

# Structure–Property Relationships in Polymer Systems:

From Functional Microgels to Dynamic Polymer Solutions and Melts

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# Abstract

Structure–property relationships in polymer materials connect microscopic parameters to macroscopic quantities. In this thesis, three studies are presented to better understand the structure– property relationships in stimuli-responsive and dynamic polymer compounds.

In a first study, the dynamic covalently cross-linked polydimethylsiloxane (PDMS) networks that are known to display molecular rearrangement in the presence of anionic end groups are investigated. PDMS networks are prepared by anionic ring-opening polymerization. Oscillatory shear rheology measurements show that the amount of initiators and cross-linkers used during synthesis directly correlates to the mechanical strength of the resulting material. Probing stress relaxation and self-healing properties with a purpose-built force-monitoring piercing device show fast self-healing rates at ambient temperature. Piercing test force measurements determine an elastic energy storage within the material during piercing that is suggested to be a prerequisite for the self-healing process.

In a second study, volume and interfacial interaction changes during the volume phase transition of poly(*N*-isopropylacrylamide) (pNIPAAm) hydrogels are decoupled from one another. For this purpose, thermosensitive pNIPAAm cores are encapsulated inside non-thermosensitive poly-acrylamide (pAAm) shells to create core-shell microgels. Both pNIPAAm cores and the pNIPAAm-AAm core-shell microgels are templated via droplet-based microfluidics. The distribution of particle sizes is narrow and well defined. The core–shell microgels Young's modulus at the microgel's surface at temperatures above and below the volume phase transition temperature (VPT) of pNIPAAm is determined by colloidal probe force mapping using atomic force microscopy. Stiffening of the surface's Young's modulus upon deswelling of the pNIPAAm core, accompanied by a small but reproducible size reduction of the pAAm-shell, above the VPT is found. It is attributed to an interconnection between the core- and the shell network in the microgels that drags the shell toward the center of the core upon deswelling. Interfacial interactions that changes during the volume phase transition of pNIPAAm are shown to remain constant, which opens pathways for the rational design assemblies of microgel layers or aggregate-substrates with the ability to independently regulate their elasticity.

A third study investigates the interplay of supramolecular and macromolecular dynamics of linear associating supramolecular polymers in semi-dilute solution. For this purpose, linear poly(ethylene glycol) functionalized with terpyridine moieties that can form transient metallo-supramolecular bonds are synthesized. Oscillatory shear rheology experiments show that shorter precursors and stronger transient bonds form longer and more stable chain assemblies, whereas longer precursors and weaker transient bonds form shorter and less stable ones. The upper boundary of the supramolecular chain extension is estimated by covalent chain extension with a photocrosslinkable unit. Viscosity calculations reveal that the assemblies display Rouse-type relaxation behavior, with assemblies having a strong metallo–supramolecular bond deviating more towards reptative motion than those with a weaker transient bond. Data is modelled with the time marching algorithm to calculate number-average degrees of chain extension, number-average molar masses, effective relaxation times and dissociation constants as much as six orders of magnitude faster than the free metal–ligand complex. This acceleration depends on the length of the polymer precursor chain the complex is attached to with longer chain segments yielding faster dissociation times, which indicates that metal–ligand bond destabilization is caused by the dynamic activity of the polymer chain itself.

# Zusammenfassung

Struktur-Eigenschafts-Beziehungen in Polymermaterialien verbinden mikroskopische Parameter mit makroskopischen Eigenschaften. In dieser Arbeit werden drei Studien vorgestellt, welche die Struktur-Eigenschafts-Beziehungen in stimuli-responsiven und dynamischen Polymeren untersuchen.

In einer ersten Studie werden dynamisch kovalent vernetzte Polydimethylsiloxannetzwerke (PDMS) untersucht, welche in Gegenwart anionischer Endgruppen ein dynamisches Netzwerk ausbilden. Diese werden mittels anionischer Ringöffnungspolymerisation dargestellt. Oszillatorische Scherrheologie-Experimente zeigen, dass die Menge der während der Synthese eingesetzten Initiatoren und Vernetzer direkt mit den mechanischen Eigenschaften des Materials korrelieren. Die Spannungsrelaxation und Selbstheilungseigenschaften werden mit einer speziell entwickelten Stecktestversuchsandordnung mit simultaner Messung der auftretenden Kräfte gemessen und zeigen schnelle Selbstheilungsraten bei Raumtemperatur. Die Stecktests bestimmen eine elastische Energiespeicherung während des Einstechens, die als Voraussetzung für den Selbstheilungsprozess angenommen wird.

In einer zweiten Studie werden Volumen- und Grenzflächenwechselwirkungsänderungen während des Volumenphasenübergangs von Poly(N-Isopropylacrylamid) (pNIPAAm)-Hydrogelen voneinander entkoppelt. Zu diesem Zweck werden temperatursensitive pNIPAAm-Kerne in nicht-temperatursensitive Poly(*N*-Isopropylacrylamid)-Schalen eingeschlossen, um Kern-Schale-Mikrogele zu erzeugen. Sowohl die pNIPAAm-Kerne als auch die pNIPAAm-AAm-Kern-Schale-Mikrogele werden mittels tröpfchenbasierter Mikrofluidik hergestellt. Die Größenverteilung der Partikel ist eng und gut definiert. Der Elastizitätsmodul der Kern-Schale-Mikrogele an der Oberfläche der Mikrogele bei Temperaturen oberhalb und unterhalb der Volumen-Phasenübergangstemperatur (VPT) von pNIPAAm wird mittels der Rasterkraftmikroskopie durch Bestimmung von Kraft-Abstandskurven gemessen. Der Elastizitätsmodul der Mikrogeloberfläche steigt beim Entquellen des pNIPAAm-Kerns an, was von einer kleinen und reproduzierbaren Volumenverkleinerung der pAAm-Schale begleitet wird. Dies wird auf eine Verbindung der Kern- und Schalennetzwerke zurückgeführt, welche die Schale beim Entquellen in Richtung des Kerns zieht. Grenzflächenwechselwirkungen während des Volumenphasenübergangs werden konstant gehalten, was Wege für eine rationale Gestaltung von Mikrogelschichten oder Aggregatsubstraten mit individuell einstellbarer Elastizität eröffnet.

Eine dritte Studie untersucht das Zusammenspiel supramolekularer und makromolekularer Dynamik in linear-assoziierenden supramolekularen Polymeren in halbverdünnter Lösung. Dafür werden lineare Polyethylenglykole (PEG) dargestellt, welche mit Terpyridin-Einheiten funktionalisiert sind, die transiente metallo-supramolekulare Bindungen ausbilden. Oszillatorische Scherrheologie-Messungen zeigen, dass kürzere PEG-Ketten und stärkere transiente Bindungen längere und stabilere Kettenaggregate bilden, wo hingegen längere PEG-Ketten und schwächere transiente Bindungen kürzere und weniger stabile Kettenaggregate bilden. Die Obergrenze der supramolekularen Kettenverlängerung wird durch kovalente Kettenverlängerung mit einer foto-vernetzbaren funktionellen Gruppe abgeschätzt. Viskositätsberechnungen zeigen, dass die Kettenaggregate Rouse-artige Relaxation zeigen, wobei Aggregate mit einer starken metallo-supramolekularen Bindung anteilig reptative Relaxation aufweisen. Der "Time Marching Algorhythmus" wird angewandt, um Zahlenmittel der Kettenverlängerung, Zahlenmittel der Molmassen, effektive Relaxationszeiten und Dissoziationskonstanten zu bestimmen. Letztere sind bis zu sechs Größenordnungen größer als die einer freien Komplexbindung. Dieser Effekt ist von der PEG-Kettenlänge abhängig, wobei längere Kettensegmente schnellere Dissoziationszeiten ergeben, was darauf hindeutet, dass die Destabilisierung der Metall-Ligand-Bindung durch die dynamische Aktivität der Polymerkette selbst verursacht wird.

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# List of Abbreviations and Symbols

а	tip-sample contact radius	h	hour
AAm	acrylamide	H <sub>2</sub> O	water
AFM	atomic force microscopy	HCOONa	sodium formate
APS	ammonium persulfate	HRMS	high-resolution mass
BIS	N,N-methylenebisacrylamide		spectroscopy
bis-D4	bis(heptamethylcyclo-	Ι	moment of inertia
	tetrasiloxanyl)ethane	IR	infrared
с	concentration	kв	Boltzmann constant
с*	overlap concentration	<i>k</i> <sub>c</sub>	the cantilever spring constant
C∞	characteristic ratio	k <sub>diss</sub>	dissociation constant
d	cantilever-detector distance	L	length
d	diameter	LCST	lower critical solution
Ð	polydispersity		temperature
D	tip-sample separation	MeOH	methanol
D <sub>4</sub>	octamethylcyclotetrasiloxane	<i>M</i> <sub>n</sub>	number-average molar mass
DBPO	dibenzoyl peroxide	mol%	molar percentage
DMMI	dimethylmaleimide	M <sub>w</sub>	weight-average molar mass
DMMIAAm	2-(dimethylmaleimide)-N-	Ν	degree of polymerization
	ethyl acrylamide	n	number of possible positions
DMSO	dimethylsulfoxide	N <sub>agg</sub>	aggregation number
Ε	elastic / Young's modulus	NIPAAm	N-isopropylacrylamide
E*	reduced elastic modulus	NMR	nuclear resonance
eq(s).	equation(s)		spectroscopy
exp	experimentally	р	poly
F	force	р	polymer
FDA	United States Food and Drug	PBA	poly( <i>n</i> -butyl acrylates)
	Administration	PDMS	polydimethylsiloxane
<i>G</i> ''	loss modulus	PE	polyethylene
G	shear modulus	PEG	poly(ethylene glycol)
<i>G</i> '	storage modulus	PFG	pulsed field gradient
G*	complex shear modulus	ppm	parts per million
Gp	elastic plateau modulus	PSD	position sensitive detector

R	universal gas constant	Zc	cantilever deflection
R <sub>H</sub>	hydrodynamic radius	Zp	position of the piezoelectric
RT	room temperature		element
S	solvent; sample	γ	shear strain; shear amplitude
SANS	small angle neutron scattering	δ	phase angle; chemical shift;
stat.	statistical		deformation
Т	temperature	$\Delta G_{\rm mix}$	Gibbs free energy of mixing
t	time	$\Delta H_{\rm mix}$	energy of mixing
t	tip	$\Delta_{PSD}$	laser beam travel distance
tan δ	loss tangent	$\Delta S_{mix}$	entropy of mixing
t <sub>c</sub>	thickness of the cantilever	3	strain
TEMED	tetramethylethylenediamine	η	viscosity
theo	theoretical	η*	complex viscosity
TMA	time marching algorithm	λ	persistence length,
ТМАН	tetramethylammonium		wavelength
	hydroxide	ν	Poisson ratio; Flory exponent
TMS	trimethylsilane	σ	stress
tpy	terpyridine	τ	relaxation time
TXS	thioxanthone disulfonate	$ au_0$	relaxation time of a polymer
UV	ultraviolet		chain building block
ν	molar concentration of	$\tau_{break}$	bond lifetime
	elastically effective crosslinks	$\tau_{break}^{*}$	renormalized bond lifetime
<i>v</i> / <i>v</i>	percentage by volume	T <sub>eff</sub>	effective relaxation time
Vis	visible	τ <sub>R</sub>	Rouse time
W	width	$\tau_{rep}$	reptation time
w/w	percentage by weight	φ	volume fraction
$X_n; \overline{L}$	number-average degree of	χ	Flory–Huggins polymer-
	polymerization		solvent-interaction parameter
X <sub>w</sub>	weight-average degree of	ω	angular frequency
	polymerization		

# 1. Introduction

## 1.1. Polymer Gels

## 1.1.1. Definition and Applications

The term *polymer gels* defines a three-dimensional polymer network that is swollen in a solvent. Many classifications of polymer gels are known: If a gel is described according to its swelling medium, it is commonly termed *hydrogel* when swollen in water, or *organogel* when swollen in organic solvents. Classification according to their size yields the terms *microgels* for gels in the size range of a few nanometers up to several hundred micrometers, and *macrogels* for gels of larger sizes. Determination according to the nature of the cross-links that form the three-dimensional network separates polymer gels in either *chemical gels*, in which the cross-links are created by covalent bonds, or *physical gels*, in which the cross-links are of a transient, non-covalent nature. The *International Union of Pure and Applied Chemistry* defines a gel as a "Nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid."<sup>1, 2</sup>



**Figure 1.1**. Schematic representation of **(A)** a polymer macrogel with above-millimeter size that is visible to the naked eye, and **(B)** a spherical polymer microgel with dimension between 10 nm and 1000  $\mu$ m that can only be seen with the aid of a microscope.

Polymer gels have gained great importance in industrial applications as well as in scientific research. Superabsorbent polymers, namely sodium polyacrylate, which creates a polymer gel that can absorb up to 300 times its own weight, is found in many household items such as diapers, candles and wound dressings.<sup>3, 4</sup> Hydrogels made from non-toxic polymers such as collagen or agarose are used in tissue engineering<sup>5-10</sup> or drug delivery<sup>11-15</sup> because of their inherent softness that can be tuned to mimic native tissue while still providing mechanical integrity. They are an excellent scaffold for cells proliferation, as they mimic the mechanicals properties of the extracellular matrix and at the same time are permeable for low molar mass substances such as nutrients and metabolites that are necessary for the cells survival.<sup>16</sup> Other applications include regenerative medicine,<sup>10, 17, 18</sup> cell encapsulation,<sup>10, 16</sup> filtration technology,<sup>19-21</sup> catalysis<sup>22</sup> and contact lenses.<sup>23</sup>

## 1.1.2. Polymer Gel Synthesis

Covalent polymer gels can be synthesized using one of the following pathways: (i) polymerization of either structurally identical or different (copolymerization) mono- and multifunctional monomers,<sup>24-26</sup> (ii) cross-linking of linear polymer chains containing cross-linkable side groups,<sup>27</sup> (iii) end-linking of linear polymer chains functionalized with reactive end groups to multifunctional cross-linkers<sup>28</sup> or (iv) interconnection of star-shaped macromonomers whose arms are capped with suitable functional groups.<sup>29</sup>

Covalent polymer networks in the context of this work were prepared by either pathway (i) or (ii). The simplest way to facilitate pathway (i) is the free radical polymerization mechanism that uses the high reactivity of free radicals to grow polymeric chains. On the upside, free radical polymerizations are easy to handle and work in variety of solvents at various temperatures and atmospheric pressure to generate high molecular weight polymers. On the downside, they lack reaction control due to the high reactivity of the free radicals. They will react not only with other monomer units to propagate chain growth, but will also undergo various side reactions, compromising polymer dispersity and structural controllability. A general reaction scheme for a free radical polymerization is shown in Scheme 1.1.

A free radical polymerization is subdivided into three steps. The reaction is initiated by homolytic bond cleavage of an initiator molecule, either thermally, photo- or electrochemically (*initiation*, Scheme **1.1**A). The free radical then reacts with a monomer unit while creating a new radical, which in turn reacts with another monomer and so forth, causing the growth of the chain (*propagation*, Scheme **1.1**B). It is at this point, that the high reactivity of the free radical becomes problematic, because there are numerous other potential reaction partners in addition to the next requested monomer molecule.



**Scheme 1.1**. Reaction pathway of a free radical polymerization. **(A)** Free radicals are generated by a suitable initiator. **(B)** The radical cleaves a double bond of a monomeric unit and thus reacts with it. The ensuing radical reacts with another monomeric unit. This process is repeated multiple times, leading to chain propagation, until **(C)** two chain radicals meet and either disproportionate or recombine. Both events result in the termination of the polymerization reaction.

These side reactions can be summed up in to two classes: chain transfer reactions and termination reactions.<sup>24</sup> Termination reactions always result in the annihilation of two free radicals, of which there are two types, of which the reaction products are shown in Scheme 1.1C.<sup>25</sup> The first is *recombination*: Two polymer chains carrying a terminal radical recombine to form one chain. The second is *disproportionation*: Here, a  $\beta$ -hydrogen atom of the carbon radical, which also carries radical, is transferred from one chain to another. This results in two different compounds: one with a saturated and another with an unsaturated terminal carbon–carbon bond.

Chain transfer reactions are another type of side reaction. Several substrates can be exposed to chain transfer reactions: Due to a homolytic cleavage of a covalent bond by a radical species, the radical character is transferred to the reactive substrate, whereas the entering radical is saturated. Chain transfer reactions are possible to polymer, monomer and solvent molecules. The purposeful addition of chain transfer agents allows for molar mass control during a free radical polymerization.<sup>30, 31</sup>

To create a polymer network, cross-linker molecules are added to the reaction mixture. These crosslinkers carry at least two reactive groups within their structure and are thus able to connect multiple polymer strands to a three-dimensional network. The mechanical properties of the resulting material can be controlled by the amount of cross-linker and polymerization initiator molecules. In a free radical polymerization, they are incorporated statistically, which leads to an undefined and polydisperse distribution of the cross-links. Often, dense clusters form at the beginning of the reaction, which are then interconnected at later reaction stages.<sup>32, 33</sup> Stemming from this are locally different viscosities. If they are too high, they can cause a dangerous autoacceleration reaction, the Trommsdorf–Norrish effect, in which termination reactions decrease by a factor of four, causing the overall rate of the polymerization to double.<sup>34</sup>

#### 1.1.3. Microfluidics

The structural polydispersity associated with a free radical polymerization can be negated to a certain extent by employing an alternative experimental procedure.<sup>32, 35-37</sup> The reaction volume can be separated into many smaller "reaction chambers" instead of producing a macrogel in a batch reaction, thus creating a relatively homogenous polymer network, as well as avoiding the above-mentioned Trommsdorff–Norrish effect. This procedure is called *microfluidics*, and describes the manipulation and processing of small amount of fluids  $(10^{-9} - 10^{-18} \text{ liters})$  through small channels that are only a few micrometers in thickness.<sup>38</sup> This produces particles with a diameter of 10–1000 µm.







**Figure 1.2.** Depending on the length-scale, gels can show different types of inhomogeneities. Colloidal microgels, or nanogels, are synthesized from the core outwards, which creates *radial inhomogeneities* (top left). Macrogels are *spatially inhomogeneous*. During their reaction, clusters with many cross-links are created first, and only later interconnected by areas of lesser cross-linking density (top right). Above-colloidal microgels, which are in the size-range of  $10-1000 \,\mu$ m, constitute the best compromise between the two former variants. Their relatively high homogeneity, coupled with a fast response time to external stimuli due to their small size, makes them perfect candidates to investigate polymer gel thermodynamics. Here, *d* is the diameter of the network structure. Reprinted with permission from A. Habicht, W. Schmolke, F. Lange, K. Saalwächter, S. Seiffert, *Macromol. Chem. Phys.* **2014**, *215*, 1116-1133. Copyright 2014, Wiley VCH.

Microgels are particularly homogeneous, when are they are prepared from polymer solutions that are connected by suitable cross-linking reactions such as photocross-linking.<sup>32, 33, 39</sup> An exemplary photoreactive cross-linking unit is dimethylmaleimide (DMMI), which has been shown to form stable, covalently cross-linked polymer gels,<sup>40, 41</sup> in which the nature of the cross-linking bond is dependent on the solvent.<sup>42</sup> The inhomogeneities associated with various experimental procedures of a free radical polymerization are shown in Figure 1.2.

Depending on the size of the microgel droplets, two different techniques are used. For the synthesis of particles within the size range of a 100  $\mu$ m or more, glass capillary devices are the method of choice. They are easily built from blunt syringe tips and standard glass slides used for optical microscopy and are therefore very cost effective. The device consists of a round glass capillary with a tapered end, which is placed inside a glass tube with a square profile. It is important that both capillaries have equal diameters to achieve coaxial alignment. If two immiscible fluids are pumped through device from opposite sides, which is the case for an aqueous polymer solution (*dispersed phase*) and an oil (*continuous phase*), droplets are formed through flow focusing at the tip of the inner glass capillary, as shown in Figure 1.3A. Particle sizes can be tuned with high accuracy by adjusting the flow rate of each phase.

If smaller particles are desired, custom designed polydimethylsiloxane (PDMS) chips made by soft- or photolithography are used.<sup>43</sup> Such microfluidic devices are fabricated from high-resolution photomasks, on which the microfluidic channel designs are printed, and are then transferred onto a photoreactive substrate. After UV-treatment, the result is a positive mold of the photomask, into which PDMS is poured, hardened, peeled off, and bound to a glass slide by oxygen plasma treatment.<sup>44</sup> The dispersed phase is injected into the central inlet, whereas the continuous phase is injected into the two side inlets. The fluids meet at the cross-junction where drops are formed, as shown in Figure 1.3B. Again, particle size can be very accurately controlled by adjusting the liquids' flow rates. Figure 1.4 displays an overview of the entire manufacturing process.



**Figure 1.3.** (A) Sketch of a glass capillary microfluidic device. Both phases meet at the tapered end of a glass capillary, where the dispersed phase is flow-focused by the continuous phase, thereby creating miniature droplets. Adapted with permission from G. T. Vladisavljevic, H. Shahmohamadi, D. B. Das, E. E. Ekanem, Z. Tauanov, L. Sharma, *J. Colloid Interface Sci.* **2014**, *418*, 163-170. Copyright 2014 Elsevier. (B) Sketch of a polydimethylsiloxane microfluidic device. Both phases meet at four-way cross-junction. The continuous phase (here: mineral oil) meets the dispersed phase (here: water) from both sides. This leads to flow-focusing that, in turn, creates the microfluidic droplets. Adapted with permission from T. Ward, M. Faivre, M. Abkarian, H. A. Stone, *Electrophoresis* **2005**, *26*, 3716-3724. Copyright 2005, Wiley VCH.

In addition to simple spherical shapes, microfluidic devices can also fabricate more sophisticated microgel shapes, such as multi-emulsions, which are drops encapsulated in larger drops. In glass capillary devices, such structures can be formed by concurrent co-flow and flow-focusing.<sup>36, 39, 43, 45</sup> PDMS microfluidic devices employ multiple cross junctions in conjugation.<sup>45, 46</sup> Both methods are shown in Figure 1.5. The use of suitable substrates greatly increases the number of applications for microfluidics. If the particles are designed to be biocompatible, they can be used for drug targeting, decreasing the load of pharmaceuticals needed for treatment by transporting the drug within the microgel to the desired location within the organism and then releasing it.<sup>47</sup> It has been shown that it is possible to encapsulate living cells, keep them alive inside the particle and release them controllably.<sup>16, 48</sup>



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Figure 1.5. Fabrication of multi-emulsions using either (A) glass capillary or (B) polydimethylsiloxane microfluidic devices. Reprinted from (A) L. Y. Chu, A. S. Utada, R. K. Shah, J. W. Kim, D. A. Weitz, *Angew. Chem., Int. Ed. Engl.* 2007, *46*, 8970-8974, and (B) A. R. Abate, D. A. Weitz, *Small* 2009, *5*, 2030-2032. Copyright 2007 and 2009, Wiley VCH

Particles prepared by a microfluidic experiment are highly monodisperse, as long as the liquid flow rates are kept constant.<sup>43, 49, 50</sup> This fact, coupled with the microgels' homogeneous structure, render them a suitable material platform to study polymer thermodynamics. Because they are small enough to equilibrate in reasonable timescales, they are particularly useful to investigate processes such as swelling.

## 1.1.4. Poly(*N*-isopropylacrylamide) and its Volume Phase Transition

Suitable candidate for the investigation of polymer gel swelling are hydrogels made from poly(*N*-isopropylacrylamide), or pNIPAAm, because they show a volume phase transition caused their lower critical solution temperature (LCST) of the NIPAAm-unit of 33.6 °C.<sup>51</sup> Other uses of pNIPPAm gels include biomedical applications,<sup>52, 53</sup> drug delivery,<sup>54, 55</sup> chemical sensors,<sup>40, 56</sup> and chemo-mechanical valves.<sup>57</sup>

Poly(*N*-isopropylacrylamide) hydrogels are most commonly synthesized by free radical polymerization using the cross-linker molecule *N*,*N*-methylenebisacrylamide (BIS).<sup>58</sup> More homogeneous gels can be created by copolymerization with a suitable reactive comonomer such as 2-(dimethylmaleimide)-*N*-ethyl acrylamide (DMMIAAm) and subsequent cross-linking of the polymer chains, in this case by a photochemical reaction.<sup>32, 33, 41</sup>

The volume phase transition of pNIPAAm hydrogels is caused by its unique chemical structure that is depicted in Figure 1.6A. The polymer is composed of a largely unpolar backbone and an unpolar side group that both disfavor interactions with water, but it also has a polar amide group that can form hydrogen bonds with the polar water molecules. This promotes mixing, but only up to certain temperature, the so-called Lower Critical Solution Temperature (LCST). Below the LCST, mixing is mainly provided by hydrophobic hydration around the side chain carbon atoms, which is achieved by cage-like water formations.



**Figure 1.6. (A)** Ensemble of poly(NIPAMM-*co*-DMMIAm) microgels in aqueous solution at **(A)** 25 °C in their fully swollen state, and **(B)** in at 40 °C in their fully deswollen state. Images were taken with an optical microscope at 4x magnification.

The LCST phase transition occurs when these cage-like structures are disrupted by increasing the temperature above the LCST. During this process, significant amounts of water molecules are released, and the local water-ordering is reduced and the polymer precipitates.

The degree of this precipitation, which manifests itself as a pronounced deswelling of the gel, as well as the nature of transition (continuously or dis continuously) is influenced, by the cross-linking density within the gel,<sup>59-62</sup> polymerization temperature,<sup>63-66</sup> or the pH-level of the solvent amongst other things.<sup>66-68</sup> Figure 1.6A and B show micrographs of an ensemble of pNIPAAm microgels in water below (B) and above (C) their LCST.

The volume phase transition of pNIPPAm is best described by the Flory–Huggins theory, which is a simplified approach to polymer thermodynamics: it appraises the entropy of mixing,  $\Delta S_{mix}$ , based on a combinatorial argument, and the energy of mixing,  $\Delta H_{mix}$ , based on mutual average interactions in a mean-field treatment. <sup>69-71</sup> Both can be expressed by the Gibbs free energy of mixing,  $\Delta G_{mix}$ , which must be negative for two components to readily mix with each other.

$$\Delta G_{\rm mix} = \Delta H_{\rm mix} - T \Delta S_{\rm mix} \tag{1}$$

Entropy always favors mixing, because it decreases the order of the system, whereas enthalpy most likely disfavors mixing, because that would force the components to interact with each other rather than with themselves.

The Flory–Huggins model places all molecules, be it solvent, low-molar mass compounds or polymers, on a lattice model. The entropy of mixing,  $\Delta S_{mix}$ , for a solvent–polymer mixture is then given as

$$\Delta S_{\rm mix} = -k_{\rm B}(n_{\rm s} \ln \phi_{\rm s} + n_{\rm p} \ln \phi_{\rm p}) \tag{2}$$

Here,  $k_{\rm B}$  is the Boltzmann constant,  $n_{\rm s}$  and  $n_{\rm p}$  are the number of possible positions on the lattice for the solvent and polymer molecules, respectively, and  $\phi_{\rm s}$  and  $\phi_{\rm p}$  their respective volume fractions.

The enthalpy of mixing,  $\Delta H_{mix}$ , is given as

$$\Delta H_{\rm mix} = k_{\rm B} T \chi n_{\rm s} \phi_{\rm p} \tag{3}$$

The dimensionless parameter  $\chi$  is called the Flory–Huggins polymer-solvent-interaction parameter and describes the differences in energies before and after mixing per  $k_{\rm B}T$ -increment. It generally assumes values higher than zero,  $\chi > 0$ , as mixing is generally disfavored energetically. The polymer molecules rather want to interact with themselves than with one the solvent. Only in cases where secondary interactions such as hydrogen bonding can outweigh the intrinsic energy penalty of mixing is the Flory–Huggins polymer-solvent-interaction parameter smaller than zero,  $\chi < 0$ .<sup>72, 73</sup>

Inserting both eqs. (2) and (3) into expression (1) yields the Flory–Huggins equation for the Gibbs free energy of mixing,  $\Delta G_{mix}$ :

$$\Delta G_{\rm mix} = k_{\rm B} T \left( n_{\rm s} \ln \phi_{\rm s} + n_{\rm p} \ln \phi_{\rm p} + \chi n_{\rm s} \phi_{\rm p} \right) \tag{4}$$

The above equation is valid for a polymer–solvent system. For any two components, A and B, the expression is:

$$\Delta G_{\rm mix} = k_{\rm B} T \left( \frac{\phi_{\rm A}}{N_{\rm A}} \ln \phi_{\rm A} + \frac{\phi_{\rm B}}{N_{\rm B}} \ln \phi_{\rm B} + \chi \phi_{\rm A} \phi_{\rm B} \right)$$
(5)

Here,  $\phi_A$  and  $\phi_B$  are the volume fractions of components A and B, and  $N_A$  and  $N_B$  are their degrees of polymerization,

Using the Gibbs free energy of mixing  $\Delta G_{mix}$ , miscibility of any two compounds A and B can be predicted by constructing phase diagrams.

#### **1.2.** Atomic Force Microscopy

#### 1.2.1. Introduction and Measurement Principle

Atomic Force Microscopy, or AFM, describes a range of scanning probe microscopes that were invented in the 1980s by G. Binning, C. F. Quate and Ch. Gerber.<sup>74</sup> An AFM microscope employs a silicon<sup>75, 76</sup> or silicon nitride<sup>77</sup> cantilever with a very sharp tip that is moved by applying a voltage to a piezoelectric translator to scan over a sample's surface. As the tip approaches the surface, the close-range, attractive force between the surface and the tip causes the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip contacts it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface. The deflection is then measured using a laser beam focused on the back of the cantilever, whose reflection is captured by a position sensitive detector, or PSD, that converts it into an electric signal.<sup>78</sup> The intensity of this signal will be proportional to the deflection of the cantilever. The experimental setup of an AFM measurement is shown in Figure 1.7.

The AFM was designed originally to image surfaces with atomic resolution. Surfaces can be mapped with a resolution of 0.1 Å<sup>79</sup> by plotting the deflection of the cantilever versus its position near the sample surface. In such a measurement, the distance of the cantilever is kept constant, which results in a map of the surface structure of atomic resolution. Alternatively, the cantilever is oscillated up and down near its resonance frequency.



**Figure 1.7.** An atomic force microscope setup: The deflection of the cantilever tip that is caused by attractive or repulsive interactions with the surface is detected by a photodetector that measures the change of direction of a reflected laser beam. Reprinted with permission from H. J. Butt, B. Cappella and M. Kappl, *Surf. Sci. Rep.* **2005**, *59*, 1-152. Copyright 2005, Elsevier.

The interaction of forces acting on the cantilever when the tip comes close to the surface, such as Van der Waals forces, dipole-dipole interactions or electrostatic forces, cause the amplitude of the cantilever's oscillation to change as the tip gets closer to the sample. This amplitude change is used as a parameter that is processed by a regulatory circuit connected to the piezoelectric translators. The original amplitude is recovered through adjustment of the cantilever's position, and from this adjustment an image of the sample can be calculated.

However, the interactions between the cantilever tip and the sample can also be used to investigate the mechanical properties of the sample, the tip, or the medium in between. These measurements are known as *force measurements*. In such a force measurement, the tip attached to the cantilever spring is slowly moved towards the surface. As with the imaging techniques the attraction or deflection of the tip is recorded but is not translated into movement of the cantilever itself; it is instead quantified and converted into to force-versus-distance curves.

To determine the force associated with the cantilever's displacement, its tip is pressed against the sample surface. The cantilever's position, both vertically and laterally, is adjusted by piezoelectric elements. The experimental result is a measure of the cantilever's deflection  $Z_c$  versus the position of the piezoelectric translator  $Z_p$  normal to the surface. Since  $Z_c$  is captured by using a laser beam and a PSD, it is recorded as the current of the photodiode detector  $I_{PSD}$ . To calculate the applied force F, the  $I_{PSD}$ -values need to be transformed.<sup>80</sup> For the cantilever, this is done by multiplying the cantilever spring constant  $k_c$  with its deflection  $Z_c$ .

$$F = k_{\rm c} Z_{\rm c} \tag{6}$$

The distance between the tip and the sample, the so-called tip–sample separation D, is calculated as the sum of the cantilever deflection  $Z_c$  and the position of the piezoelectric element  $Z_p$ :

$$D = Z_{\rm c} + Z_{\rm p} \tag{7}$$



**Figure 1.8.** Schematic side view of a cantilever with a force at its end. *X* is the horizontal coordinate originating at the basis of the cantilever, Z(X) is the cantilever deflection at the position *X*,  $Z_c$  being the cantilever deflection at its end. Reprinted with permission from H. J. Butt, B. Cappella and M. Kappl, *Surf. Sci. Rep.* **2005**, *59*, 1-152. Copyright 2005, Elsevier.

Upon contact with the sample, the cantilever bends under the resulting stress and the laser beam's reflection changes it position. If the cantilever possesses a rectangular cross-section, the change of the cantilever slope is given as:

$$\frac{dZ_c}{dX} = \frac{6FL^2}{Ewt_c^3} = \frac{FL^2}{2EI}$$
(8)

Here, w denounces the width, L the length and  $t_c$  the thickness of the cantilever, whereas E describes the Elastic Modulus of the cantilever material. The moment of inertia I for a rectangular cantilever is:

$$I = \frac{wt_c^3}{12} \tag{9}$$

The relations from equation (8) are visualized in Figure 1.8.

If the distance *d* from the cantilever to the PSD is known, the travel distance of the laser beam  $\Delta_{PSD}$  can be approximated as:

$$\Delta_{PSD} = 2d \tan \alpha = \frac{FL^2 d}{EI}$$
(10)

Figure 1.9 illustrates the correlation between the cantilever deflection  $Z_c$  and the laser beam's travelling distance  $\Delta_{PSD}$ .

Since the detected signal at the PSD is proportional to the cantilever slope, the deflection can be put as:

$$Z_{c} = \frac{2}{3}L\frac{dZ_{c}}{dX} = \frac{4FL^{3}}{Ewt_{c}^{3}} = \frac{FL^{3}}{3EI} = \frac{\Delta_{PSD}L}{3d}$$
(11)

Here, *d* is the distance between the cantilever and the PSD.



**Figure 1.9.** Correlation between the cantilever deflection  $Z_c$  and the travelling distance  $\Delta_{PSD}$  of the laser beam. Here, *d* is the distance between the end of the cantilever and the PSD, and  $Z_c$  is the cantilever deflection. Reprinted with permission from H. J. Butt, B. Cappella and M. Kappl, *Surf. Sci. Rep.* **2005**, *59*, 1-152. Copyright 2005, Elsevier.

The cantilever's spring constant  $k_c$ , needed to calculate the applied force F as shown in equation (6), is a key parameter of an AFM force measurement. Combining expressions (6) and (11) generates a new equation for the spring constant  $k_c$ :

$$k_{\rm c} = \frac{F}{Z_{\rm c}} = \frac{Ewt_{\rm c}^{\ 3}}{4L^3}$$
(12)

Calculated values for  $k_c$  often differ significantly from experimentally determined ones. This can be attributed to small changes in the thickness of the cantilever  $t_c$ , because its composition is never perfectly homogeneous. It enters (12) to the power of three, which causes tiny alterations to have a profound effect on the calculation of the spring constant  $k_c$ . In most cases, the back of cantilevers is coated with a gold layer or another highly reflective substance to increase reflectivity. The thickness of this layer is not a known quantity. To alleviate these problems, the spring constant is experimentally determined before each measurement.

#### 1.2.2. The Hertz Model

Data analysis of the curves obtained from force measurements is not trivial, especially for viscoelastic materials such as hydrogels.<sup>41</sup> The primary result of the force measurement is the electric current of the photodiode detector  $I_{PSD}$  against the position of the piezoelectric translator  $Z_p$ . To obtain a force curve, both these values need to be converted into measures of force and deflection.<sup>80</sup> This can only be done if the tip–sample separation *D*, or *zero-distance*, is known. However, it cannot be determined independently but must be inferred from the force curve measurement itself.

In an ideal system without deformation of the surface or the cantilever tip and without any attractive or repulsive forces, the force curve consists of two linear parts. The zero-distance D is then identical to the point at which the first change in the electric current of the photodiode detector  $I_{PSD}$ , which corresponds to the force F, is recorded. In reality, however, both repulsive and attractive forces have a major impact on the zero-distance D.



**Figure 1.10.** A force–distance curve, representative of a colloidal probe AFM force measurement on a soft matter sample. Adapted with permission from R. W. Carpick, M. Salmeron, *Chem. Rev.* **1997**, *97*, 1163-1194. Copyright 1997, American Chemical Society.

This results in a loss of linearity in the contact regime of the force curve and appropriate mathematical models have to be developed to describe it. This becomes especially important for soft materials, as the cantilever tip may be immersed within sample. In this case, the deformation  $\delta$  and contact area are constantly changing with the applied force. To minimize the degree of indentation, spherical cantilever tips, called colloidal probes, are used to spread the force load over a wider surface.<sup>41,81</sup>

If all those factors are considered, the resulting force curve will look as shown in Figure 1.10. (i) When the tip and sample are separated, there are neither attractive nor repulsive forces present. (ii) As the two approach each other, attractive forces usually accredited to van der Waals interactions set in, bending the cantilever towards the sample. (iii) As soon as the interaction forces exceed the spring constant of the cantilever  $k_c$ , the tip jumps onto the sample surface, resulting in a steep drop of the force curve. This point is called *jump-in* or *snap-in*. The total jump distance is related to the jump-in distance, the indentation  $\delta$  of the sample as well as tip and sample deformation. This makes it practically impossible to determine the zero-distance  $D.^{82}$  (iv) As the load increases, the cantilever bends in relation to the sample surface due to attractive interactions. Now the cantilever is bent in the opposite direction, resulting in a tensile load. (vi) The cantilever detaches from the surface as soon as the tensile load overcomes the interaction forces, causing a steep incline in the force curve. This point is called *jump-off* or *snap-out*.

The indentation of the cantilever tip often leads to plastic deformations. However, for soft samples such as polymeric gels, these deformations can be neglected, and the contact regime can be described using models in which tip and sample are assumed to be continuous elastic media.

To draw any conclusion about the mechanical behavior of the sample, the contact regime of the force curve is analyzed. The deformation  $\delta$  is directly related to the sample's elastic modulus *E*, and therefore characterizes the material's stiffness. For a quantitative analysis of the deformation  $\delta$ , the Hertz model

describing the contact of two elastic bodies is used.<sup>83</sup> According to the model, the applied force *F* can be written as a function of the deformation  $\delta$ :

$$F(\delta) = E^* R^{0.5} \delta^{1.5}$$
(13)

Here, *R* denotes the cantilever tip's radius, whereas  $E^*$  denotes the reduced elastic modulus, which is given by:

$$\frac{1}{E^*} = \frac{3}{4} \left( \frac{1 - v_s^2}{E_s} + \frac{1 - v_t^2}{E_t} \right)$$
(14)

 $E_s$  and  $E_t$  are the elastic moduli of the sample and the cantilever tip, respectively, whereas  $v_s$  and  $v_t$  are their respective Poisson ratios.

Often, the cantilever material is so rigid, that elastic deformation of the cantilever can be neglected. The equation can be simplified to:

$$\frac{1}{E^*} = \frac{3}{4} \left( \frac{1 - v_s^2}{E_s} \right)$$
(15)

The spring constant of the sample, the sample stiffness  $k_s$ , is closely related to the reduced elastic modulus  $E^*$ . Using tip–sample contact radius a, an expression for the sample stiffness  $k_s$  can be found:

$$k_{\rm s} = \frac{3}{2}aE_{\rm tot} = 2a(\frac{E_{\rm s}}{1 - v_{\rm s}^2}) \tag{16}$$

The tip–sample contact radius *a* is calculated from the reduced elastic modulus *E*\*:

$$a = \sqrt[3]{\frac{RF}{E^*}}$$
(17)

It is related to the sample deformation  $\delta$  by:

$$\delta = \frac{a^2}{R} \tag{18}$$

Sneddon has shown that for any punch that can be described as a solid of revolution of a smooth function the load–displacement relationship can be written as:<sup>84</sup>

$$F = \alpha \delta^n \tag{19}$$

Here,  $\alpha$  and *n* are material constants. For Hertzian behavior, *n* assumes typical values, depending on the geometry of the cantilever tip (*n* = 1 for flat cylinders, *n* = 2 for cones, *n* = 1.5 for spheres and paraboloids).

It is important to note that the Hertz model makes many simplifications. It neglects any positive or negative interaction forces such as adhesion or repulsion. As a consequence, it can only be applied when the adhesive forces are much smaller than the maximum load applied during the AFM experiment. Additionally, the bodies have be considered elastic half-spheres, which means that the area of contact needs to be much smaller than the radius of the body under investigation for Hertz theory to apply. Problems that can be solved despite these simplifications are called *Hertzian*.

If a particular problem violates the above stated approximations, it is referred to as *non-Hertzian*. The most likely reason for non-Hertzian behavior is the existence of significant adhesion. Many theories have been developed to describe the work of adhesion, of which the JKR and DMT theories are the most prominent examples. JKR theory, formulated by Johnson, Kendall, and Roberts, utilizes a balance between the stored elastic energy and the loss in surface energy.<sup>85</sup> Thus, the JKR model considers the effect of contact pressure and adhesion *inside* the area of contact. DMT theory, developed by Derjaguin, Müller and Toporov, employs a similar approach but crucially considers adhesive forces *outside* the area of contact.<sup>86</sup> In practice, JKR theory is applied for experiments using large cantilever tips on soft, deformable samples where large adhesion is observed, whereas DMT theory is used for experiments with a small cantilever tip on stiff samples with small adhesion. Maugis has shown that the JKR and DMT models are limits of the same underlying theory.<sup>87</sup>

# **1.3.** Oscillatory Shear Rheology

## 1.3.1. Fundamentals

A prime method to investigate the deformation and flow of polymeric materials is the *oscillatory shear rheology*. The term *rheology* derives from the Greek word *rheos*, meaning "flow", and *logos*, meaning "study of", so it describes the study of the flow of matter.

Polymer solutions, melts and gels are *viscoelastic* materials, meaning that their mechanical behavior cannot be described by the boundary cases of an ideal elastic solid or an ideal viscous fluid, but display contributions of both cases.

In an ideal elastic solid, the energy of a uniaxial deformation is stored within the material and released again after the deformation has ended. The material regains its original state. The extent of the deformation, or strain  $\varepsilon$ , to the stress  $\sigma$  that is applied, is captured by Hooke's law:

$$\sigma = E \cdot \varepsilon \tag{20}$$

Here, *E* is the elastic modulus, also called Young's modulus, the material-specific constant of proportionality between stress  $\sigma$  and strain  $\epsilon$ .



**Figure 1.11.** Schematic representation of a setup for an oscillatory shear rheology experiment. The sketch shows the most common gemoetries to investigate the dynamics of (supramolecular) polymer solutions, melts and gels. Measurements are carried out using either (A) a plate–plate, or (B) a cone–plate configuration. Reprinted with permission from W. Schmolke, S. Seiffert, *Physical Chemistry of Polymers Part 2, 2<sup>nd</sup> Edition*, Mainz, **2019**.

In an oscillatory shear rheology experiment, the sample is not deformed uniaxially, but is sheared. In this case, the parameters shear deformation, or shear strain y, to the stress  $\sigma$  that is applied, is used:

$$\sigma = G \cdot \gamma \tag{21}$$

Here, *G* is the shear modulus, the material-specific constant of proportionality between stress  $\sigma$  and shear strain  $\gamma$ .

In an ideal viscous fluid, the stress,  $\sigma$ , is proportional not to the shear deformation itself but to its rate,  $\frac{d\gamma}{dt}$ , which causes the material to remain in its deformed state after stress application has ceased. There is no energy storage, but instead energy is dissipated as heat during shear deformation, rendering it irreversible. This is captured by Newton's law:

$$\sigma = \eta \cdot \frac{\mathrm{d}\gamma}{\mathrm{d}t} \tag{22}$$

Here,  $\eta$  is the viscosity, a material-specific constant of proportionality between stress and the rate of shear deformation.

The viscoelastic properties of polymeric compounds are commonly investigated by an oscillatory shear rheology experiment, because it measures the elastic and viscoelastic contributions simultaneously and can therefore determine the viscoelastic properties in a single measurement. For the measurement, the sample is placed onto an even plane lower plate. An upper plate is then lowered onto it, which is either another even plane or a very shallow cone. The former one has the advantage that it allows user-defined gap size, whereas the latter eliminates disruptive shear-force gradients throughout the sample, but is limited to a predetermined gap size. Polymer solutions are therefore often measured with cone-plate geometries that enhance sensitivity, whereas polymer gels and melts are mostly measured using plate-plate geometries. Both measurement configurations are depicted in Figure 1.11. The motor of the rheometer then turns the upper part in an oscillatory fashion, resulting in a torque that is exerted by the resistance of sample-medium in between the two plates. During a dynamic experiment, a sinusoidal stress  $\sigma = \sigma_0 \cdot \exp(i\omega t)$ , is applied to the sample, and the time-dependent strain  $\gamma$  is recorded, as depicted in Figure 1.12.



**Figure 1.12.** During an oscillatory shear rheology experiment, a sinusoidal stress  $\sigma$  is applied to a sample and the timedependent shear strain  $\gamma$  is recorded. The phase angle  $\delta$  reflects the individual contribution of the elastic and viscous parts of the sample. Reprinted with permission from W. Schmolke, S. Seiffert, *Physical Chemistry of Polymers Part 2, 2<sup>nd</sup> Edition*, Mainz, **2019**.

A purely elastic sample generates an answer, in which both stress and strain are in phase, because both quantities are directly proportional to each other at each time in accordance to Hooke's law, eq. (21). The resulting phase angle  $\delta$  is zero. For purely viscous compounds, it is not the strain itself but its derivative that is proportional to the applied stress in accordance to Newton's law, eq. (22). The sample generates a response that corresponds to a cosine, resulting in phase angle  $\delta$  of  $\pi/2$ . A viscoelastic compound will give an answer that is a mix of the purely elastic and purely viscous responses, thus resulting in a phase shift of a phase angle  $\delta$  between  $0 < \delta < \pi/2$ . From  $\delta$ , the individual contribution of the elastic and viscous parts of the viscoelastic sample can be calculated. The closer  $\delta$  is to zero, the higher is the elastic contribution, whereas the closer  $\delta$  is to  $\pi/2$ , the higher is the viscous contribution.

As mentioned above, the shear modulus *G* reflects the ratio of stress,  $\sigma$ , to shear strain,  $\gamma$ . In case of an oscillatory shear rheology experiment, it is generated as a *complex quantity*, *G*<sup>\*</sup>, connecting the ratio of the sinusoidal stress  $\sigma$ , the shear strain  $\gamma$  and the phase angle  $\delta$ :

$$G^* = \frac{\sigma}{\gamma} = \frac{\sigma_0 \exp(i\omega t)}{\gamma_0 \exp(i(\omega t - \delta))} = \frac{\sigma_0}{\gamma_0} \exp(i\delta)$$
(23)

Euler's formula allows for the separation of the complex shear  $G^*$  modulus into a real and imaginary part, G' and G'':

$$G^* = \frac{\sigma_0}{\gamma_0} (\cos \delta + i \sin \delta) = G' + iG''$$
(24)

The first part, G', is called the *storage modulus*, as it captures the compound's elastic properties:

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \tag{25}$$

The second part, G", is called the *loss modulus*, which captures the compound's viscous properties:

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \tag{26}$$

The extent of the storage and the loss modulus contributions to the complex shear modulus  $G^*$  can be estimated from the ratio of the loss and the storage modulus, G''/G'.

$$\frac{G''}{G'} = \frac{\frac{\sigma_0}{\gamma_0} \sin \delta}{\frac{\sigma_0}{\gamma_0} \cos \delta} = \frac{\sin \delta}{\cos \delta} = \tan \delta$$
(27)

The result, the tangent of  $\delta$ , is the so-called the *loss tangent*. It is a measure of the elastic and the viscous parts to a sample's viscoelastic properties. According to eq. (27), a loss tangent value smaller than one, tan  $\delta < 1$ , signifies that the compound's viscoelastic properties are dominated by its elastic contribution. A loss tangent value larger than one, tan  $\delta > 1$ , on the other hand signifies that the compound's viscoelastic properties are dominated by its viscous contribution. Both the elastic and the viscous parts contribute equally, when the loss tangent has a value of one, tan  $\delta = 1$ .

#### 1.3.2. The Maxwell Model

Many mechanical models exist to mathematically describe the unique properties of viscoelastic materials. The two most prominent are the *Maxwell model* and the *Kelvin–Voigt model*.<sup>88</sup> Whereas the latter is commonly used to predict the creep of soft materials under stress, the former is the best suited to model the relaxation behavior of polymers after a stress load is removed.<sup>89</sup> Stress relaxation, in particular the relaxation time  $\tau$  that describes the time a material needs to return from a perturbed state back to equilibrium, is a key parameters in the study of polymer dynamics. The Maxwell model is represented by a purely viscous damper and a purely elastic spring that are connected in series, the so-called *Maxwell* element shown in Figure 1.13.

When a stress load  $\sigma$  is applied to Maxwell element by an external deforming force, the elastic spring deforms instantly. This is then followed by a delayed and irreversible deformation of the viscous damper that tries to relax the stress in the deformed spring. Residual stress is stored elastically in the system when relaxation is not allowed to come to completion. Once the stress  $\sigma$  is released, only the elastic spring snaps back to its original position. The viscous damper remains deformed irreversibly. The applied stress  $\sigma$  is equal in both parts of the Maxwell element:

$$\sigma = \sigma_1 = \sigma_2 \tag{28}$$

The total shear strain is the sum of the strains of the two individual parts:

$$\gamma = \gamma_1 + \gamma_2 \tag{29}$$



**Figure 1.13.** Schematic of a *Maxwell* element, which is a purely viscous damper and a purely elastic spring connected in series. Reprinted with permission from W. Schmolke, S. Seiffert, *Physical Chemistry of Polymers Part 2, 2<sup>nd</sup> Edition*, Mainz, **2019**.

Deriving the time dependence of eqs. (28) and (29) and solving the resulting differential equation for the boundary condition of constant deformation yields an expression for the time-dependent stress  $\sigma(t)$ :

$$\sigma(t) = \sigma_0 \cdot \exp\left(-\frac{Gt}{\eta}\right) = \sigma_0 \cdot \exp\left(\frac{-t}{\tau}\right)$$
(30)

Here,  $\boldsymbol{\tau}$  is the relaxation time that is given as

$$\tau = \frac{\eta}{G} \tag{31}$$

The *relaxation time* connects the shear modulus *G* and the viscosity  $\eta$ . In a viscoelastic medium,  $\tau$  is the *characteristic time of molecular rearrangement*. On timescales longer than the relaxation time  $\tau$ , the molecules are able to fully rearrange themselves, and viscous flow dominates the viscoelastic properties. By contrast, on timescales shorter than the relaxation time  $\tau$ , the molecules do not have sufficient time to rearrange themselves, and elastic energy storage dominates the viscoelastic properties.

Applying the Maxwell model to an oscillatory shear rheology experiment generates:

$$G^* = \frac{\sigma}{\gamma} = \frac{\sigma_0 \exp(i(\omega t + \delta))}{\gamma_0 \exp(i\omega t)}$$
(32)

This expression can also be written as:

$$G^* = \frac{G_p \cdot \tau \cdot i\omega}{\tau \cdot i\omega + 1} = G' + iG''$$
(33)

Here,  $G_p$  is the plateau modulus. It denominates the maximal value of the storage modulus G' on very short timescales.

Again, we can split the complex shear modulus  $G^*$  into the storage modulus G' and the loss modulus G'' according to eq. (24):

$$G'(\omega) = G_{\rm p} \cdot \frac{\omega^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} \tag{34}$$

$$G''(\omega) = G_{\rm p} \cdot \frac{\omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} \tag{35}$$

At low frequencies,  $\omega^2 \cdot \tau^2 \ll 1$  and the numerator of eqs. (34) and (35) dominate the expressions, leading to straight-line graphs when plotted in a double-logarithmic representation, with a slope determined by the exponent of the frequency  $\omega$ .



**Figure 1.14.** Double-logarithmic representation of the frequency-dependent shear modulus  $G(\omega)$  according to the Maxwell model, eqs. (34) and (35).

Figure 1.14 shows such a log–log plot, in which we find a slope of two for the storage modulus G', and a slope of one for the loss modulus G''. In this regime, the polymer system can relax fully, as the polymer chains have enough time to relax back to their equilibrium conformations after shear deformation. The material's mechanical properties are dominated by its viscous contribution. At high frequencies,  $\omega^2 \cdot \tau^2 >> 1$ , so that many of the variables in the numerator and in the denominator cancel out. For the storage modulus G', no frequency dependence remains, such that its graph is a flat line that corresponds to the plateau modulus G<sub>p</sub>. For the loss modulus G'', a frequency dependence of  $\omega^{-1}$ remains. In this regime, there is not enough time for full relaxation of the system, and the material behaves as an elastic solid. This becomes more and more dominant the shorter the timescale is. Both the storage and the loss modulus, G' and G'', have the same value of one half of the plateau modulus G<sub>p</sub> at the terminal relaxation time  $\tau_0$ . It denotes the time the polymer chains take to rearrange themselves over a distance that is equal to their own size. Polymers display terminal relaxation times  $\tau_0$ in the milliseconds to seconds range.

#### **1.4. Supramolecular Polymers**

#### 1.4.1. Introduction

Upon receiving the Nobel Prize in chemistry for his work on host–guest chemistry, Jean-Marie Lehn called supramolecular chemistry a "chemistry beyond the molecule". His argument is based on the fact that supramolecular compounds in general, and supramolecular polymers specifically, employ *non-covalent* secondary interactions such as hydrogen bonding<sup>90-92</sup>, metal–ligand coordination,<sup>93-95</sup>  $\pi$ – $\pi$  stacking,<sup>96, 97</sup> or host–guest interactions.<sup>98, 99</sup> An overview of the different kinds of transient chemical bonds and their respective energies are shown in Figure 1.15. The transient bonds render supramolecular materials inherently dynamic,<sup>100-103</sup> and they are therefore able to respond to external stimuli or changes in their chemical environment. It is possible to introduce defined structural changes on adjustable time scales into well-known and otherwise chemically stable polymeric materials by combining supramolecular binding motifs with polymer chemistry.



**Figure 1.15.** Overview of binding energies corresponding to the nature of the (transient) bond. Reprinted with permission from E. Van Ruymbeke, *J. Rheol.* **2017**, *61*, 1099-1102. Copyright 2017, The Society of Rheology.

This makes supramolecular polymer systems a promising platform for self-healing,<sup>104, 105</sup> drug delivery,<sup>106, 107</sup> or shape memory<sup>108, 109</sup> materials. Nowadays, supramolecular polymer chemistry research has many active fields of research that investigate topics such as supramolecular polymers,<sup>100, 103, 110</sup> host–guest complexes<sup>111-113</sup> or self-assembly processes.<sup>97, 114-116</sup>

Supramolecular polymers can be synthesized mainly by two different approaches. In the first, low molar mass compounds that can form transient bonds are used. These precursors carry multiple functional groups that are either homocomplementary (A–A type) or heterocomplementary (A–B type). Upon formation of the transient bonds, nanometer-scale aggregates are formed, sometimes with exquisite structural control.<sup>97, 116, 117</sup> This process is called *supramolecular polymerization*. In the second approach, polymeric compounds are functionalized with transient binding motifs *after the initial polymerization* has already taken place, either along the polymer chain or at its ends. The transient bonds then act as supramolecular cross-linker units so that these compounds undergo dynamic supramolecular chain-extension<sup>118, 119</sup> or formation of supramolecular networks.<sup>120-122</sup>

## 1.4.2. Poly(ethylene glycol)

Many supramolecular polymers are based on linear poly(ethylene glycol), or PEG. Its structure is depicted in Scheme 1.3. It is a commercially available polyether backbone polymer that is prepared by anionic polymerization of ethylene oxide and can be purchased in a wide range of molar masses. It has very low polydispersity due to the anionic synthesis pathway. Its free hydroxyl end-groups are easy to chemically convert into other functionalities such as azides,<sup>95, 119</sup> epoxides,<sup>123, 124</sup> amines<sup>94, 125</sup> or active esters.<sup>119, 124</sup> Additionally, various architectures of PEG such as linear, dendrimer and multi-arm can be prepared. PEG is highly soluble in water and many organic solvents such as methanol, chloroform, tetrahydrofuran, toluene, and dimethyl sulfoxide. All these reasons render PEG a versatile material platform for model system studies to investigate supramolecular polymer gels and solutions.



**Scheme 1.3.** Chemical structure of linear poly(ethylene glycol).

Additionally, PEG as well as PEG-based hydrogels are believed to be non-toxic and unable to facilitate cell or protein interaction,<sup>126</sup> which is why the United States Food and Drug Administration (FDA) has cleared them for use.<sup>127</sup> As a consequence, PEG and PEG-containing formulations are widely found in cosmetics, as food additives, and have been studied extensively as possible medical drug carriers<sup>128-130</sup> or cell encapsulation,<sup>127</sup> although there are some warning signs that FDA clearance might have been premature.<sup>131</sup>

#### 1.4.3. Supramolecular Poly(ethylene glycols) and Metal–Ligand Coordination

Supramolecular polymers based on PEG are made via the second pathway to supramolecular polymers mentioned in section 1.4.1: the transformation of functional groups attached to an already polymerized compound. In the case of PEG, it is end-group functionalization, specifically, as the polyether backbone is not reactive. Different supramolecular PEG polymers can be synthesized according to the architecture of the PEG precursor. A supramolecular polymer made from multi-arm PEG will result in a supramolecular polymer network,<sup>29, 95, 118, 124</sup> whereas supramolecular polymers made from linear PEG lead to either dimerization (functionalization of only one end group)<sup>132</sup> or chain-extension (functionalization of both end groups).<sup>118, 119, 133</sup>

Supramolecular PEG polymers can be prepared from various secondary interactions. Out of these many possibilities, metal complexation is of particular interest. Judging from Figure 1.15, metal–ligand coordination is somewhat of an odd entry. Its binding energy  $(30–300 \text{ kJ} \cdot \text{mol}^{-1})$  lies in between those of weaker transient bonds  $(\pi-\pi \text{ stacking: } 1-10 \text{ kJ} \cdot \text{mol}^{-1}; \text{ hydrogen bonding: } 5-100 \text{ kJ} \cdot \text{mol}^{-1}$  and covalent bonds  $300-1000 \text{ kJ} \cdot \text{mol}^{-1}$ ).<sup>134</sup> Metal–ligand coordination binding energies span the entire gap from purely supramolecular to purely covalent bonds, which makes it a suitable candidate for model studies.<sup>95, 119, 135</sup> The binding energies can be adjusted by simply choosing different ligand–metal ion combinations to represent the entire range from a weak transient bond to a covalent bond.

One of the most prominent ligand system is based on terpyridines (tpy).<sup>118-120, 136-139</sup> This ligand forms stable trivalent chelate complexes with many transition metal ions, as shown in Scheme 1.4. In a seminal publication, Schubert and co-workers copolymerized methyl methacrylate with a terpyridine-functionalized methacrylate comonomer, and showed that addition of transition metal ions at low concentrations led to a marked increase in viscosity.<sup>140</sup> They attributed this to the formation of a metal–terpyridine metallo-supramolecular bond, which they could prove by UV measurements that revealed the characteristic absorption of the metal complex, as well as systematic variations of the complexes' binding strength by employing different metal ions and the observation of a corresponding trend in the viscosity variation. Schubert *et al.* were also the first to combine the terpyridine metallo-supramolecular binding motif with a PEG backbone.<sup>141</sup> They reacted the hydroxyl-termini of linear PEGs with a chlorine-functionalized terpyridine-derivative under basic conditions to generate end-capped tpy-PEG polymers. The work-up, however, was tedious because of the reaction mixture contained both mono- and bifunctionalized tpy-PEGs and required preparative size exclusion chromatography.



Scheme 1.4. Chemical structure of the terpyridine–metal(II) ion metallo-supramolecular bond. Adapted with permission from *Phys. Chem. Chem. Phys.*, 2019, *21*, 19623-19638. Copyright 2019, PCCP Owner Societies.

Recently, a more efficient way to synthesize tpy-PEG compounds on a multi-gram scale has been developed. It is a multi-step synthesis based on the transformation of the terminal hydroxyl groups into azide functionalities and subsequent copper-less thermal azide–alkyne cycloaddition with a suitable alkyne terpyridine-derivative at elevated temperatures.<sup>95, 120</sup> The cycloaddition is carried out under high vacuum to avoid decomposition of the PEG backbone.<sup>142</sup> A copper-catalyzed azide–alkyne cycloaddition cannot be used due to the disruptive effect of the ensuing highly-stable terpyridine–copper metallo-supramolecular bond.<sup>143, 144</sup> A modification of this synthetic pathway to regenerate the hydroxyl group, albeit as a secondary one, has also been published.<sup>123</sup> This is particularly useful to introduce chemical markers such as fluorescent dyes making it possible to investigate the dynamics of these metallo-supramolecular tpy-PEG systems.<sup>124, 145</sup>

#### 1.4.4. Dynamics in Linear Associating Metallo-Supramolecular Solutions and Melts

To describe the dynamics of metallo-supramolecular polymer systems, both in the melt state and in solution, the polymer chain relaxation process described by the relaxation time  $\tau$  is separated into two contributions. The first contribution originates from the diffusive motion of the entire supramolecular polymer assembly, in which the dynamics are either a Rouse-type motion characterized by the Rouse relaxation time  $\tau_{R}$ , or a reptative motion characterized by the reptation time,  $\tau_{rep}$ . This depends on the presence of entanglements between polymer chains: assemblies that do not exhibit entanglements are described by the Rouse time  $\tau_{R}$ , whereas the presence of entanglements leads to a prolonged relaxation process that is captured by the reptation time,  $\tau_{rep}$ . The second contribution stems from the dynamics of the metallo-supramolecular binding motif itself. This is reflected by their bond lifetime  $\tau_{break}$ , which is directly connected to the association-dissociation kinetics of the metallosupramolecular bond. For a low molar mass metal-ligand compound, the bond lifetime  $\tau_{\text{break}}$ corresponds directly to the inverse dissociation constant of the complex itself, k<sub>diss</sub><sup>-1</sup>. However, this is often not the case when a metal-ligand bond is connected to a polymer backbone. Topological factors such as the mobility of the polymer chains, which is markedly different in solutions compared to melts, cause an apparent stability<sup>132, 146, 147</sup> or instability<sup>119</sup> of the metal–ligand bond when compared to their low molar mass counterparts. In these cases, the bond lifetime needs to be renormalized to reflect the changes imparted on the material by their environment. On the theoretical side, Rubinstein and Semenov developed the concept of the renormalized bond lifetime  $\tau_{break}^{*}$  to take this into account.<sup>148</sup>, <sup>149</sup> The more prominent case is a bond lifetime renormalization to longer bond lifetimes. The polymer chain cannot create sufficient spatial separation after the occasional opening of a metal-ligand bond for the non-coordinated ligand to find a new binding partner due to the crowded environment, but instead reassociates with its former binding partner. This effect is amplified when the concentration of non-bonded partners is low or the binding affinity of the associating groups is strong, which is
particularly true for metallo-supramolecular complexes.<sup>143, 144</sup> Loop formation has been shown to be a significant factor altering the viscoelastic spectrum in linear associating supramolecular poylmers.<sup>150, 151</sup> Bond lifetime renormalization is commonly encountered in metallo-supramolecular networks, both in solution<sup>120, 152</sup> and in melt,<sup>110, 122</sup> where the topological constraints are caused by multiple associating motifs on a single molecule, and which rarely open simultaneously to allow for the polymer chain to move freely. Linear associating metallo-supramolecular polymer systems in the melt state show the same markedly prolonged bond lifetime.<sup>132, 146, 147</sup> There are indications that bond lifetime renormalization is reversed when the linear polymer chain is allowed to move more freely. Seiffert *et al.* recently published a study in which they investigated the dynamics in telechelic terpyridine-capped PEG assemblies in the semi-dilute regime. Their results suggest that a polymer chain, once freed from topological constraints, might exert a dragging force on the transient bonds, as the determined dissociation constants of the metal–ligand complexes attached to a polymer backbone were many magnitudes faster compared to a low molar mass compound carrying the same binding motif. This indicates the possible presence of a crossover concentration, after which the transient bond lifetime is prolonged instead of shortened.

A prime technique to investigate the complex dynamics of dynamic metallo-supramolecular solutions and melts is the frequency-dependent oscillatory shear rheology. As elaborated in section 1.3, a key parameter in polymer dynamics, the relaxation time  $\tau$ , is accessible by this method, although it is determined as an effective relaxation time that is composed of the various individual contributions as discussed above. Model studies that systematically vary parameters such as chain length, polymer concentration and metallo-supramolecular bond strength are aimed to explain the complex interplay of metallo-supramolecular and macromolecular dynamics. Figure 1.16A shows an example of such a study, where the authors varied the strength of the metal–ligand coordination by employing different transition metal ions, using a terpyridine-functionalized poly(*n*-butyl acrylate) polymer system.<sup>118</sup> The shift in effective relaxation times  $\tau_{eff}$  (in Figure 1.16A: relative relaxation times  $\tau_{rel}$ ) is immediately noticeable. The authors could show that the effective relaxation times  $\tau_{eff}$  increases in a systematic fashion with the increase in strength of the metallo-supramolecular bond.



**Figure 1.16. (A)** Frequency-dependent storage and loss moduli, *G*<sup>'</sup> and *G*<sup>''</sup>, of linear associating terpyridine-functionalized poly(*n*-butyl acrylate) chains in melt complexed with Ni<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> transition metal ions. The reference corresponds to a polymer without metal ions. Full symbols denote the storage modulus *G*<sup>'</sup>, open symbols denote the loss modulus *G*<sup>''</sup>. Reprinted with permission from F. Zhuge, J. Brassinne, C. A. Fustin, E. van Ruymbeke, J. F. Gohy, *Macromolecules* **2017**, *50*, 5165-5175. Copyright 2017, American Chemical Society. **(B)** Frequency-dependent storage and loss moduli, *G*<sup>'</sup> and *G*<sup>''</sup>, of linearly associating acrylic acid-functionalized poly(*n*-butyl acrylate) chains in melt, grouped into four characteristic relaxation domains. The solid curve denote the storage modulus *G*<sup>'</sup>, the dotted line denote the loss modulus *G*<sup>''</sup>. Reprinted with permission from L. G. D. Hawke, M. Ahmadi, H. Goldansaz, E. van Ruymbeke, *J. Rheol.* **2016**, *60*, 297-310. Copyright 2016, Society of Rheology.

Van Ruymbeke has developed a theoretical model to analyze the experimental rheology data obtained from such studies.<sup>153-155</sup> Originally created to quantitatively predict the linear viscoelastic properties of entangled linear polymers such as the molecular weight distribution, the entanglement and the elastic plateau modulus  $G_0$ , it has been developed further in recent years to better understand the dynamics of linear associating supramolecular polymers.<sup>118, 132, 146, 147</sup> They could show that the relaxation behavior of such polymer systems can be grouped into four relaxation regimes, as shown in Figure 1.16B.<sup>147</sup> In the high frequency regime (zone i), Rouse motion occurs. There, time-scales are so short that only segments of the polymeric assembly can relax. The regime is characterized by a slope of 0.5 for both the loss and the storage modulus, G' and G'', in a log-log representation. In the next regime (zone ii), chains are able to relax either via reptation or contour-length fluctuations but are still trapped due to entanglements. An elastic plateau exists due to the presence of binary associations on top of these entanglements. Both the binary associations as well as the entanglements are considered frozen on this time-scale and the chain segments between two binary associations or entanglements cannot relax by longer range Rouse processes. In zone iii, time-scales are long enough for the binary associations to open and polymer chains now have sufficient time to escape the entanglements and fully relax. The contribution of the supramolecular associations gains importance in this regime. Polymer chains that disconnect from the assembly because a supramolecular association opens can explore their surroundings faster than their still-bound counterparts. Once they reattach, their motion is slowed down again, which causes the relaxation time spectrum to broaden significantly. Whereas the smaller segments are not affected by entanglements, longer assemblies still are to varying degrees. This causes a constraint release mechanism, because entanglements between short and long chains can dissolve quickly owing to the fast relaxation of the short chains. As a consequence, a long chain relaxes more quickly than by a pure reptation process. Zone iii has a characteristic slope of 0.5 for both the storage and loss modulus, G' and G'', in a log-log representation. On long time-scales (zone iv), the terminal relaxation is delayed until the dissociation of a supramolecular binding motif. The low frequency plateau is due to the presence of supramolecular clusters which have a very long relaxation time that is not accessible experimentally.

## **1.5. Dynamic Covalent Polymer Networks**

In some cases, covalently-bonded polymer networks can exhibit dynamic properties. These dynamic polymer networks based on covalent chemical bonds often rely on external energy sources such as heat<sup>156</sup> or UV light<sup>157</sup> to become dynamic, due to the high energies necessary to break and reform such a bond (see Figure 1.15). Depending on the intended use of the material, this can become an advantage, as these external energies can be used as a trigger to iniater the molecular rearrangement for applications such as self-healing.<sup>158, 159</sup> These systems employ thermally or photochemically activated chemical pathways such as reversible Diels–Alder reactions,<sup>160-162</sup> disulfide exchange reactions<sup>163-165</sup> or imine–amine exchange reactions.<sup>166-168</sup> The number of covalent polymer networks that are dynamic at room temperature are limited. Incorporation of boronic ester motifs into polymeric networks has been shown to exhibit ambient temperature self-healing.<sup>169-171</sup> Jin *et al.* have recently reported on a polymer network based on a poly(tetramethylene oxide)glycol backbone equipped covalent ditelluride bonds and with 2-ureido-4[1*H*]-pyrimidinone moieties with supposedly rapid self-healing properties at ambient temperatures under visible light.<sup>172</sup>



Scheme 1.5. (A) Schematic view of a vitrimer network with exchange processes that preserve the total number of links and average functionality of cross-links. (B) The mechanism of the exchange process is a transesterification of hydroxy-ester networks. Reprinted with permission from D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* 2011, *334*, 965-968. Copyright 2011, American Association for the Advancement of Science.

A new class of dynamic covalent polymer networks is based on vitrimers, which change their network structure by thermally activated bond-exchange reactions.<sup>182-185</sup> At high temperatures, they flow like viscoelastic liquids, whereas at low temperatures the bond-exchange reactions are so slow that the materials can be considered "frozen" and they behave like classical thermosets. Developed by Leibler and co-workers,<sup>186-188</sup> vitrimers can be based on a variety of bond exchange mechanisms such as carboxylate transesterification, as shown in Scheme 1.5,<sup>188</sup> transamination of vinylogous urethanes,<sup>189</sup> transalkylation of triazolium salts<sup>190</sup> or olefin metathesis using a Grubbs catalyst.<sup>191-194</sup>

The common denominator in all of the above classes is that they are all based on connecting a reactive chemical group to a polymer backbone to utilize the group's reactive properties to create a dynamic polymer network based on exchange reactions of labile covalent bonds. There is, however, another approach, which creates an inherently dynamic covalent polymer network. This approach is based on a polymer that is very well known, both in research and in industry, and has been known for over a hundred years: the organosilicon polydimethylsiloxane, or PDMS. PDMS is the most widely used silicon-based organic polymer, because it is optically clear, non-flammable and non-toxic.<sup>195, 196</sup> As such, PDMS in used in commercial products like cosmetic skin and hair products,<sup>196-198</sup> lubricants<sup>199</sup>, surfactants,<sup>200</sup> or insulators.<sup>201, 202</sup> As mentioned in chapter 1.1.3, PDMS is also a well-suited material for the construction of microfluidic devices.<sup>43, 45, 46</sup> It was discovered in the 1950s, and the discovery in fact patented,<sup>203, 204</sup> that the introduction of anionic moieties into a PDMS polymer network creates a steady dynamic network-junction restructuring.<sup>205-207</sup>



Scheme 1.6. Covalent bond-exchange mechanism of a living polydimethylsiloxane network. Reprinted with permission from W. Schmolke, N. Perner, S. Seiffert, *Macromolecules* 2015, *48*, 8781-8788. Copyright 2015, American Chemical Society.

In 2012, McCarthy *et al.* drew attention to these findings and demonstrated that PDMS networks polymerized by tetramethylammonium silanolate-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(heptamethylcyclo-tetrasiloxanyl)ethane produced a compound stable to both air and water, in which anionic end groups resided in the material. These could be thermally activated at 90 °C to initiate a restructuring of the network and thus facilitate self-healing.<sup>208,</sup> <sup>209</sup> Seiffert and co-workers expanded on this work and developed a synthesis protocol to make this rearrangement mechanism accessible at ambient temperatures.<sup>105</sup> The nature of the proposed covalent bond exchange is shown in Scheme 1.6 . Additionally, the silanolate tetramethylammonium end-groups can be degraded via thermal treatment at 150 °C to transform the dynamic PDMS network into a non-dynamic one.

# 2. Scientific Goals

Stimuli-responsive and dynamic materials are promising platforms for the design of smart materials able to react to external triggers such as changes in their chemical or physical environment. To rationally design such materials, however, requires a deep and fundamental understanding of their underlying structure–property relationships. This thesis shows by three separate studies that such an understanding is vital both on a conceptual and practical level by extending accepted polymer theory through a model study and using structure–property relationships of known polymer systems to decouple linked macroscopic material parameters as well as to develop self-healing polymeric materials.

Polydimethylsiloxane (PDMS) is an optically clear polymer widely used both in research and industry applications due to its chemical robustness and easy manufacturing process. Much less known is the fact that PDMS networks can also be dynamic. PDMS networks that are anionically polymerized can be dynamic at elevated temperatures, which add self-healing capabilities to the advantageous properties of classical polydimethylsiloxane compounds. This thesis investigates how the structure–property relationship between the synthesis parameters of such anionically polymerized PDMS and the network's resulting two macroscopic properties, mechanical strength and stress-relaxation ability, can be used to introduce ambient temperature self-healing functionality into such a material. It also addresses the question whether these two parameters are connected or can be controlled individually.

Poly(*N*-isopropylacrylamide) (pNIPAAm) is a thermo-sensitive polymer that exhibits marked reversible changes of its polymer–solvent interactions at a lower critical solution temperatures (LCST) of about 32 °C, which results in a volume phase transition (VPT) of the polymer. This LCST-type behavior makes pNIPAAm networks beneficial for the investigation of polymer thermodynamics but is also a promising property for stimuli-responsive materials. During the VPT the microscopic structure is rearranged due to the changing polymer–solvent interactions that is accompanied by a concurrent change of many macroscopic parameters. The polymer's elastic properties change drastically, and so does its interfacial interaction potential. The conjoint use of both these effects can be advantageous, for example to serve in switchable cell culture substrates that allow for temperature-controlled cell adhesion and detachment. However, for a more general material design it is desired to uncouple these two parameters during the VPT process. This thesis addresses whether this is possible by incorporation of thermosensitive pNIPAAm particles in non-thermosensitive polymer shells using droplet-based microfluidics.

Supramolecular polymers have long been identified as possible "materials of the future" due to their inherent dynamic capabilities. They are based on transient interactions such as hydrogen bonding or  $\pi$ - $\pi$  stacking. Another class of transient bonds, metallo-supramolecular bonds between a ligand molecule and a metal ion, can recreate the entire energy-range from a weak transient bond to a non-dynamic covalent bond, which makes them particularly useful for model studies to better understand the interplay between the macromolecular and supramolecular contributions to the material's overall dynamics. Much is known about this interplay for linear associating polymer melts as well as metallo-supramolecular polymer networks, both in the melt state and in solution. This thesis aims to gain insight into the dynamics of linear associating polymers in the semi-dilute regime by designing a modular system based on monodisperse linear polymer chains equipped with a tunable metallo-supramolecular binding motif. Their viscoelastic properties are characterized as well as modelled to understand the structure-property relationships between molecular parameters such as transient bond strength or polymer precursor chain length, and macroscopic properties such as viscosity.

# 3. Publications

**3.1.** Dynamically Cross-Linked Polydimethylsiloxane Networks with Ambient-Temperature Self-Healing



Willi Schmolke, Norman Perner, Sebastian Seiffert, Macromolecules 2015, 48, 8781-8788.

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## Author Contributions:

<u>Willi Schmolke</u>: Polymer synthesis, polymer characterization, rheology measurements and data analysis, piercing test and data analysis, preparation of the manuscript

Norman Perner: Conception of the work, project development, manufacturing of the piercing test device, supervision of the work

Sebastian Seiffert: Supervision of the work, correction of the manuscript

In this manuscript, dynamically cross-linked polymer networks based on polydimethylsiloxane are investigated. They have promising potential to serve as self-healing materials but are often limited to occur at elevated temperature. We overcome this limitation by refinement of an earlier approach to synthesize dynamically cross-linked polydimethylsiloxane networks such to show stress relaxation and self-healing at room temperature on short time scales, which we probe by oscillatory shear rheology and piercing experiments. Our studies reveal a direct correlation between the amount of anionic groups in the polymer networks and their stress-relaxation and self-healing rates, allowing these materials to be designed in a rational fashion.

## 3.1.1. Introduction

Self-healing materials are compounds that have a structurally incorporated ability to repair mechanical damage; they have promising properties for a multitude of applications,<sup>1-14</sup> including those as biomimetics,<sup>6,15-18</sup> as renewable coatings,<sup>18-20</sup> or concrete.<sup>21,22</sup> The approach of design of these materials has two variants. One variant is to include a healing agent within the compound<sup>15-18,21-43</sup> by incorporating it within microcapsules<sup>18,29-43</sup> or hollow tubes<sup>15-17,22,24,25</sup> that are embedded in the material and that fracture if a crack occurs, thereby releasing the healing agent. Many healing agents have been studied for this purpose, including dicyclopentadiene-Grubbs' catalyst systems, 23,29-33 isocyanates<sup>34</sup>, linseed oil,<sup>35</sup> or simple organic solvents,<sup>36-38</sup> allowing even chemically inert compounds such as polydimethylsiloxanes<sup>39-44</sup> to be healed. The intrinsic disadvantage of this strategy is that healing can occur only once at a specific spot. This drawback is overcome in a second approach that realizes an intrinsic healing ability in a material.<sup>4,20,43,45-88</sup> This is achieved by designing systems based on dynamic building-block interconnection, for example, through thermally reversible Diels-Alder reactions,<sup>49-57</sup> redox or photolytically active disulfide bonding,<sup>58-62</sup> aromatic disulfide metathesis<sup>63,64</sup>, pH-responsive boronic-acid esterification,<sup>65-67</sup> as well as noncovalent bonding based on urea,<sup>68-71</sup> ionomers,<sup>72-75</sup> or diverse supramolecular motifs.<sup>20,68,69,76-82</sup> An additional strategy to realize dynamically enforced materials is based on dangling chains in a weak gel, which form reversible entanglements and exhibit cooperative diffusive mobility.<sup>83-88</sup> Furthermore, a relatively new class of self-healing materials is referred to as vitrimers.<sup>71,89-94</sup> These are covalently bonded compounds that constantly undergo thermally activated internal bond exchange. Upon application of a suitable external trigger to start the healing process, all these various systems can undergo multiple damage-healing cycles. Most of these self-healing motifs can be combined with diverse polymer backbones such as robust and versatile polydimethylsiloxane (PDMS), which is a material with prominent utility and prospect in the field of insulation.<sup>39-44,82,95</sup> In fact, a suitable approach for forming self-healing PDMS elastomeric rubbers has long been known: several 1950s patents<sup>96-98</sup> and publications<sup>99,100</sup> give descriptions of reactions that aim at the inclusion of anionic moieties into a PDMS polymer network, which entails steady dynamic network-junction restructuring. However, these early studies miss to perceive the healing abilities that can result from this. Six decades later, in 2012, this aspect was realized and described in a seminal paper by Zheng and McCarthy.<sup>44</sup> Unfortunately, however, elevated temperatures are required for several hours to enable the healing process in this existing approach.

In this article, we present a systematic investigation of the reaction parameters of PDMS dynamicnetwork synthesis such to control their dynamic characteristics, with a specific view to enable stress relaxation and self-healing at room temperature on short timescales. For this purpose, we vary the content of the ionic polymerization initiator tetramethylammonium hydroxide (TMAH). In addition, we concurrently and independently control the materials' mechanical properties by variation of the crosslinker content, which can be adjusted by the amount of the radical-formation reagent dibenzoyl peroxide (DBPO) that is used during the preceding cross-linker synthesis. To determine the mechanical properties of the dynamically cross-linked PDMS networks, we probe them by oscillatory shear rheology, whereas we conduct piercing experiments to probe their dynamic network-junction restructuring and the resulting stress relaxation and self-healing. We find appreciable stress relaxation and self-healing at our target temperature of 25 °C as well as at higher (60 °C) and lower (5 °C) temperatures. The tests also reveal a quantitative dependence of the stress-relaxation rate on the number of ionic chain-ends in the polymer network, which is determined by the concentration of TMAH during the polymerization process.

#### 3.1.2. Results and Discussion

PDMS networks can be prepared by anionic ring-opening polymerization in the presence of a crosslinker.<sup>44,96-99</sup> We prepare such a cross-linker by addition of vacuum-dried dibenzoyl peroxide (DBPO) to a hot solution of octamethylcyclotetrasiloxane, denoted D<sub>4</sub>. Thermal decomposition of the DBPO yields free radicals that cleave a hydrogen–carbon bond in the D<sub>4</sub>. Two resulting D<sub>4</sub> radicals then combine to form the cross-linker *bis*(heptamethylcyclotetrasiloxanyl)ethane (*bis*-D<sub>4</sub>), as shown in Scheme 1a. Its amount can be tuned by the amount of DBPO employed, which, in turn, determines the mechanical strength of the dynamically cross-linked PDMS networks formed thereafter: these are stiff at a high cross-linker content and soft at a low cross-linker content, thereby differing from the strong elastomeric materials originally reported by Zheng and McCarthy.<sup>44</sup>

In addition to *bis*-D<sub>4</sub>, further generation of higher siloxane oligomers has been reported;<sup>101</sup> these are created by hydrogen abstraction at a *bis*-D<sub>4</sub> unit followed by recombination with another D<sub>4</sub> to form *tris*-D<sub>4</sub>,<sup>101</sup> which may then undergo further hydrogen–carbon bond cleavage to create even higher molecular weight D<sub>4</sub>-oligomers. Despite the formation of this mixture of different D<sub>4</sub>-oligomers, however, all of them act as cross-linker molecules during the polymerization. Additional side products, such as benzene,<sup>101</sup> that may arise from decarboxylation of DBPO can be easily removed by filtration over neutral activated aluminum oxide. The <sup>1</sup>H NMR spectrum in Figure 1 confirms the existence of the cross-linker *bis*-D<sub>4</sub> as well as the successful removal of benzene, thereby confirming the purity of the D<sub>4</sub>–*bis*-D<sub>4</sub> reaction mixture.

In a second step, the ionic initiator TMAH is added to the reaction mixture at high temperature. This triggers an anionic ring-opening polymerization to yield the final gellylike product, as shown in Scheme 1b. In this process, side reactions do not occur at a perceptible extent, and the resulting material can be used without further purification. After the reaction, about 6% (v/v) of D<sub>4</sub> remain present as monomeric species in the system.<sup>102,103</sup> Due to its vapor pressure, D<sub>4</sub> evaporates with time.<sup>104,105</sup> To quantify this evaporation for the present set of samples, their weight was determined over time, denoting a loss of 0.83% (w/w) over seven days. As a consequence, long-term applications of these materials require them to be confined in a sealing containment or medium.

With this approach, we obtain a set of dynamically cross-linked PDMS networks whose mechanical properties are controlled by the amount of DBPO employed during the cross-linker synthesis. In addition, the stress-relaxation characteristics of these materials, which further correlates to their self-healing ability, is controlled by the amount of TMAH during the polymerization, because this determines the number of anionic groups in the polymer network that constitute its dynamic cross-linking. Each anionic chain-end in the network is a persistently active species able to heterolytically cleave silicon–oxygen bonds to form new bonds as well as new anionic chain-ends, respectively, as sketched in Scheme 2. This can occur both at the PDMS network chains and at the residual lower molecular weight  $D_4$ -units in the samples due to the equality of the silicon–oxygen bonds in all these compounds, thereby creating an equilibrium between cyclic oligomers and the PDMS chains.<sup>44,99,103</sup> Furthermore, evaporated  $D_4$  will be reformed in the samples by the same mechanism. This dynamics has already been described in a private communication of D. T. Hurd in 1952 as a "catalyzed chain transfer reaction",<sup>100</sup> but the implications have not been recognized until 2012.<sup>44</sup>



**Scheme 1.** (a) Synthesis of the Cross-Linker Bis- $D_{4}$ ;<sup>a</sup> (b) Subsequent Anionic Ring-Opening Copolymerization of  $D_4$  and Bis- $D_4$  yields a Dynamic Polydimethylsiloxane Network with Self-Healing Ability

<sup>a</sup> A hydrogen–carbon bond is cleaved homolytically, such that two D<sub>4</sub> radicals can combine to form bis-D<sub>4</sub>.



**Figure 1.** <sup>1</sup>H NMR spectrum of a reaction mixture of D<sub>4</sub> and bis-D<sub>4</sub> made with a DBPO content of 0.61 mol%. The abscissa denotes the chemical shift  $\delta$  relative to a tetramethylsilane standard ( $\delta$  = 0 ppm). The sample consists predominantly of unreacted D<sub>4</sub> ( $\delta$  = 0.09 ppm). (a) Magnification reveals the signal of the cross-linker molecule bis-D<sub>4</sub> ( $\delta$  = 0.46 ppm). (b) The sole detectable impurity of the reaction, benzene, can only be detected before the purification procedure at ( $\delta$  = 7.36 ppm).<sup>101,106</sup> The adjacent peak at  $\delta$  = 7.26 ppm corresponds to residual chloroform in the deuterated solvent CDCl<sub>3</sub>.<sup>106</sup>



Scheme 2. Proposed Dynamic Cross-Linking Mechanism of Ionic Polydimethylsiloxane Networks<sup>a</sup>

<sup>*a*</sup> An anionic chain end cleaves a silicon–oxygen bond via nucleophilic attack such that a new silicon–oxygen bond and a new anionic chain end are formed. The new chain end can then undergo the same reaction elsewhere in the network.

The mechanical strength of the different dynamically cross-linked PDMS networks is reflected by their elastic storage moduli, G', which we probe by oscillatory shear rheology at a constant frequency ( $\omega = 0.1$  Hz) and shearing amplitude ( $\gamma = 0.01$ ) at 25 °C, as assembled in Table 1. A high content of DBPO during the PDMS network synthesis leads to more cross-links, which, in turn, leads to a high value of G'. To quantitatively describe this interdependence, we apply the phantom network model based upon the theory of rubber elasticity.<sup>107</sup> It connects the dynamic complex shear modulus, G, to the molar concentration of elastically effective tetrafunctional cross-links, v, as v = G/(RT), with R the universal gas constant and T the temperature. Due to the relative insignificance of the viscous part of the modulus, G'', in the present set of polymer networks, G can be approximated to be dominated by its elastic part G', and hence, v can be approximated as v = G'/(RT). With this formula, we calculate  $v_{exp}$  = 3.8–4.6 mmol·L<sup>-1</sup> for a DBPO content of 0.12 mol%,  $v_{exp}$  = 6.1–6.9 mmol·L<sup>-1</sup> for a DBPO content of 0.37 mol% and  $v_{exp} = 6.3-7.7$  mmol·L<sup>-1</sup> for a DBPO content of 0.61 mol%. In a hypothetic ideal situation, every cross-linker molecule provides one elastically effective tetrafunctional connection in the network, resulting in theoretically achievable values of  $v_{theo}$  = 4.2 mmol·L<sup>-1</sup> for a DBPO content of 0.12 mol%,  $v_{theo}$  = 13.0 mmol·L<sup>-1</sup> for a DBPO content of 0.37 mol%, and  $v_{theo}$  = 21.5 mmol·L<sup>-1</sup> for a DBPO content of 0.61 mol%.

DBPO (mol%)ª	TMAH (mol%)ª	<i>G</i> ' (Pa)	<i>G</i> " (Pa)	tan δ	v <sub>exp.</sub> (mmol·L <sup>−</sup> ¹) <sup>b</sup>	v <sub>theo.</sub> (mmol·L <sup>−</sup> ¹) <sup>b</sup>
0.12	1.63	11500	2900	0.25	4.6	4.2
0.12	2.44	10500	3100	0.29	4.2	4.2
0.12	3.25	9500	3100	0.33	3.8	4.2
0.37	1.63	17100	4300	0.25	6.9	13.0
0.37	2.44	16300	4300	0.26	6.6	13.0
0.37	3.25	15200	4400	0.29	6.1	13.0
0.61	1.63	19000	2000	0.10	7.7	21.5
0.61	2.44	17700	2300	0.13	7.1	21.5
0.61	3.25	15600	2800	0.18	6.3	21.5

**Table 1.** Elastic and viscous shear moduli, G' and G'', and their ratio,  $\tan \delta = G''/G'$ , in dynamically cross-linked polydimethylsiloxane networks prepared with different concentrations of DBPO and TMAH.

<sup>a</sup>: Mol% in the prepolymer reaction mixture.

<sup>b</sup>: Polymer-network structural characteristics are estimated from the rheological data on basis of the phantom network model:<sup>107</sup> v<sub>exp</sub>: molar concentration of tetrafunctional cross-linking junctions in the polymer network, calculated as v = G'/(RT); v<sub>theo</sub>: ideal theoretically achievable molar concentration of cross-linking junctions in the polymer network calculated from the cross-linker concentration.



**Figure 2.** (a) Testing device to conduct piercing experiments on the present set of dynamic polydimethylsiloxane networks. An electric motor is connected to a pressure-sensitive sensor, to which a brass pin with a diameter of 3 mm is mounted. The sample is fixed below the pin. (b, c) Force curves of piercing experiments recorded with varying pin velocities at a constant temperature of 25 °C (b) and with a constant pin velocity of 2 mm·s<sup>-1</sup> and varying temperature (c). The tested dynamically cross-linked PDMS network was made using 0.37 mol% of DBPO and 3.25 mol% of TMAH. (b) Velocity-dependent measurements show a linear dependence of the force-curve amplitude on the pin velocity: as the movement speed of the pin is increased, positive and negative peak-force values increase in proportion. (c) Temperature-dependent force measurements show that the force needed for the piercing process is lower at higher temperature. The inset displays the relaxation part of the force curve recorded at 5 °C. Also shown is a fit to determine the relaxation time of the material according to  $F(t) = F_{\infty} + (F_0 - F_{\infty}) \exp(-t/\tau)$  (dotted line in the inset).

For the lowest DBPO content of 0.12 mol%,  $v_{exp}$  closely matches the ideal value of  $v_{theo}$ . At higher cross-linking degrees, by contrast, the experimental results differ from the ideal case. For a DBPO content of 0.37 mol%, the cross-linking efficiency is lower,  $v_{exp}/v_{theo} \approx 0.5$ , and an even lower cross-linking efficiency of just  $v_{exp}/v_{theo} \approx 0.3$  is evident at an even higher cross-linker content of 0.61 mol%. It has been reported that a higher cross-linker content during polymer network syntheses is connected to a higher probability of occurrence of non-ideal reactions such as cyclization or multiple local cross-linking.<sup>108-111</sup> We consider this conceptual picture for our system, too. On top of that, we consider another reason: during the network formation, the liquid D<sub>4</sub> and *bis*-D<sub>4</sub> become a viscoelastic transient polymer network, especially because the synthesis is carried out in bulk. This effect lowers the cross-linker mobility within the forming network, thereby leading to more heterogeneous spatial distribution of its cross-linking nodes that causes a lower degree of elastically effective cross-linking.<sup>112</sup>

The PDMS-network elasticity is also affected by the concentration of TMAH used to trigger the anionic polymerization: when this concentration is doubled at constant concentration of DBPO, G' drops by about 10%, accompanied by an increase of the viscous modulus, G'', of about 10% as well. As a result, the loss tangent, tan  $\delta = G''/G'$ , systematically increases with increasing concentration of TMAH at a given concentration of DBPO, as summarized in Table 1. We explain these findings on the basis of the dynamic network-restructuring mechanism described above: as more polymer chains are generated

at a higher concentration of the polymerization initiator, more anionic chain-ends are present in the PDMS network. This higher number of active end groups results in a higher probability of the chain transfer reaction illustrated in Scheme 2 to occur, such that the network gets more dynamic. As a result, the viscous parts of the materials' viscoelastic properties are pronounced.

To further quantify the stress-relaxation characteristics of the dynamically cross-linked PDMS networks, we probe them by piercing tests on a self-built device, as shown in Figure 2a. The experimental setup is adapted from established atomic force microscopy, where partial mechanical stress and potential damage are exerted to polymer-gel samples along with concurrent quantitative probing on a microscopic length-scale.<sup>112-114</sup> Our device is built to semi-quantitatively probe the same properties on a macroscopic length-scale that is more relevant for large-scale technical applications of PDMS. The device consists of a sled on which a pressure-sensitive sensor is mounted. This sensor is connected to a brass pin with a diameter of 3 mm carrying a conically shaped tip. The sensor-tip array can be moved on the sled by an electrical motor with speeds of  $0.1-10 \text{ mm} \cdot \text{s}^{-1}$ . The velocity can be adjusted in steps of  $\pm 0.1$  mm·s<sup>-1</sup>. The pin is pierced 6 mm deep into the sample, remains immobile for 5 s, and is then retracted with the same speed into the opposite direction. A force sensor registers shear and tensile forces that occur during this process. During piercing of the pin, the force linearly increases with a slope depending on the pin-movement speed. While resting the pin within the sample for 5 s, force relaxation becomes evident by an exponential decrease of the force until the pin is retracted by movement into the opposite direction, upon which the resulting force linearly redecreases. The force eventually drops below 0 N due to adhesion of the sample to the pin until it reaches a threshold. At this point, the widening gap between pin and sample is forcing the adhered PDMS to flow alongside the pin wall, entailing a decrease of the adhesive force. To ensure reproducibility of these data, repeat measurements were carried out over a timeframe of two months, yielding indistinguishable results. Advantageously, our experimental approach is insensitive to potential uncertainty that may arise in more microscopic methods such as atomic force microscopy due to nano- and micrometer-scale spatial heterogeneities that are common structural features in polymer networks.<sup>112</sup> This is because our self-built setup shown in Figure 2a probes the dynamically cross-linked PDMS networks on length-scales larger than such polymer-network heterogeneity, thereby averaging over it. To also prevent potential further artifacts caused by heterogeneities on larger length-scales in the samples, as they may be caused by mixing heterogeneities of the gelling components, each sample was rotated between repeat measurements to pierce and probe different sample positions with a spacing of several mm, denoting independence of the results of the measuring position.

The differences in the mechanical stiffness of our present set of samples can be determined by the amplitude of the force curves recorded in these piercing tests: generally, a lower force is necessary to drive the pin into a softer PDMS network. At 25 °C, a typical peak value at the moment of 6 mm piercing is 7.5 N for a sample prepared with a DBPO content of 0.61 mol% and a TMAH content of 2.44 mol%, whereas only 2.4 N are needed for such piercing of a sample prepared with the same TMAH amount but a lower DBPO amount of only 0.12 mol%.

The sample exhibits peak values of 4.7 N at 6 mm piercing and -1.9 N under retraction at 5°C, whereas these values drop to 2.4 N and -1.3 N, respectively, at 60 °C. We presume that a higher temperature better activates diffusive movement of the chains within the dynamic networks, thereby allowing breakage and (re-)formation of bonds to occur at higher rates, which results in a softer material.<sup>48</sup>

DBPO (mol%) <sup>a</sup>	TMAH (mol%) <sup>b</sup>	<i>Т</i> (°С)	τ (s)
0.12	1.63	5	2.17
0.12	2.44	5	2.00
0.12	3.25	5	1.92
0.37	1.63	5	2.29
0.37	2.44	5	2.20
0.37	3.25	5	2.16
0.61	1.63	5	2.49
0.61	2.44	5	2.36
0.61	3.25	5	2.26
0.12	1.63	25	1.99
0.12	2.44	25	1.93
0.12	3.25	25	1.83
0.37	1.63	25	2.11
0.37	2.44	25	2.01
0.37	3.25	25	1.90
0.61	1.63	25	2.19
0.61	2.44	25	2.09
0.61	3.25	25	2.00
0.12	1.63	60	1.75
0.12	2.44	60	1.64
0.12	3.25	60	1.51
0.37	1.63	60	1.87
0.37	2.44	60	1.74
0.37	3.25	60	1.67
0.61	1.63	60	1.97
0.61	2.44	60	1.79
0.61	3.25	60	1.69

**Table 2.** Relaxation times, τ, of dynamically cross-linked polydimethylsiloxane networks prepared with different amounts of DBPO and TMAH and probed by piercing experiments as shown in Figure 2.

<sup>a</sup>: Measurements were carried out at 5, 25, and 60 °C. The relaxation times were determined by single-exponential data fitting of the part of the force curve where the pin remains immersed within the sample and does not move. Fitting was done according to the equation  $F(t) = F_{\infty} + (F_0 - F_{\infty}) exp(-t/\tau)$ .

<sup>b</sup>: Mol% in the prepolymer reaction mixture.

The stress-relaxation characteristics of the dynamically cross-linked PDMS networks are determined by examination of the relaxation parts of the force curves, which is those parts where the pin is fully immersed within the sample but remains motionless. During these 5 s, the compounds' viscous properties and the dynamic chain exchange reaction illustrated in Scheme 2 cause a time-dependent exponential decay of the measured force. We obtain the relaxation times,  $\tau$ , by fitting these relaxation parts of the force curves with the function  $F(t) = F_{\infty} + (F_0 - F_{\infty}) \cdot \exp(-t/\tau)$ , with  $F_{\infty}$  the asymptotic relaxation plateau value at  $t \rightarrow \infty$  and  $F_0$  the initial force at t = 0. The relaxation time  $\tau$  is a measure of systems' network-junction restructuring dynamics: the shorter  $\tau$ , the better does the network accommodate the applied piercing forces by restructuring, which further correlates to better self-healing.

We presume  $\tau$  to reflect multiple contributions, among which the main contributors are expected to stem from the kinetics of the anionic chain exchange reaction, as also described for vitrimers, 71,89-92 and the topologically constrained diffusive chain mobility in the polymer network, which is both synergistically promoted by an increase of temperature.<sup>48</sup> In agreement to this presumption, we find that  $\tau$  is dependent on (i) the concentration of ionic groups in the polymer network, as determined by the amount of TMAH employed during its synthesis, (ii) the amount of cross-linker, as determined by the amount of DBPO employed during the cross-linker synthesis, and (iii) on temperature. This is plausible by considering the above-proposed dynamic network-restructuring mechanism: when the concentration of anionic chain-ends is increased, the likelihood of the chain exchange reaction sketched in Scheme 2 to occur is raised as well. The transient PDMS networks then become more dynamic, and as a result they better accommodate external forces imposed during piercing. In agreement with this conceptual picture, we observe a linear dependence of the inverse relaxation time as a function of the TMAH concentration in the range of c(TMAH) = 1.5-3.5 mol%, as shown in Figure 3. Although the changes are small, the trend is systematic and reproducible for all samples and all measurement temperatures. A similar argument is valid for temperature changes, as both the dynamic exchange reaction sketched in Scheme 2 and the diffusive movement of the chains within the network is activated by temperature.<sup>48</sup> By contrast, the DBPO content has an opposite effect, because more cross-links in the PDMS networks limit the chain diffusive movement.

In addition to  $\tau$ , also the asymptotic force-relaxation plateau value,  $F_{\infty}$ , is of interest. It does not decay to zero in all our experiments, which is because the dynamic PDMS networks probed in these are viscoelastic materials, such that some of the energy introduced to the system during the piercing process is stored elastically. This energy storage is reflected in  $F_{\infty}$ . We believe that this finite elastic energy storage is in fact an important prerequisite for a fully functioning self-healing process. The stored energy is released as soon as the pin is retracted, such that the surfaces of the specimen inside the cavity created by the pin are brought into contact again, and only when they touch can the dynamic chain exchange reaction sketched in Scheme 2 take place to cause self-healing. On top of that, if there was no elastic component in the viscoelastic response of these samples, they would flow away in the longtime limit, preventing them to be used in applications.



**Figure 3.** Inverse relaxation time,  $\tau^{-1}$ , as a function of the anionic initiator concentration *c*(TMAH). Dynamically cross-linked PDMS networks were probed at a temperature of 25 °C. The dashed line denotes a DBPO concentration of 0.12 mol% during the synthesis, the dotted-dashed line denotes a DBPO concentration of 0.37 mol%, and the dotted line denotes a DBPO concentration of 0.61 mol%.



**Figure 4.** Images of a piercing experiment carried out at 25 °C (conducted by hand). The tested dynamically cross-linked PDMS network was made using 0.61 mol% of DBPO and 3.25 mol% of TMAH. The top-left labels denote the experimental timescale. First, (10 s exp. time) a pin is driven into the PDMS from the top and then (30 s exp. time) retracted from the sample after remaining immobile within the sample for 5 s. Directly after the pin retraction, (45 s exp. time), traces of the pin's movement are still visible in the sample (encircled region), but just 15s later, (60 s exp. time) these traces have disappeared.

We find that the residual force value  $F_{\infty}$  depends on the amount of DBPO used during the polymernetwork synthesis.  $F_{\infty}$  is roughly 40% of the peak force value for a DBPO content of 0.12 mol%, 50% for a DBPO content of 0.37 mol%, and 60% for a DBPO content of 0.61 mol%, independent of the number of active chain-ends as well as the measurement temperature. This finding is in qualitative agreement to the above rationale: as  $F_{\infty}$  is related to elastic-energy storage in the materials, it is related to G', which, in turn, was found to be proportional to the amount of DBPO used during the polymernetwork synthesis, as discussed above.

To demonstrate the ability of the dynamically cross-linked PDMS networks for rapid self-healing at room temperature, we further inspect one of our piercing experiments, as shown in Figure 4. Upon retraction of the pin from the material, a damaged trace is left within the sample for about 15 s. Afterwards, however, this trace fully disappears and the material has healed. Repetition of the piercing experiment at the exact same spot produces the same result repeatedly. Experiments conducted at different temperatures show healing times slightly longer (+3 s) at 5 °C or slightly shorter (-2 s) at 60 °C, in agreement to the related tendencies in the temperature-dependence of the relaxation time.

#### 3.1.3. Conclusion

Dynamically cross-linked PDMS networks can be prepared by anionic ring-opening polymerization of octamethylcyclotetrasiloxane (D<sub>4</sub>) and its dimeric form *bis*-D<sub>4</sub>. Variation of the concentration of dibenzoyl peroxide (DBPO) and tetramethylammonium hydroxide (TMAH) during this synthesis allows the mechanical strength and stress-relaxation ability of the resulting networks to be tuned independently; in particular, suitable choice of these parameters allows them to be formed with the ability to heal at ambient temperatures on a timescale of just several seconds. These dynamically cross-linked PDMS networks have the advantageous properties of classical polydimethylsiloxane rubbers, including chemical robustness, non-toxicity, and hydrophobicity, but they also exhibit room-temperature stress relaxation and self-healing. Even though evaporation of persistent monomeric D<sub>4</sub> necessitates potential long-term applications of these materials to be realized in a sealed environment, the present approach still can add room-temperature self-healing as a beneficial property to many of the established applications of classical polydimethylsiloxane networks.

#### 3.1.4. Experimental Section

**Chemicals:** Octamethylcyclotetrasiloxane (D<sub>4</sub>) was purchased from ABCR and stored over molecular sieves. Dibenzoyl peroxide (DBPO) was purchased from Alfa Aesar. Tetramethylammonium hydroxide pentahydrate (TMAH) was purchased from Sigma Aldrich. All these chemicals were used without further purification. All reactions were carried out under dry conditions.

**Spectroscopy:** <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 400 digital FT-spectrometer at 400 MHz in CDCl<sub>3</sub> at 25 °C. Chemical shifts reported in ppm are referenced to trimethylsilane (TMS) as an internal standard using  $\delta$ (TMS) = 0 ppm. IR spectra were recorded on a Nicolet iS10 FT-IR-spectrometer with a DTGS-detector by Thermo Scientific.

Synthesis of the octamethylcyclotetrasiloxane–*bis*(heptamethylcyclotetrasiloxanyl)ethane (D<sub>4</sub>– *bis*-D4) reaction mixture: Dibenzoyl peroxide (DBPO) was placed in a Schlenk flask and subjected to high vacuum for at least 15 min. Octamethylcyclotetrasiloxane (D<sub>4</sub>) was added, and the solution was heated to 120 °C for 2 h. The solution was then filtered over neutral activated aluminum oxide 90 and stored over molecular sieves. If yellowish-colored side products were formed, this was interpreted as an indication for insufficient drying of the DBPO; the reaction was then dismissed and repeated after more extensive drying. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.46 (s, -CH<sub>2</sub> of *bis*-D<sub>4</sub>), 0.09 (s, -CH<sub>3</sub> of D<sub>4</sub>). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.56. 0.96. <sup>29</sup>Si-NMR (79 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –18.72.

Synthesis of the dynamically cross-linked polydimethylsiloxane (PDMS) networks: A mixture of octamethylcyclotetrasiloxane (D<sub>4</sub>) and *bis*(heptamethylcyclotetrasiloxanyl)-ethane (*bis*-D<sub>4</sub>) was poured in a Schlenk flask and heated to 110 °C. Tetramethylammonium hydroxide pentahydrate (TMAH) was added quickly under rapid stirring. The onset of solidification was observed by a marked increase of the viscosity as well as by turbidity that later faded during the reaction. After 4 h the reaction was finished and the hot, highly viscous pre-polymer fluid could be poured into a custom mold for solidification. IR (thin film)  $v_{max}$  (cm<sup>-1</sup>): 2962 (m), 1412 (w), 1257 (s), 1070 (s), 1010 (vs), 864 (m), 787 (vs), 699 (m).

**Evaporation test:** A sample of 14.279 g of a dynamically cross-linked polydimethylsiloxane PDMS made with 0.12 mol% of DBPO and 3.25 mol% of TMAH was poured into a glass vial with a cross section of 19.63 cm<sup>2</sup> (r = 2.5 cm) and left to stand at room temperature for evaporation over a time of seven days. The mass of the sample was determined twice p)r day. The weight loss due to seven-day evaporation was measured to be 118 mg or 0.83% (w/w) of the initial sample mass.

**Rheology:** Rheological studies were performed on a strain-controlled Rheometrics Fluids Spectrometer II with parallel plate–plate geometry (plate diameter 25 mm) at a temperature of 25 °C. For sample preparation, a slice of each compound was cut using a scalpel and placed on the lower plate. Then the upper plate was lowered until contact. The gap between the plates was determined before each measurement due to differences in the PDMS slice thicknesses. Each sample was measured for at least 1 h at a constant shearing amplitude ( $\gamma = 0.01$ ) and frequency ( $\omega = 0.1$  Hz).

**Piercing tests:** Piercing experiments were performed on a self-built testing device consisting of a software-controlled motorized sled opposed by a sample retainer at 5 °C, 25 °C, and 60 °C. The sled carries a mounting for pins with a diameter of 2–6 mm and can be precisely moved over a distance of 25 cm with a speed of 0.1–10 mm·s<sup>-1</sup>. The pin was pierced 6 mm deep into the sample, remained immobile for 5 s, and was then retracted with the same speed into the opposite direction. A force sensor registered shear and tensile forces occurring during this process. The sample was rotated in

between reapeat measurements. In addition, reproducibility was checked by repeat measurements over a timeframe of two months.

## 3.1.5. Acknowledgement

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3.2. Core–Shell Microgels with Switchable Elasticity at Constant Interfacial Interaction

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## Author Contributions:

Maximilian Seuss: Colloidal probe atomic force microscopy measurements and data evaluation, interfacial interaction calculations, swelling measurements and data evaluation, preparation of the manuscript

**Willi Schmolke:** Polymer synthesis and functionalization, polymer characterization, construction of microfluidic devices, microfluidic templating and encapsulation, colloidal probe atomic force microscopy measurements and data evaluation, swelling measurements and data evaluation, preparation of the manuscript

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In this work, Hydrogels based on poly(*N*-isopropylacrylamide) (pNIPAAm) exhibit a thermo-reversible volume phase transition from swollen to deswollen states. This change of the hydrogel volume is accompanied by changes of the hydrogel elastic and Young's moduli and of the hydrogel interfacial interactions. To decouple these parameters from one another, we present a class of sub-millimeter sized hydrogel particles that consist of a thermo-sensitive pNIPAAm core wrapped by a non-thermo-sensitive polyacrylamide (pAAm) shell, each templated by droplet-based microfluidics. When the microgel core deswells upon increase of the temperature to above 34 °C, the shell is stretched and dragged to follow this deswelling into the microgel interior, resulting in an increase of the microgel surficial Young's modulus. However, as the surface interactions of the pAAm shell are independent of temperature at around 34 °C, they do not considerably change during the pNIPAAm-core volume phase transition. This feature makes these core–shell microgels a promising platform to be used as building blocks to assemble soft materials with rationally and independently tunable mechanics.

#### 3.2.1. Introduction

Thermo-sensitive polymers exhibit marked reversible changes of their polymer–solvent interactions at critical solution temperatures, rendering them promising for diverse applications. A particularly favorable type of thermo-sensitive polymer system is poly(*N*-isopropylacrylamide) (pNIPAAm) in water, which displays such responsivity at a lower critical solution temperature (LCST) of ~32 °C.<sup>1, 2</sup> As an effect of this temperature-dependent polymer-solvent interaction,<sup>3, 4</sup> cross-linked polymernetwork hydrogels based on pNIPAAm exhibit a reversible volume phase transition from swollen to deswollen states <sup>5, 6, 7, 8</sup> and a significant increase of the water contact angle<sup>9, 10</sup> as the temperature exceeds the LCST. This property renders pNIPAAm-based hydrogels useful for a plethora of applications, which has been particularly explored for microscopic pNIPAAm gel particles.<sup>11, 12, 13</sup> In these systems, the particle swelling-deswelling transition causes a change of the microgel volume fraction<sup>14</sup> and of the microgel interaction potential.<sup>15, 16</sup> The conjoint use of both these effects can serve to induce temperature-controlled transitions between pNIPAAm-based microgel glasses, suspensions, and gels,<sup>17</sup> thereby offering rich versatility for *in-situ* tuning of the state of pNIPAAm microgel-based soft matter. Furthermore, when a pNIPAAm hydrogel or microgel deswells, it exhibits drastic changes of its mechanical properties such as the gel's elastic<sup>18</sup> or Young's modulus.<sup>19, 20</sup> Again, the conjoint use of both these effects can be beneficial, for example, to serve in switchable cell culture substrates that allow for temperature-controlled cell adhesion and detachment.<sup>21, 22</sup> However, whereas these specific applications use the conjoint change of the coupled variables mentioned above, it is desirable to change just one of them while keeping the others constant in more general rational materials design. For example, *in-situ* tuning the elasticity of gel substrates is desirable in view of studying its effect on attached cells<sup>21</sup> but this should occur without concurrently influencing the cell adhesion.<sup>23</sup> For this and other purposes, it is desired to use temperature to easily and reversibly change the gel's elastic or Young's modulus without conjointly changing the gel hydrophilicity.<sup>24</sup>

In this paper, we present a design approach for microgel particles that allow their elastic and Young's moduli to be changed by variation of temperature without exhibiting perceptible accompanying changes of their hydrophilicity and adhesion. These particles are core-shell microgels consisting of a thermo-sensitive pNIPAAm hydrogel core wrapped by a non-thermoresponsive polyacrylamide (pAAm) hydrogel shell, as sketched in Figure 1. Whereas the core can be swollen and deswollen in response to changes in temperature around 34 °C, the shell is just indirectly affected by this process.



**Figure 1.** Volume phase transition of core–shell microgels with a thermo-responsive poly(*N*-isopropylacrylamide) pNIPAAm core and a non-thermo-responsive polyacrylamide (pAAm) shell. When the core and shell are connected and exhibit some interpenetration at their interface, temperature-dependent deswelling of the pNIPAAm core forces the pAAm shell to contract as well, thereby leading to an increase of the particles surficial Young's modulus. While this happens, however, the particles' surficial hydrophilicity does not change, because the polymer–solvent interaction of the outer pAAm material is not strongly temperature dependent around 34 °C.

Due to some interfacial polymer interpenetration and connection of the pNIPAAm core to the pAAm shell, as illustrated in Figure 1, its thermo-sensitive contraction can force the pAAm shell to contract as well, as also illustrated in Figure 1, thereby affecting the Young's modulus on the particle surface at elevated temperatures. This thermo-mechanical effect on the non-responsive shell is expected to depend on the shell thickness and its polymer-network composition, which are two design criteria focused on in this study. While the gels get contracted, however, the surface interactions of the pAAm shell are unaffected by small changes in temperature. These microgels therefore hold good promise to be used as building blocks to assemble larger layers or aggregates<sup>25</sup> that allow their elasticity to be switched within determined ranges without conjoint perceptible change of their interfacial interaction potential and adhesion energy per area.

In earlier work, similar core–shell gel particles with sizes from tens of nanometers to about one micrometer have been used to combine the response of different core and shell materials to create multiply stimuli-sensitive,<sup>26, 27, 28</sup> or two-step responsive materials.<sup>29, 30, 31</sup> Zhao et al. covered temperature-responsive pNIPAAm nanogels by a non-responsive hydrophobic PMMA shell.<sup>32</sup> Richtering et al. produced colloidal core–shell microgels from temperature-responsive polymers with different LCSTs. By small angle neutron scattering<sup>29</sup> and theoretical calculations<sup>33</sup> they verified the interpenetration of the core and shell polymers and the resulting mutual influence of their temperature-responsive swelling. These papers also report network,<sup>27</sup> and the cross-linking density<sup>30</sup> on the particle response. To complement this existing work, the present study combines thermo-responsive pNIPAAm cores with sizes in the above-colloidal domain with a soft, non-responsive polymer shell, taking advantageous use of the exquisite control on the particle fabrication provided by droplet-based microfluidic templating.<sup>34</sup>



**Figure 2.** Preparation of core-shell microgels that each consist of a thermo-responsive poly(*N*-isopropylacrylamide) (pNIPAAm) hydrogel core and a non-thermo-responsive polyacrylamide (pAAm) hydrogel shell by droplet-based microfluidics. A), B) pNIPAAm microgels are first prepared by emulsification of an aqueous solution of monomeric NIPAAm and the cross-linker BIS by an external phase of parraffin oil in a microfluidic device with a single flow-focusing cross-junction geometry. C), D) Core-shell microgels are subsequently prepared in a microfluidic device with sequential double cross-junction geometry. In the first junction, the pNIPAAm microgels from the preceding experiment are wrapped by a solution of pre-polymerized p(AAm-*co*-DMMIAAm) and the photosensitizer TXS. In the second junction, pre-core-shell microgel droplets are formed by emulsification of the resulting fluid stream with paraffin oil, which are then photo-gelled by UV irradiation.<sup>35</sup>

#### 3.2.2. Results and Discussion

#### 3.2.2.1. Microfluidic Fabrication of pNIPAAm–pAAm Core–Shell Microgels

Our idea of preparing microgels with independently tunable elasticity is based on sub-millimeter sized gel particles with core-shell geometries. In previous work, microgels consisting of thermo-responsive polymer-gel shells that surround non-responsive or differently responsive polymer-gel cores have been fabricated with colloidal sizes by seed-microgel precipitation polymerization<sup>27</sup> and with abovecolloidal sizes by microgel encapsulation in droplet-based microfluidics.<sup>34</sup> We adopt the latter approach to form above-colloidal core-shell microgels, each consisting of a thermo-sensitive core surrounded by a non-thermo-sensitive shell. To realize this idea, core microgels consisting of crosslinked pNIPAAm are first made by droplet-based microfluidic templating at  $(23 \pm 1)$  °C. For this purpose, we use a polydimethylsiloxane (PDMS) microfluidic device with a single flow-focusing cross-junction geometry to fabricate monodisperse pre-microgel droplets of a NIPAAm solution (100 g  $L^{-1}$ ) containing 1.36 g  $L^{-1}$  of N,N'-methylenebisacrylamide (BIS) as a cross-linker. Subsequent cross-linking copolymerization of these monomers within the droplets yields pNIPAAm microgels in the size-range of 20 µm in radius (Figure 2A, B). After fabrication of these pNIPAAm microgels, we pack them by sedimentation and then use the resulting microgel paste in a second microfluidic step, wherein which they are encapsulated into surrounding non-thermo-sensitive polymer shells to form the anticipated core-shell particles.

To obtain a non-thermo-sensitive polymer for wrapping the thermo-sensitive pNIPAAm microgels, we synthesize photo-cross-linkable polyacrylamide (pAAm). This is done by radical copolymerization of acrylamide with the photochemically dimerizable comonomer dimethylmaleinimidoacrylamide (DMMIAAm, 1.3 mol% rel. to AAm),<sup>35, 36, 37</sup> employing sodium formate as a chain transfer agent for

molecular-weight control.<sup>38</sup> The resulting polymer is then used in a consecutive microfluidic experiment conducted in a device with two sequential cross–junction channels, again at  $(23 \pm 1)$  °C. In the first junction, the pre-fabricated pNIPAAm microgels are surrounded by a stream of a semidilute solution (100 g  $L^{-1}$ ) of the photo-cross-linkable polyacrylamide, along with a triplet photosensitizer, thioxanthone-2,7-disulfonate (TXS).<sup>35</sup> In the second junction, this fluid stream is flow-focused by immiscible paraffin oil, thereby creating core-shell droplets, each containing a single pNIPAAm microgel. Whereas the position of the core inside the shell is not controllable in this process, the distribution of particle sizes resulting from the two consecutive microfluidic experiments is narrow and well defined. Subsequent UV irradiation of these droplets gels their pAAm polymer shells, thereby yielding pNIPAAm–pAAm core–shell microgels (Figure 2C, D). If this experiment is conducted such that the shell gelpoint is passed not before some diffusive interpenetration of the shell polymer into the core microgel, the resulting core-shell microgels are obtained with interconnected core and shell, as illustrated in Figure 1. After the microfluidic experiment, the core-shell microgels are removed from the templating emulsion and washed with water, wherein which they swell to equilibrium sizes. While the core size is determined by the first microfluidic experiment, the shell thickness can be adjusted by the flow rates as well as the microchannel geometry in the second microfluidic experiment.

## 3.2.3. Optical Characterization

We focus our study on two batches of core-shell microgel particles, each prepared with the same pNIPAAm cores but with different shell thicknesses. Additionally, plain pNIPAAm microgels taken from the core-microgel stock, and plain pAAm microgel particles templated from the shell-polymer solution in a microfluidic experiment as shown in Figure 2A that is conducted at conditions as used during the second core-shell batch formation, are used as references. Images of the microgels are taken by optical microscopy during stepwise variation of the temperature from 28 °C to 38 °C. For this purpose, the particles are immobilized on a glass surface by sedimentation, and measurements are performed in a fluid cell with included temperature control in water. At each temperature, the microgels are equilibrated with their environment for at least 30 min. From these images, the core and shell radii of the microgels are determined. A temperature-independent average radius of  $(32.6 \pm 1.5) \mu m$  is found for 9 plain pAAm particles. For an ensemble of 9 plain pNIPAAm particles, deswelling from an average radius of  $(23.2 \pm 3.2) \,\mu\text{m}$  to  $(9.1 \pm 1.1) \,\mu\text{m}$  is observed when the temperature increases from 28 to 38 °C. Out of a total of 18 core-shell particles investigated, Figures 3A and B show the deswelling curves for two representative microgel particles from batch 1 (A) and 2 (B), with the core radius and the total particle radius as a function of temperature. Deswelling curves of further core-shell particles and the reference particles are compiled in the Supporting Information (Figure S1).

In batch 1, we find core–shell particles with core radii between 18  $\mu$ m and 23  $\mu$ m and a relatively thin shell between 8  $\mu$ m and 14  $\mu$ m thickness at 28 °C. As the core positions exhibit some variation and asymmetry in the ensemble of particles, we refer to average values of the shell thickness, which are calculated from the core and shell diameters irrespective of the core position within the shell. While increasing the temperature, the typical LCST behavior of pNIPAAm is observed for the core, resulting in a decrease of its radius. For example, the particle shown in Figure 3A exhibits such a decrease of its core radius down to 14  $\mu$ m at 40 °C. The core deswelling is accompanied by a decrease of the entire particle radius by 5  $\mu$ m.



**Figure 3.** Temperature (*T*) dependent radii (*r*) of pNIPAAm–pAAm core–shell microgel particles in water, along with light microscopy images recorded at 20× magnification. Open blue circles represent the total particle radius, whereas full red circles represent the core radius. The lower critical solution temperature (LCST) is indicated by a dashed vertical line. Scale bars in the micrographs represent 50  $\mu$ m. A) For particles from batch 1, the overall particle size decreases above the LCST, because the non-thermo-responsive shell gets dragged to follow the deswelling of the core. B) By contrast, a temperature-independent overall particle radius is observed for batch 2 although the core still deswells above the LCST.

As a consequence of the more pronounced deswelling of the core compared to the effect on the overall particle radius, the pAAm shell gets radially stretched by ~3.5  $\mu$ m; its total volume, however, reduces to 78% of its original value during this process. Similar behavior is found for all particles from this batch (see Supporting Information Figure S1). The second batch of core–shell microgels contains particles with a larger total radius ranging from 35  $\mu$ m to 37  $\mu$ m and smaller core radii between 15  $\mu$ m and 20  $\mu$ m below the LCST. Consequently, the pAAm shell of the second batch is on average twice as thick as in batch 1. Again, the typical deswelling of the pNIPAAm core is observed at increasing temperature, as shown for one representative core–shell particle in Figure 3B. In contrast to the first batch, however, the entire particle radius does not change with temperature for all particles of this batch. Thus, the shrinking of the core in the batch-2 particles appears to be compensated by the stretching of the shell towards the particle interior. In case of the core–shell particle shown in Figure 3B, a shell stretching of 2.5  $\mu$ m is observed.

The temperature-dependence of the size of the pNIPAAm–pAAm core–shell microgel particles indicates that the shell thickness is a relevant design parameter: while the LCST-based deswelling of the core is comparable for both batches, a thin shell is more prone to follow this deswelling than a thick shell.

#### 3.2.4. Thermo-Sensitive Change of the Microgel Young's Moduli

To quantify the surficial mechanical properties of the core–shell microgels, we probe them by indentation exerted by atomic force microscopy (AFM) using the colloidal probe technique.<sup>39</sup> With this

method, temperature-dependent changes of the microgel Young's modulus can be determined with high accuracy. After equilibration at a given temperature for at least 30 min, a silica sphere of 23  $\mu$ m radius (in case of the plain pNIPAAm particles) or 2  $\mu$ m radius (in case of the plain pAAm and the coreshell particles) fixed at the free standing end of the cantilever is aligned centrically above the microgel particle under optical control with an inverted optical microscope. Then, approach–retract cycles are performed at a constant speed of 2  $\mu$ m s<sup>-1</sup> to record force–deformation (F–D) curves. In addition to optical control, axisymmetric contact of the microgel and the spherical probe is ensured by sampling a spatially resolved grid of F–D curves, resulting in a topographical image of the microgel (see Supporting Information Figure S2). Then, the temperature is increased stepwise, and the measurements are repeated for exactly the same particles.

To establish a reference system for the mechanical properties of our core–shell microgel particles, we first investigate plain pNIPAAm and plain pAAm microgel particles at varying temperatures. Figure 4 depicts representative F–D measurements on one pAAm as well as on one pNIPAAm particle at five different temperatures. The microgel stiffness is reflected by the slope of the F–D plots. It is almost temperature-independent in case of the plain pAAm particles, as indicated by very similar F–D datasets (Figure 4, dashed lines) in the investigated temperature range. By contrast, the F–D curves recorded on the plain pNIPAAm microgels become drastically steeper with increasing temperature, reflecting the microgel deswelling and stiffening.<sup>22</sup>

To quantify the mechanical properties, several theories modeling contact mechanics are available.<sup>40,</sup> <sup>41, 42, 43</sup> In the field of colloidal probe force spectroscopy, the Hertz model and the Johnson–Kendall– Roberts (JKR) theory are frequently used. Both theories describe the contact formation and elastic compression of two isotropic spherical bodies under external axisymmetric load. The Hertz model neglects interparticle forces such as adhesion or friction, whereas additional stress contributions due to adhesion forces within the contact area are accounted for in the JKR theory, which transitions into the Hertz equation as adhesion vanishes. Since the measured adhesion forces between both types of homogenous microgels and the colloid probe are small, the Hertz model is used in this study:

$$F = \frac{4}{3} E R^{0.5} D^{1.5} \tag{1}$$

with

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$
(2)

and

$$\frac{1}{E} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}$$
(3)

In Equation 1, the applied force, F, is related to the measured deformation, D, by a characteristic power of 1.5 and some effective parameters of the system, which are the radius, R, and the elastic or Young's modulus, E, as given by Equation 2 and 3. The indexes in these equations refer to the two materials in contact, and v is the Poisson ratio, which is assumed to be 0.5 for incompressible isotropic elastic materials.



**Figure 4.** Temperature-dependent force (*F*) vs. deformation (*D*) measurements performed on plain pNIPAAm (solid lines) and plain pAAm (dashed lines) microgel particles as a reference. For each type, representative approach measurements in the range between 30 and 38 °C (temperature is color-coded) are shown for one particle. The stiffness of the pAAm particles is almost independent of the temperature, as indicated by their very similar behavior under load. By contrast, temperature-dependent stiffening is observed for the pNIPAAm particles while exceeding the LCST.

In our study, we limit the mechanical characterization to the small deformation regime below 500 nm to avoid plastic effects and only probe the surficial properties of the microgels. Such small deformation is also beneficial to minimize the potential complex influence of the asymmetry of the core--shell geometries on the interaction forces. Validity of the Hertz model for each F–D experiment is assumed when its power law dependence falls in the range between 1.45 and 1.55, according to Equation 1 (see Supporting Information Figure S2). The resulting Young's moduli for plain pAAm and pNIPAAm microgel particles and their thermo-responsive swelling-deswelling are shown in Figure 5.

As expected, the Young's modulus of the plain pAAm microgel particles (Figure 5, squares) is found to be insensitive to temperature, with values in the range between 20 to 50 kPa. The scattering of the data is assumed to be an unfavorable artifact due to a broad distribution of the conversion of the photocross-linking reaction achieved during the consecutive microfluidic experiment.



**Figure 5.** Temperature (*T*) dependent Young's moduli (*E*) of single plain pNIPAAm (green circles) and plain pAAm (blue squares) microgel particles recorded by colloidal probe AFM. Dashed lines are to guide the eye. Each point represents the average value of at least five F–D measurements. Values for the Young's modulus of three different particles are shown for each system. In case of pAAm, the Young's modulus is temperature independent and in the range of 20 to 50 kPa. Contrary, at low temperatures, the Young's modulus of pNIPAAm is around 1 kPa and increases up to 250 kPa above the LCST (33–34°C).



**Figure 6.** Force (*F*) vs. deformation (*D*) measurements conducted on one pNIPAAm–pAAm core–shell microgel particle with temperature-controlled colloidal probe AFM. Temperatures are color-coded as denoted in the legend. As indicated with the horizontal arrow, the deformability of the particle first stays constant between 30 and 34.5 °C. Upon further heating that causes deswelling of the pNIPAAm core beyond 35 °C, however, the core–shell particle gradually stiffens with increasing temperature, as highlighted by the vertical arrow.

In contrast, the plain pNIPAAm microgels are found to be softer, with a modulus of just around 1 kPa at low temperatures, but they stiffen up to 250 kPa at temperatures above the LCST. The variation in the apparent LCST for the three pNIPAAm particles shown in Figure 5 is probably due to temperature gradients within the setup of the liquid cell in the AFM. Besides the variation in the absolute values of the Young's modulus for both systems, their relative temperature-induced changes are characteristic for both systems. The values for plain pAAm remain constant with temperature, while plain pNIPAAm particles stiffen by two orders of magnitude upon temperature increase.

After establishing the plain-microgel reference system, we focus on our core–shell microgel particles. The F–D data recorded on these microgels are nearly identical if the temperature is below the LCST of pNIPAAm, as seen in Figure 6 for one particle. This is because both hydrogel materials do not show appreciable thermal sensitivity in this temperature range. Upon exceeding the LCST, however, a change of the mechanical response is observed: in this temperature range, gradual steepening of the F–D curves is recognized while the temperature is raised to 40 °C. This is a first indication that the temperature-responsive microgel core mechanically affects the per-se non-thermo-sensitive microgel shell.

Following this qualitative interpretation, quantification of these mechanical changes is desired to compare the core-shell microgel thermo-mechanical response to that of their plain hydrogel components. Classical theories such as the Hertz and JKR models, however, are derived on the assumption of homogenous isotropic bodies. Following earlier work of finite-element simulations on comparable soft core-shell particles that indicates a good estimation of the effective elastic modulus by the Hertz theory,<sup>44</sup> we apply Equation 1 in the small deformation regime for mechanical quantification. The validity of this approach is further supported by the resulting elastic moduli in the low kPa range and the measured F–D power-law dependence (see Supporting Information Figure S2). Elastic moduli estimated for representative core-shell particles from both batches in the small deformation regime (< 500 nm) are shown in Figure 7. In this deformation regime, only the elastic contributions of the shell material are measured. At low temperatures, the Young's modulus for both particles is temperature-independent. Above the LCST of the encapsulated core, however, a non-linear increase of the elastic modulus of the shell is observed for both core-shell particles. Furthermore, the absolute values of representative particles below the LCST differ strongly with  $(6.7 \pm 0.2)$  kPa for Figure 7A and  $(32.2 \pm 0.4)$  kPa for Figure 7B. Both trends hold as well for a statistical analysis of several particles (see Supporting Information Figure S3).



**Figure 7.** Temperature (*T*) dependent Young's moduli (*E*) of the two pNIPAAm–pAAm core–shell microgel particles shown in Figure 3 at varying temperatures. Each data point represents averaged values of at least five F–D curves, and the dashed lines are a guide to the eye. Absolute values of the Young's modulus are plotted to the left axis. Relative changes in Young's modulus are given by the right axis. Values measured on one core–shell particle of batch 1 are shown in A) and one particle of batch 2 in B), respectively.

As discussed in the context of Figure 5, the differences in the absolute Young's moduli of the pAAm shells are presumed to be due to a varying extent of photocross-linking achieved during the core–shell microgel preparation. In the following, we therefore focus on a discussion of the relative temperature-induced changes.

We interpret the elasto-thermal effect of the per-se non-responsive pAAm-shell with the following conceptual picture comprising two scenarios depicted in Figure 8. In both scenarios, a redistribution of the shell polymer network is triggered by the temperature-induced shrinking of the core. Due to the interconnection between the core- and the shell network in the microgels, the deswelling core drags the shell towards the center of the core.

In the first scenario (Figure 8A), which corresponds to the situation observed for batch 1, the total particle radius reduces with temperature. As a result, the shell volume reduces, and water is squeezed out of the shell. This observation agrees with earlier experimental results and model calculations for core–shell colloidal hydrogels by Richtering et al.<sup>29, 33</sup> In this earlier work, it is conceived that thin swollen shells are subject to lateral contraction exerted by a collapsing core, which reduces the shell size. Although this model does not focus on mechanical changes induced by that, one can deduct from the shell-volume reduction that the polymer concentration in the shell is increased during this process. According to the Flory–Rehner theory,<sup>45,46</sup> this leads to an increase of the elastic modulus of the polymer gel, which would explain the observed stiffening of the particles in batch 1 of our work.



**Figure 8.** Schematic illustration of the changes in the pAAm shell polymer network upon deswelling of the pNIPAAm core at increasing temperature. The polymer chains in the shell are not drawn to scale but sketched such to illustrate their radial stretching and the change of their segmental density upon core deswelling. Darker colors indicate an increased polymer concentration. In A), the deswelling of the core results in a decreasing total particle radius, release of water out of the shell network to the surrounding environment, an increasing polymer density, and radial stretching of the network. In B), by contrast, the total particle radius stays constant, the shell polymer density decreases, but still the network is radially stretched.

The second scenario, schematically depicted in Figure 8B, focuses on particles that do not change their total size upon core collapse, which is typical for batch 2. Here, the reasons for the observed stiffness changes are less clear. They could be induced by radial stretching of the shell polymer network towards the shrinking core. Again, this assumption is supported by earlier core—shell microgel modeling by Gernandt and Richtering.<sup>33</sup> Their model predicts that close to the interface of a collapsed core, the shell is predominately laterally contracted. With increasing distance from the interface, the radial stretching of the shell outweighs this lateral contraction due to decreasing mechanical stresses from the core and due to the swelling tendency of the shell. As a result, hydrogels with thicker shells – as our particles from batch 2 – mainly experience radial stretching. A possible explanation for a mechanical stiffening resulting from this stretching could be that the shell polymer segments between cross-links become more rigid due to a loss of entropy upon stretching, thereby increasing the elastic modulus.<sup>47</sup>

In general, the magnitude of radial stretching and lateral contraction of the shell polymer chains might be further influenced by the network constitution, which is primarily determined by parameters such as its initial cross-linking density and the spatial distribution of cross-links within the shell. We do not have direct information on these parameters on a single-particle level, but yet the general trends seem hold.

#### 3.2.5. Interfacial Interaction

Plain pNIPAAm hydrogel particles exhibit conjoint changes of both their mechanical and their adhesion properties upon the thermo-responsive volume phase transition.<sup>22</sup> By contrast, the interfacial properties of pAAm hydrogels are supposed to be temperature-independent in the range covered in our study, which should result in constant adhesive properties. We therefore presume that the interfacial properties of our core–shell microgel particles should be constant and decoupled from their mechanical switchability shown above.



**Figure 9.** Adhesion properties of plain and core–shell microgels against a spherical silica probe measured by AFM. A) Force (*F*) vs. deformation (*D*) upon approach (red line) and retraction (blue line) recorded on a core–shell particle. The blue shaded area enclosed by the force curve and the abscissa represents the work of adhesion required to remove the probe from the sample. B) Work of adhesion ( $W_{Adh}$ ) for plain pAAm (blue circles), plain pNIPAAm (orange triangles), and pAAm–pNIPAAm core–shell (green squares) microgels at varying temperatures (*T*). The data points represents the averaged values of 17 core–shell, 9 plain pAAm, and 8 plain pNIPAAm particles, while for each particle and temperature combination at least 20 F–D curves were evaluated.

To investigate this hypothesis, we analyze the F–D curves recorded during retraction of the sphere to determine adhesion forces and energies. If present, adhesive interaction forces cause an attraction between the silica probe and the hydrogel particles, which becomes dominant when the loading force of the cantilever vanishes during retraction. Upon further retraction of the probe, the adhesive attraction between the surfaces causes them to stick together, resulting in a net-negative force measured. The sphere stays in contact with the surface until the cantilever force overcomes the adhesion force and the probe jumps out of contact.

Often, the negative force maximum is used to describe the adhesion. A more global measure of adhesion is the total energy needed to pull the probe off the surface, which is referred to as the work of adhesion. It equals the area enclosed by the negative part of the force curve and the abscissa (Figure 9A, blue shaded area). The adhesive properties of the three different microgel systems as a function of temperature are presented in Figure 9B. Starting at low temperatures, a high work of adhesion of  $(1.25 \pm 0.39)$  pJ between the hydrophilic swollen plain-pNIPAAm microgel particles and the hydrophilic silica probe is measured at 28 °C. While increasing the temperature, the adhesion only slightly decreases. The imminent collapse of the hydrogel particles can be noticed as a first drop in the work of adhesion before reaching the lowest value at 38 °C. The temperature-dependent adhesion of pNIPAAm was studied by many researchers. Both decrease<sup>48, 49</sup> and increase<sup>50, 51, 52</sup> of the adhesion

with increasing temperature were reported, depending on the properties of the interacting surfaces and the experimental setup.

For the plain pAAm hydrogel particles, the work of adhesion is very low,  $(2.82 \pm 0.24) \times 10^{-3}$  pJ, and it is not affected by temperature variation. In contrast to the two-order-of-magnitude changes of the adhesive properties of the plain-pNIPAAm microgels, the work of adhesion estimated for the core-shell particles stays nearly constant at low values over the whole temperature range probed. We do not find any significant change between 28 °C and 38 °C with a work of adhesion of (0.56 ± 0.26) pJ and (0.44 ± 017) pJ, respectively. Thus, the adhesion behavior of the core-shell-system appears to be dominated by the shell layer and hardly affected by temperature changes.

## 3.2.6. Conclusion

Core-shell microgels that consist of a thermo-responsive pNIPAAm core and a non-responsive pAAm shell exhibit tunable elastic properties. This is achieved by chemical or topological interconnection between their cores and shells, transferring the collapse of the core to a surficial stiffening of the shell at elevated temperatures. The deswelling core drags the cross-linked shell inwards, thereby changing the shell volume and polymer segmental concentration, and radially stretching the shell network. For a given core size and composition, we find that the relative shell stiffening is more effective for particles with a thinner and softer shell. In case of thicker and more rigid shells, the surficial stiffening gets attenuated but is still present. In contrast to plain pNIPAAm microgels, these effects occur without marked changes in the outer microgel hydrophilicity, and the adhesiveness remains constant. Hence, these composite microgels exhibit an independently tunable elasticity without accompanying change of other relevant parameters. Further correlating the impact of the core collapse and the core interconnection properties with the shell to the mechanical stiffening might be used to rationally design assemblies of microgel layers or aggregate-substrates with the ability to independently regulate their elasticity.

## 3.2.7. Experimental Section

**Materials:** All chemicals were used without further purification and purchased from Sigma Aldrich, unless stated otherwise. 1,4-dioxane and n-hexane were purchased from Roth. 1H,1H,2H,2H-perfluorooctanol was purchased from Alfa Aesar. Octadecyltrimethoxysilane was purchased from Acros Organics. The modified polyether–polysiloxane surfactant ABIL EM 90 was donated by Evonik, which we gratefully acknowledge. The perfluorinated oil Novec HFE-7500 was purchased from 3M. Acrylamide was recrystallized twice from chloroform prior to use. If not noted further, purified water from a Milli Q water purifier with a resistance of 18.2 M $\Omega$ ·cm (T = 25 °C) was used. Dialyses were done with tubes from regenerated cellulose 132703 (SpectraPor) with a molecular weight cutoff of 12–14 kg mol<sup>-1</sup>.

**Equipment:** <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 400 digital FT-spectrometer at 400 MHz at T = 25 °C. Chemical shifts reported in ppm are referenced to trimethylsilane (TMS) as a standard using  $\delta$ (TMS) = 0 ppm. High-resolution mass spectroscopy (HRMS) with electron-spray ionization (ESI) was carried out on an Ionspec QFT-7 from Varian Inc. Atomic force measurements were carried out on a MFP-3D atomic force microscope equipped with a BioHeater closed fluid cell with a

polyethylenimine-coated glass surface, both from Asylum Research. A MikroMasch NSC12 no Al backside coating tipless cantilever made from n-type silicon, bought from Nanoworld AG, was used. The AFM was coupled to an AxioObserver Z1 inverted optical microscope by Carl Zeiss for optical control of the cantilever placement. Samples were suspended in purified water from a Milli Q water purifier with a resistance of 18.2 M $\Omega$ ·cm (T = 25 °C). Data analysis was done with IGOR Pro 6.3.6.4 by WaveMetrics software, which was supplemented by the 120804+1702 add-on package for AFM analysis by Asylum Research. Microgel swelling and deswelling measurements were carried out on the same BioHeater closed fluid cell from Asylum Research mentioned above. The temperature of each sample was varied from 28 °C to 38 °C. After equilibration for 30 min, an optical micrograph was taken at each temperature with a high-resolution digital camera from Carl Zeiss. The pictures were analyzed to determine the particle sizes using ImageJ 1.49 software.

**Synthesis of tert-butyl (2-aminoethyl)carbamate:** Ethylendiamine (61.57 ml, 0.92 mol) was dissolved in 1,4-dioxane (300 ml). A solution of di-tert-butyl-dicarbonate (26.19 g, 0.12 mol) in 1,4-dioxane (300 ml) was added dropwise, upon which the solution turned turbid. After rapid stirring for 18 h, the resulting sticky precipitate was filtered off. The solvent and excess ethylendiamine were removed in vacuo. Addition of water (500 ml) caused precipitation of di-tert-butyl ethane-1,2-diyldicarbamate, which was filtered off. The aqueous phase was saturated with sodium chloride and extracted five times with dichloromethane (150 ml) each. The organic phase was then dried over sodium sulfate, filtered, and the solvent removed in vacuo. The crude product (16.26 g) was obtained as a yellowish oil. After distillation at 7 × 10<sup>-2</sup> mbar and 130 °C, the product was obtained in 82% yield (15.76 g) as a colorless oil. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl3):  $\delta$  = 1.40 (s, 9H, 3CH3, Boc), 1.89 (s, 2H, NH2), 2.77 (m, 2H, CH2-NH2), 3.15 (m, 2H, CH2-NH), 5.10 (br. s, 1H, NH) ppm.

Synthesis of tert-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)carbamate: Tertbutyl (2-aminoethyl)carbamate (15.76 g, 98.37 mmol) and dimethyl maleic anhydride (12.08 g, 95.81 mmol) were dissolved in toluene (300 ml) and refluxed for 3 h using a water separator. Upon heating, a strong increase of turbidity of the mixture was observed, which cleared after about 15 min of refluxing. After removal of the solvent in vacuo and drying in high vacuum, the product was obtained in 98% yield (25.27 g) as a white solid. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl3):  $\delta$  = 1.39 (s, 9H, tBu-O), 1.95 (s, 6H, 2CH3, maleic), 3.30 (br. m, 2H, CH2-NH), 3.61 (t, *J* = 5.7 Hz, 2H, CH2-N), 4.80 (br. s, 1H, NH) ppm.

2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethan-1-aminium **Synthesis** of 2,2,2trifluoroacetate: Tert-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl) carbamate (25.27 g, 94.19 mmol) was dissolved in dichloromethane (70 ml). After addition of trifluoroacetic acid (100 ml), gas evolution was observed. Bubbling ceased after an hour of rapid stirring. The solvent was removed in vacuo to yield the crude product (47.18 g) as a reddish-brown oil. Water (250 ml) was added to the solution, which immediately turned cloudy, but cleared again after a few seconds. Diethylamine was added until pH = 8 to eliminate excess trifluoroacetic acid. The aqueous phase was then extracted four times with ethyl acetate (200 ml). The organic phase was dried over magnesium sulfate, filtered, and the solvent removed in vacuo to yield the product as a solid suspended in a bright red oil, which turned out to be excess diethylamine. For separation, the mixture was suspended in dichloromethane, and the solid was filtered off. After drying overnight in high vacuum, the product was obtained in 75% yield (19.86 g) as a white solid. <sup>1</sup>H NMR (400 MHz, 25 °C, DMSO-d6):  $\delta$  = 1.88 (s, 6H, 2CH3), 2.96 (t, J = 6 Hz, 2H, CH2-NH3+), 3.62 (t, J = 6 Hz, 2H, CH2-N), 7.92 (s, 3H, NH3<sup>+</sup>) ppm.

Synthesis of N-(2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl) acrylamide (DMMIAAm): Tert-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl) carbamate (16.74 g, 59.30 mmol) and sodium carbonate (18.86 g, 0.18 mol) were dissolved in dichloromethane (150 ml). A solution of acryloyl chloride (5.90 g, 65.23 mmol) at 0 °C was added dropwise, yielding a white suspension. The mixture was allowed to warm to ambient temperature while being stirred for two days. The crude solution was filtered to remove excess sodium carbonate, dried with magnesium sulfate, and the solvent removed in vacuo. The product was obtained in 85% yield (10.01 g) as a white solid. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl3):  $\delta$  = 1.96 (s, 6H, 2CH3), 3.51 (m, CH2-NH), 3.70 (m, H, CH2-N), 5.62 (dd, *J* = 10.3, 1.2 Hz, 1H, =CH2), 6.06 (dd, *J* = 17.0, 10.3 Hz, 1H, =CH2), 6.22 (dd, *J* = 17.0, 1.2 Hz, 1H, =CH2), 6.25 (s, 1H, NH) ppm; HRMS (ESI) m/z: [M + H] calcd for C11H14N2O3, 245.0902; found, 245.0904.

Synthesis of shell precursor polymer p(AAm-co-DMMIAAm): Acrylamide (AAm) (7.93 g, 111.55 mmol) and DMMIAAm (0.77 g, 3.45 mmol) were dissolved in water (250 ml) at a concentration of 0.46 mol L<sup>−</sup> <sup>1</sup>.<sup>35</sup> The solution was purged with argon for 30 min at room temperature. Ammonium persulfate (APS) and tetramethylethylenediamine (TEMED) were added to the reaction mixture in form of 4.6 ml aliquots of aqueous stock solutions with concentrations of  $c(APS) = 0.2 \text{ mol} \cdot L^{-1}$  and  $c(\text{TEMED}) = 0.5 \text{ mol}\cdot L^{-1}$ . To control the molecular weight of the forming polymers, sodium formate (0.35 g, 5.17 mmol) was added as a chain transfer agent.<sup>38</sup> The mixture was stirred at room temperature under an argon atmosphere. To monitor the reaction, samples were taken at 30 min intervals to check for precipitation of p(AAm-co-DMMIAAm) after addition of equivalent volumes of methanol to the aliquots. After 120 min, a perceptible precipitation was noticed, and the reaction was quenched by adding a threefold excess (750 ml) of methanol. After addition of 3 wt.% of hydrochloric acid (25 wt.% HCl in water), the precipitate could be isolated and filtrated. The crude polymer was dissolved in water, dialyzed against water for one week, and isolated by freeze drying. The product was obtained in 25% yield (2.18 g) as a fluffy white solid. The compositions of the copolymers were estimated from the integrals of the corresponding NMR signals.<sup>35</sup> Setting the integral of the broad signal at  $\delta$  = 3.20–3.75 ppm to 4, the molar ratio of AAm to DMMIAAm groups in the copolymer is obtained from the integral x of the broad high-field NMR signal at  $\delta = 2.4$  ppm in the following fashion: x was first reduced by 9 (3 backbone protons plus 6 methyl protons in each DMMIAAm residue) and afterwards divided by 3 (3 protons per acrylamide residue). The resulting number is the ratio of AAm to DMMIAAm in the copolymer. <sup>1</sup>H NMR (400 MHz, 100 °C, D2O):  $\delta$  = 1.30–2.40 (br. m, polymer backbone and DMMIAAm methyl protons), 3.20–3.75 (br. m, 4H, CONH–(CH2)2–DMMI) ppm.

**Microfluidic setup for microgel synthesis:** Microfluidic devices were manufactured using soft lithography.<sup>53</sup> A polydimethylsiloxane (PDMS) / cross-linker mixture (Sylgard 184 silicone elastomer kit, Dow Corning, base: curing agent = 10:1) was poured onto a silicon wafer that has been patterned with SU-8 photoresist (MicroChem Corp.) before. After curing for 1 h at 65 °C, the solidified PDMS was attached to a glass slide by plasma bonding. Two types of microfluidic devices were fabricated. The device for core-microgel formation had single cross-junction geometry with a channel height and width of 25  $\mu$ m. The encapsulation device used for core-shell microgel formation had a sequential double cross-junction geometry with a channel height of 40  $\mu$ m and a channel width of 50  $\mu$ m. To render the devices hydrophobic, octadecyltrimethoxysilane was injected into the channels, allowed to sit for 1 min, and then removed by subsequent rinsing with 2-propanol and water.

In all microfluidic experiments, pumps used were PhD Ultra Syringe Pumps (Harvard Apparatus), operating with disposable syringes (1-5 ml, Becton Dickson) and Intramedic Clay Adams PE Tubing
"PE 20" (Becton Dickinson). To monitor the droplet formation, all devices were operated on an optical microscope (Zeiss PrimoVert) connected to a digital camera (UK1155-M, ABS GmbH, Jena, Germany). All experiments were carried out at ambient temperature  $(23 \pm 1 \text{ °C})$ .

**Microfluidic fabrication of p(NIPAAm-co-BIS) core microgels:** A NIPAAm monomer solution with a concentration of 100 g L<sup>-1</sup> containing 1 mol% of the cross-linker *N*,*N*'-methylenebisacrylamide (BIS) was emulsified by flow-focusing with fluorinated oil Novec HFE-7500 (3M) containing 1.8 wt.% of Krytox (DuPont) as a surfactant. APS and TEMED were used to initiate the polymerization. APS was pre-mixed to the monomer solution at a concentration of 8 g L<sup>-1</sup>, whereas TEMED was pre-mixed to the Novec HFE-7500 oil phase at a concentration of 3 vol%. Flow rates were 40 µl h<sup>-1</sup> and 160 µl h<sup>-1</sup> for the NIPAAm–BIS solution and the oil phase, respectively. The resulting pre-microgel droplets were collected and stored overnight to assure completion of the free radical polymerization; this long reaction time also assures even distribution of all components by diffusion within the gelling droplets. The pre-microgel suspension was covered by a thin layer of paraffin oil to suppress solvent evaporation during this process. After storage, paraffin and HFE-7500 oils were removed by depipeting, and the microgels were washed with Novec HFE-7500 containing 20 wt.% of 1H,1H,2H,2H-perfluorooctanol (1×), plain Novec HFE-7500 (2×), n-hexane containing 1 wt.% of the surfactant Span 80 (Sigma Aldrich) (2x), n-hexane (2×), isopropyl alcohol (4×), 1,4 dioxane (4×), and dest. water (4×).

**Microfluidic fabrication of pNIPAAm–pAAm core–shell microgels:** A p(AAm-*co*-DMMIAAm) solution with a concentration of 100 g L<sup>-1</sup> containing 10 mmol L<sup>-1</sup> of the triplet photosensitizer sodium 2,7-thioxanthonedisulfonate, prepared according to Kronfeld and Timpe,<sup>54</sup> was used to encapsulate the p(NIPAAm-*co*-BIS) core microgels. The microfluidic device and the tubing were wrapped in aluminum foil to prevent gelation of the p(AAm-*co*-DMMIAAm) solution by ambient light. The syringe containing the aqueous pNIPAAm microgel suspension was inserted into the syringe pump beforehand and stored over night with the tip facing down to induce sedimentation of the microgels within the syringe. The corresponding tubing was made hydrophobic by coating with octadecyltrimethoxysilane. Core–shell pre-microgel droplets were formed, using low viscous paraffin oil containing 2 wt.% of the modified polyether–polysiloxane surfactant ABIL EM 90 as the continuous phase. Flow rates were 40 µl h<sup>-1</sup> (pNIPAAm microgels), 20 µl h<sup>-1</sup> (pAAm-co-DMMIAAm) and 80 µl h<sup>-1</sup> (paraffin oil). Upon exiting the microfluidic device, the droplets were exposed to UV light (Blak-Ray B-100AP high intensity UV lamp,  $\lambda = 365$  nm, intensity = 100 W). After collection in a vial, the obtained microgel emulsions were washed several times with water to remove the paraffin oil.

**Colloidal probe atomic force microcopy:** All AFM experiments were performed on a MFP-3D Bio from AsylumResearch, an Oxford Instruments company. For calibration of the cantilever, the inverse optical lever sensitivity (InvOLS) was determined by line fitting the repulsive part of F–D curves on a glass surface. Assuming that the glass is not deformable, a direct correlation between the cantilever deflection in nm and the measured output voltage is established. The spring constant of each cantilever (NSC 12 noAl, k = 0.1-1 N m<sup>-1</sup>, MikroMasch) was calibrated prior to attachment of the colloidal probe with the thermal noise method.<sup>55</sup> Glass beads with a radius of 23 µm and 2 µm were used as colloidal probes. Young's moduli derived from measurements with different probe sizes are quantitatively comparable since the Hertz equation takes into account the probe radius. They were glued onto the free standing end of cantilever with a two-component epoxy glue (UHU endfest) using a micromanipulator (MP-285, Sutter Instruments) mounted on an inverted microscope (AxioVert, Zeiss).

Prior to the experiments, the glass surface of the BioCell was cleaned with isopropanol and water, and the colloidal probe cantilever was cleaned in O<sub>2</sub> plasma for 30 sec. For the mechanical characterization of the pNIPAAm particles, the colloidal probe was not plasma cleaned but coated with a polyethylenglycol-poly-L-lysine layer to suppress adhesive forces. About 100  $\mu$ l of each sample solution were spread on the glass surface, and particles were allowed to sediment for at least 30 min before the fluid cell was completely filled with MilliQ water. For some experiments, the glass surface was additionally coated with a polyethylenimine layer to improve the fixation of the hydrogel particles on the glass surface. Fixation and location of the particles were controlled with an inverted optical microscope and the topview optics of the AFM. After equilibration at a given temperature for at least 30 min, the colloidal probe was aligned centric above each hydrogel particle under optical control with the microscope. The force-setpoint for F–D curves was adjusted for each particle type to achieve sufficient deformation (>= 500 nm) for mechanical evaluation. Furthermore, the distance range of the F–D was adjusted such that the probe comes out of contact during retraction. For all experiments, a cantilever speed of 2  $\mu$ m s<sup>-1</sup> was used. To ensure axisymmetric contact between probe and sample, force maps (spatially resolved force-distance curve) were collected giving a topographical image of the particle. From this force map a set of about 10 F-D which are closest to the apex of the sample are picked for further evaluation (see Supporting Information Figure S2). For each temperature, a set of particles was probed before the temperature was increased. Subsequent validation of the InvOLS was performed before and after each measurement.

**Mechanic and adhesion evaluation:** All raw data measured as movement of the *z*-piezo and the deflection signal of the cantilever on the segmented photodiode were processed in a homemade IgorPro procedure. First, the deflection of the cantilever in the non-contact regime was set to zero by rotating the F–D curve. The contact point between probe and sample was determined by the onset of a restoring force in the approach direction and set to zero deformation. The pure deformation of the sample was calculated by subtracting the absolute deflection of cantilever, given by the product of measured photodetector signal and the InvOLS, from the piezo movement in contact. Finally, the deflection signal in volt of the photodetector is transformed to force by multiplication with the InvOLS and the spring constant.

The elastic modulus was determined by fitting the F–D curve up to a deformation of 500 nm by the Hertz equation (equation 1). This deformation range includes sufficient data points for proper fitting and ensures that the underlying core layer has no direct mechanical influence. Typically, underlying layers are assumed to only influence the Young's modulus determination if deformation is larger than 10% of the film thickness.<sup>56</sup> Our core–shell microgels exhibit a minimum shell thickness of 7  $\mu$ m, which is significantly larger than the maximal deformation of just 0.5  $\mu$ m in AFM. During the fitting, the first 50 nm of deformation were not considered because the forces associated to these small deformations are low, resulting in a high contribution to the experimental error. In addition to visual control of the fits, only measurements with a contact exponent in F–D between 1.45 and 1.55 were considered for averaging. For each elastic modulus, an error was calculated by solving equation 1 for *E* and performing error propagation in the fit range. For this purpose, the residual of the fit and measurement was used as a variable parameter. Further, constant errors for the colloidal probe radius of ±0.5  $\mu$ m and 10% for the InvOLS as well as the spring constant were considered.

The work of adhesion between probe and sample was determined by integrating the retraction part of force–deformation plots between zero force in contact (before minimum force) and the first point at which the baseline is reached again.

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## 3.2.10. Supporting Information



#### Figure S1: Further temperature-dependent deswelling curves of core-shell and plain hydrogels

**Figure S1.** Geometrical changes of pNIPAAm–pAAm core–shell microgel particles as well as plain pNIPAAm and pAAm particles determined by optical microscopy at varying temperature in water. The equilibration time at each temperature was at least 30 min. In A) & B), open blue symbols correspond to the total particle radius, whereas full red symbols correspond to the core radius only. A) shows radii of three core–shell particles from batch 1, and B) shows radii of three core–shell particles from batch 2. C) Radii from four different spherical plain pAAm microgel particles at varying temperatures. D) Temperature-dependent deswelling of three different spherical plain pNIPAAm particles, which were used as core material for the core–shell particles.



Figure S2: Overview of the mechanical characterization procedure

**Figure S2.** AFM force spectroscopy data acquisition, evaluation, and validation of axisymmetric contact of the probe and the sample. All data shown were recorded at a constant temperature of 32 °C. A ) AFM height image of one core–shell microgel particle recorded as a force-map (at every pixel, a single force-deformation curve is recorded) with a colloidal probe  $(R_{probe} = 1.7 \ \mu m)$ . Recording such force maps is essential to ensure axisymmetric contact, since bare optical alignment of the probe with an inverted optical microscope, also done here prior to recording the force map, would typically result in force–deformation curves recorded at positions 0  $\mu m \times 0 \ \mu m \times 15 \ \mu m$ , or the center of the force map. Furthermore, note that the force map shown is already recorded by applying x–y piezo offsets to the cantilever to finally record the apex of the sample and the first neighbors as indicated with the red square in A. All curves are very uniform and show the typical exponential behavior in contact. D ) Double logarithmic plot of the 9 force-deformation curves in contact to examine the power law



Figure S3: Statistical analysis of the core-shell thermo-mechanical behavior

**Figure S3.** Young's modulus of six additional pNIPAAm-pAAm core–shell microgels particles at varying temperatures. Particles from batch 1 are shown in blue trapezoids and green bow-tie symbols. Batch 2 particles are represented by red triangles, black circles, blue crosses, and purple squares. A) Absolute Young's modulus and B ) relative Young's modulus at temperatures between 25 and 40 °C.

**3.3.** Enhancement of metallo-supramolecular dissociation kinetics in telechelic terpyridine-capped poly(ethylene glycol) assemblies in the semi-dilute regime



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### Author Contributions:

<u>Willi Schmolke</u>: Polymer synthesis, polymer characterization, rheology measurements and data analysis, piercing test and data analysis, preparation of the manuscript

Mostafa Ahmadi: Computational analysis and adaptation of the Time Marching Algorithm, preparation of the manuscript

Sebastian Seiffert: supervision of the work, correction of the manuscript

In this work, the dynamics of supramolecular polymer assemblies that governed by that of their polymeric building blocks and that of the transient bonds between them, are investigated. Entrapment of such bonds by topological crowding often causes renormalization of the bond lifetimes towards prolonging. In the present study, by contrast, we show that this effect can also be inverse in the case of telechelic metallo-supramolecular polymers in semi-dilute solution. We focus on linear poly(ethylen glycols) capped by terpyridine binding motifs at both ends that can form metal–ligand coordinative bonds with various transition metal ions, thereby creating transient metallo-supramolecular assemblies of varying length and binding strength. Oscillatory shear rheology measurements along with theoretical modelling of the mechanical spectra of these samples reveals a pronounced enhancement of the complex dissociation kinetics that is dependent on the length of the polymeric chain segment, with longer segments yielding faster dissociation times up to six orders of magnitude shorter than described for the free complexes. This finding indicates that the dynamic activity of the polymer chain itself causes complex destabilization.

### 3.3.1. Introduction

Supramolecular chemistry provides powerful tools to design stimuli responsive materials. This is because compounds composed of non-covalently bonded mono-, oligo-, or polymeric building blocks are inherently dynamic<sup>1-4</sup> through their transient physical bonding, which is typically realized through hydrogen bonding<sup>5-7</sup>, metal–ligand coordination,<sup>8-10</sup>  $\pi$ – $\pi$  stacking,<sup>11, 12</sup> or host–guest interactions;<sup>13, 14</sup> some covalently bonded compounds can accomplish the same when they contain reversible bonds such as disulfide bridges,<sup>15, 16</sup> hydrazones,<sup>18</sup> oximes,<sup>19</sup> or reactive chain-ends.<sup>20, 21</sup> Metal–ligand coordinative bonding is an odd entry in this list, as its binding energy (30–300 kJ·mol<sup>-1</sup>) is in between those of weak transient bonds (for example,  $\pi$ – $\pi$  stacking: 1–10 kJ·mol<sup>-1</sup>; hydrogen bonding: 5–100 kJ·mol<sup>-1</sup>) and covalent bonds (300–1000 kJ·mol<sup>-1</sup>).<sup>22</sup> It can thus be considered to lay at the verge of a supramolecular and a covalent bond. This situation renders metal–ligand coordination a suitable candidate for model studies, because the binding energy can be adjusted by mere choice of a metal ion as the linker to represent the entire range from a weak transient bond to a covalent bond.

By combining supramolecular binding motifs with polymer chemistry, it is possible to introduce defined structural changes on adjustable time scales into well-known and otherwise chemically stable polymeric materials. This ability renders supramolecular polymers and polymer systems a promising platform for self-healing,<sup>21, 23</sup> drug delivery,<sup>24, 25</sup> or shape memory<sup>26, 27</sup> materials. To make this truly useful, a detailed understanding of the structure–property relationships, and therefore of the interplay of supramolecular and macromolecular dynamics in the transiently linked polymers, is essential when such materials are to be tailored from the molecular level. Whereas this interplay has been intensely studied for supramolecular cross-linked polymer networks and gels, it is far less understood for linear telechelic polymers, which have a linear architecture and carry the same associative end group on both sides, especially in semi-dilute solution.

The dynamics of any supramolecular polymer system is governed primarily by the effective relaxation time of the assembly,  $\tau_{eff.}$ . This time is composed of two major contributors, as illustrated in Figure 1, both in polymer networks and in linear telechelic assemblies, both in bulk and solution. The first contributor is the diffusive motion of the supramolecular assembly, which can be either a Rouse-type motion with the corresponding Rouse relaxation time,  $\tau_{R}$ , or a reptative motion described by the corresponding reptation time,  $\tau_{rep}$ , depending on the absence or presence of entanglements. The second contributor is the dynamics of the supramolecular associative motifs that hold the assembly together, which is determined primarily by their effective bond lifetime,  $\tau_{break}$ . For a free associative motif that is not connected to an oligo- or polymeric backbone,  $\tau_{break}$  corresponds to the inverse dissociation constant of the complex itself,  $k_{diss}^{-1}$ . For an associative motif that is connected to an oligoor polymeric backbone, however,  $\tau_{break}$  is often markedly prolonged, because the low mobility of the polymer chain attached to the binding motif, often further restrained by topological constraint in a crowded environment, hinders the complex to effectively open. This is because occasional breakage of a supramolecular complex in such an environment is not quickly followed by substantial spatial separation of the former binding partners to allow for association with new partners, but instead, the old partners most likely re-associate with one another again after breakage. This situation is especially relevant when the concentration of non-bonded partners is low due to a strong binding affinity of the associating groups. Consequently, such a transient bond might break and reform many times before its motifs find new different partners, which prolongs the effective lifetime of the complex measurably, as described by Rubinstein's and Semenov's theoretical concept of the renormalized bond lifetime,  $\tau_{break}^{*}$ .<sup>28, 29</sup>



**Figure 1.** Schematic representation of the interplay between the polymer chain motion (left zoom) and metallosupramolecular association of its building blocks (right zoom) for telechelic linear polymers in the semi-dilute regime. Depending on the length of the polymeric building block and the strength of the metallo-supramolecular association, the chain aggregates either relax via a Rouse-type motion or by reptation.

To probe this conceptual picture, several experimental studies have been conducted during the last decade. Van Ruymbeke and co-workers showed that the renormalized bond lifetime  $\tau_{break}^*$  plays a significant role in telechelically extended metallo-supramolecular assemblies in the melt state.<sup>30, 31</sup> They investigated the viscoelastic properties of a series of terpyridine end-capped poly(n-butyl acrylates) (PBAs) with different structural architectures by oscillatory shear rheology. Whereas monofunctional linear polymer chains were found to form binary assemblies and to display Maxwelltype viscoelasticity, bifunctional compounds were found to form a polydisperse distribution of assemblies with different molar masses, leading to a complex viscoelastic behavior. The metal-ligand bond of these assemblies, whose lifetime is tunable by selection of the transition metal ion, shifts the terminal relaxation time  $\tau_{eff.}$  to lower frequencies compared to the non-associated compound. This shift was found to be directly related to the renormalized bond lifetime  $\tau_{break}^*$ , as the probability of any open binding motif to find a new binding partner is lowered upon increase of the metallosupramolecular bond strength. The association was determined to be much stronger, and thus longer lived, when the complexing terpyridine motif is attached to a polymer backbone than it would be for a free terpyridine unit. The same effect can also be found in solution-based system comprised of either side-chain associating<sup>32-34</sup> or star-shaped polymers.<sup>10, 35</sup>

Contrary to these findings, Richter and co-workers showed that the renormalized bond lifetime  $\tau_{break}^*$  does not play a significant role in rapidly exchanging and weakly associating systems. They studied the association of a telechelic poly(ethylene glycol) (pEG) in the melt within different experimental time frames using pulsed field gradient NMR (PFG-NMR), small angle neutron scattering (SANS), and oscillatory shear rheology.<sup>36</sup> The molar mass of their pEG chains ( $M_n = 1.97 \text{ kg} \cdot \text{mol}^{-1}$ ) was chosen to be close to its melt-state entanglement molar mass ( $M_e \approx 1.6-2.2 \text{ kg} \cdot \text{mol}^{-1}$ ),<sup>37-39</sup> and the chain termini were capped with hetero-complementary thymine (A) and diaminotriazine (B) moieties that form A–B-type associations via triple hydrogen bonding. Richter *et al.* reported a seemingly profound inconsistence between the structure (as studied by SANS) and dynamics (as studied by PFG-NMR and rheology) of these assemblies. Structurally, aggregation numbers  $N_{agg}$  of 6–13 were determined, whereas dynamically, Rouse-type relaxation was observed even though these aggregates' molar masses were all well above the entanglement threshold, such that the telechelic chains should actually undergo reptation. This result was discussed in terms of the hydrogen bond lifetime of the end group association, which must be short enough to allow for diffusion of the buildings blocks of the

supramolecular aggregates during the determined diffusion time. So in short, whereas the compound forms long chain aggregates in a time-average, from a dynamical viewpoint, these break up (and reform) too fast for the diffusing chain to experience entanglement constraints.

The exact effect of the interplay between the motion of the supramolecular assemblies and the dynamics of the supramolecular association in transient telechelic polymers is both complex and not yet fully understood. To our knowledge, most available studies on telechelics focus on polymers in the melt state<sup>30, 31, 36, 40, 41</sup>. This is reasonable, because in the melt, the polymer chain motion is sufficiently slowed down to successfully separate both contributors to the dynamics and to study the renormalized bond lifetime  $\tau_{\text{break}}^*$  on experimentally accessible time scales. Studies on solution-based systems mainly focus on polymers that form transient *networks*, such as side-chain associating polymers or starshaped and dendritic structures<sup>33-35, 42, 43</sup>. Studies of purely linear telechelically associating polymers in solution, by contrast, are rare, thereby leaving an incomplete picture.<sup>44</sup>

In this paper, we employ a modular system based on telechelic terpyridine-functionalized pEG to study the interplay of polymer chain motion and metallo-supramolecular intrachain dynamics in the semidilute regime, as visualized in Figure 1. We chose pEG in particular for its high chain flexibility, its good solubility in different media, and its well-defined terpyridine-based coordinative polymer chemistry,<sup>45,</sup> <sup>46</sup> which allows us to fine-tune the strength of the metallo-supramolecular association by selecting different transition metal ions (Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>).<sup>46-49</sup> We intentionally use metallo-supramolecular bonds, as they are quite strong in terms of their binding energies compared to other supramolecular interactions,<sup>22</sup> and therefore amplify the influence of the transient association; on top of that, they are tunable by mere exchange of the central ion without any structural changes on the polymeric level accompanying that. The mechanical properties of such a material reflect the influence of both the assemblies own diffusive motion and the dynamics of the metallo-supramolecular association. Based on such data, we systematically investigate the chain dynamics in dependence of classical polymer physical parameters such as the molar mass and concentration of the pEG compound, whereas the supramolecular associative dynamics is determined by parameters such as the bond lifetime and association strength of the transient bonds. We probe the systems by oscillatory shear rheology and evaluate the data with a modified version of the tube-based time marching algorithm (TMA) developed by van Ruymbeke et al.<sup>50</sup> In this endeavour, it is to realize that transforming rheological data into a detailed molecular picture is a challenge, because the viscoelastic response of the metallosupramolecular assemblies is a summation of the chain's own movement as well as all other chemical and physical interactions. To alleviate this, we have simplified our system whenever possible and stay within the confines of accepted methodology.<sup>30, 31, 50, 51</sup>

# 3.3.2. Experimental section

**Chemicals:** All poly(ethylene glycols) were purchased from Sigma Aldrich and used without further purification, unless stated otherwise. Solvents were purchased from Acros Organics *Acroseal* in bottles equipped with a septum cap and stored over molecular sieves. Chemical reagents were purchased from various suppliers. A full list of compounds, including supplier and purity, is given in the supplemental information.

**Spectroscopy:** <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 400 digital FT-spectrometer at 400 MHz in either  $CDCl_3$  or  $DMSO-d_6$  at 25 °C. Chemical shifts reported in ppm are referenced to

trimethylsilane (TMS) as a standard using  $\delta$ (TMS) = 0 ppm. UV spectra were recorded on a V-760 spectrophotometer (JASCO) using analytical grade solvents (Uvasol, Merck). IR spectra were recorded on a FT/IR-4700 Fourier Transform Infrared Spectrometer (JASCO). High-resolution mass spectroscopy (HRMS) with electron-spray ionization (ESI) was carried out on an Ionspec QFT-7 from Varian Inc.

**2.3 Synthesis** All synthetic steps were carried out for pEGs with a molar mass range of  $M_w = 4-12$  kg·mol<sup>-1</sup>. Molar masses and polydispersities as determined by size exclusion chromatography (SEC) are compiled in Table 1. The polydispersity did not change for any intermediate or final product upon chemical end-group modification.

Compound	<i>M</i> n (kg·mol <sup>−1</sup> )¹	<i>M</i> <sub>w</sub> (kg·mol <sup>−1</sup> ) <sup>1</sup>	PDI
pEG-4K	4.54	4.66	1.03
pEG-6K	5.88	6.08	1.03
pEG-8K	8.30	8.78	1.06
pEG-10K	8.95	9.56	1.07
pEG-12K	12.63	13.97	1.13

 Table 1. Molar masses and polydispersities of pEG-OH precursors, as determined by size exclusion chromatography (SEC).

<sup>1</sup>: Linear poly(ethylene glycol) standards obtained from PSS GmbH (Mainz, Germany) were used as references in SEC to evaluate the molar mass distribution.

**Synthesis of pEG-epoxide:** pEG-OH-4K (12.0 g, 3.00 mmol) was dried at 80 °C *in vacuo* until bubbling ceased, indicating complete evaporation of residual water. The compound was then cooled to room temperature and dissolved in anhydrous tetrahydrofuran (250 ml). Sodium hydride (3.60 g, 90.00 mmol, 60% suspension in mineral oil) was added slowly to the solution at room temperature, upon which it turned turbid yellow, and then stirred for 3 h. Epichlorohydrin (18.82 ml, 240.00 mmol) was added, and the solution was stirred for another 48 h. It was then cooled to 0 °C and quenched with water. Brine was added (100 ml), and the mixture extracted with dichloromethane (3 x 400 ml). The organic layer was collected, dried over sodium sulfate, and concentrated *in vacuo*. The concentrate was precipitated into cold diethyl ether, collected by filtration and dried under high vacuum to yield the product as a colorless solid (11.27 g, 91%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 3.70 (dd, *J* = 11.6, 2.8 Hz, 2H), 3.55–3.46 (m, pEG-backbone), 3.25 (dd, *J* = 11.6, 6.4 Hz, 2H), 3.09 (ddt, *J* = 6.4, 4.2, 2.8 Hz, 2H), 2.72 (dd, *J* = 5.1, 4.2 Hz, 2H), 2.54 (dd, *J* = 5.1, 2.7 Hz, 2H) ppm.

**Synthesis of pEG-hydroxy-azide:** Sodium azide (3.57 g, 54.84 mmol) and ammonium chloride (5.87 g, 109.71 mmol) were added to a solution of pEG-epoxide (11.27 g, 2.74 mmol) in dimethyl-formamide (100 ml) and stirred for 72 h at a temperature of 60 °C. Dimethylformamide was then removed *in vacuo*. The residue was dissolved in dichloromethane (50 ml). Brine was added (100 ml), and the mixture was extracted with dichloromethane (3x 400 ml). The organic layer was collected, dried over sodium sulfate, and concentrated *in vacuo*. The concentrate was precipitated into cold diethyl ether, collected by filtration, and dried under high vacuum to yield the product as a colorless solid (10.99 g, 96%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 5.25 (d, *J* = 5.2 Hz, 2H), 3.77 (td, *J* = 5.9, 3.7 Hz, 2H), 3.68 (dd, *J* = 5.9, 3.7 Hz, 2H), 3.55–3.46 (m, pEG-backbone), 3.27 (dd, *J* = 12.7, 3.7 Hz, 2H), 3.19 (dd, *J* = 12.7, 6.6 Hz, 2H) ppm. IR: v = 2882 (m), 2099 (azide, w), 1467 (m), 1360 (w), 1342 (m), 1280 (m), 1241 (m), 1146 (m), 1101 (s), 1061 (m), 961 (m), 842 (m).

**Synthesis of Propargyl-terpyridine:** 2,6-Bis(2-pyridyl)-4(1*H*)-pyridone (4.00 g, 16.05 mmol) and predried potassium carbonate (13.31 g, 96.28 mmol) were suspended in anhydrous acetonitrile (100 ml). After dropwise addition of propargyl bromide (2.15 ml, 19.26 mmol, 80 wt% in toluene), the suspension was heated to 60 °C and stirred for 24 h. Then, the reaction mixture was cooled to room temperature and precipitated into ice-cold water. The crude product was collected by filtration, washed with ice-cold water and dried *in vacuo*. A saturated solution of the crude product was prepared in boiling *n*-heptane, which was then cooled to room temperature to add 2 wt% of activated charcoal. The suspension was refluxed for 10 min, and the product isolated by hot filtration as colorless needles (4.09 g, 89%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.68 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.60 (dt, *J* = 8.0, 1.2 Hz, 2H), 8.09 (s, 2H), 7.83 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 2H), 7.32 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H), 4.93 (d, *J* = 2.4 Hz, 2H), 2.59 (t, *J* = 2.4 Hz, 1H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.83, 157.26, 155.90, 149.09, 136.77, 123.88, 121.34, 107.55, 77.59, 77.36, 77.05, 76.73, 76.33, 55.83 ppm. Mass spectra (250.0 V, ESI-TOF). m/z calculated for [C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>O + Na]<sup>+</sup>: calculated 310.0956, found 310.1000.

**Synthesis of pEG-hydroxy-terpyridine:** Propragyl-terpyridine (0.82 g, 2.86 mmol) was added to a melt of pEG-hydroxy-azide (4.00 g, 0.95 mmol). The melt was stirred at a temperature of 90 °C for 18 h under high vacuum. Then, the reaction mixture was allowed to cool down to room temperature and dissolved in dichloromethane (25 ml). This solution was precipitated into cold diethyl ether, collected by filtration, and dried under high vacuum to yield the product as a colorless solid (10.99 g, 96%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 8.72 (d, *J* = 5.1 Hz, 4H), 8.62 (d, *J* = 7.9 Hz, 4H), 8.21 (s, 1H), 8.09 (s, 4H), 8.01 (t, *J* = 7.4 Hz, 4H), 7.88 (s, 1H), 7.50 (t, *J* = 6.6 Hz, 4H), 5.61 (s, 1H), 5.45 (s, 2H), 5.33 (dd, *J* = 38.2, 5.6 Hz, 2H), 4.54 (dd, *J* = 68.2, 14.6 Hz, 2H), 4.36 (ddd, *J* = 58.1, 14.1, 8.0 Hz, 2H), 4.01 (d, *J* = 39.6 Hz, 2H), 3.55–3.46 (m, pEG-backbone) ppm.

Synthesis of *Tert*-butyl (2-aminoethyl)carbamate: Diaminoethane (61.57 ml, 920.0 mmol) was dissolved in 1,4-dioxane (300 ml). A solution of Di-*tert*-butyl dicarbonate (25.10 g, 115.0 mmol) was added dropwise at room temperature over a period of 3 h, upon which the reaction mixture turned turbid. The mixture cleared after stirring for 18 h, indicating full conversion. Any precipitate was filtered off, and the filtrate was concentrated *in vacuo* to remove solvent and residual diaminoethane. After addition of 500 ml of water, the disubstituted product, bis-*N*,*N*'-*tert*-butyloxycarbonyl)-1,2-diaminoethane, could be removed by filtration. The aqueous filtrate was washed with dichloromethane (5x 150 ml). The organic layer was collected, dried over sodium sulfate, and removed *in vacuo* to yield the crude product as a yellow oil. Purification by vacuum distillation (130 °C, 7·10<sup>-</sup> <sup>2</sup> mbar) yielded the product as a colorless oil (15.76 g, 86%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.10 (s, 1H), 3.15 (q, *J* = 6.0 Hz, 2H), 2.77 (t, *J* = 5.9 Hz, 2H), 1.89 (s, 2H), 1.40 (s, 9H) ppm.

Synthesis of *Tert*-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)ethyl)carbamate: *Tert*-butyl (2-aminoethyl)carbamate (15.76 g, 98.3 mmol) and dimethyl maleic anhydride (12.40 g, 98.3 mmol) were dissolved in toluene (300 ml) and heated to 130 °C for 3 h using a reflux condenser equipped with a water trap. Removal of the solvent *in vacuo* and drying under high vacuum yielded the product as a colorless solid (25.27 g, 98%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.80 (s, 1H), 3.61 (t, *J* = 5.7 Hz, 2H), 3.30 (q, *J* = 4.6 Hz, 2H), 1.95 (s, 6H), 1.39 (s, 9H) ppm.

**Synthesis of 1-(2-Aminoethyl)-3,4-dimethyl-1H-pyrrole-2,5-dione trifluoroacetate:** Trifluoroacetic acid (148.0 g, 1.3 mol) was added to a solution of *tert*-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)carbamate in dichloromethane (70 ml). The solution was stirred for 1 h at room temperature until all bubbling ceased, indicating complete deprotection. Residual trifluoroacetic acid

was removed *in vacuo*. The residue was dissolved in water (250 ml) and the pH set to eight using diethylamine. The mixture was extracted with ethyl acetate (4x 200 ml). The organic layer was collected, dried over sodiumm sulfate, and removed *in vacuo* to yield the product as a colorless solid (19.86 g, 75%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.94 (s, 3H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.35 (s, 1H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.50 (d, *J* = 2.5 Hz, 1H), 1.90 (s, 6H) ppm.

**Synthesis of pEG-***p***-Nitrophenylcarbonate:** pEG-OH 6K (3.0 g, 0.5 mmol) was dried at 80 °C *in vacuo* until bubbling ceased, indicating complete evaporation of residual water. The compound was then cooled to room temperature and dissolved in anhydrous dichloromethane (20 ml). Anhydrous pyridine (241.7 µl, 3.0 mmol) and *p*-nitrophenylchloroformate (302.3 mg, 1.5 mmol) were added, and the resulting suspension was stirred for 18 h. Brine was added (25 ml), and the mixture was extracted with dichloromethan (3x 100 ml). The organic layer was collected, dried over sodium sulfate and concentrated *in vacuo*. The concentrate was precipitated into cold diethyl ether, collected by filtration, and dried under high vacuum to yield the product as a colorless solid (2.92 g, 94%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 8.32 (d, *J* = 9.2 Hz, 4H), 7.57 (d, *J* = 9.2 Hz, 4H), 4.42–4.33 (m, 4H), 3.82–3.63 (m, 8H), 3.55–3.46 (m, pEG-backbone), 3.32 (s, 1H), 2.50 (t, *J* = 1.9 Hz, 9H) ppm.

**Synthesis of pEG-DMMI:** pEG-*p*-Nitrophenylcarbonate (2.92 g, 0.47 mmol) was dissolved in dimethylformamide (100 ml). Triethylamine (0.26 ml, 1.89 mmol) was added to the solution, followed by 1-(2-aminoethyl)-3,4-dimethyl-1*H*-pyrrole-2,5-dione trifluoro-acetate (0.34 g, 1.42 mmol). The reaction mixture was stirred for 18 h at room temperature. Brine was added (100 ml), and the mixture was extracted with dichloromethan (3x 200 ml). The organic layer was collected, dried over sodium sulfate, and concentrated *in vacuo*. The concentrate was precipitated into cold diethyl ether, collected by filtration, and dried under high vacuum to yield the product as a colorless solid (1.68 g, 87%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.28 (s, 2H), 4.01 (s, 4H), 3.55–3.46 (m, pEG-backbone), 3.09 (s, 4H), 2.94 (s, 2H), 1.90 (d, *J* = 9.8 Hz, 12H) ppm.

**Sample preparation for oscillatory shear rheology:** Samples were prepared by mixing equal volumes of polymer and cross-linking metal-ion solutions (0.50 mL each) in chloroform–methanol (volume ratio 1:1). The polymer solutions consisted of pEG-hydroxy-terpyridine precursor polymer at concentrations between 200 and 500 g·L<sup>-1</sup>, thereby giving metallo-supramolecular assemblies with concentrations between 100 and 250 g·L<sup>-1</sup> after mixing with the cross-linking metal-ion solutions. Each of the metal-ion solution was prepared such that two terpyridine-units can complex to exactly one metal-ion upon mixing these components. Sample equilibration was performed directly on the lower plate of the rheometer. The upper plate was then lowered and raised again twice while rotating, thereby thoroughly mixing the two compounds.

**Oscillatory shear rheology:** Rheological studies were performed on a stress-controlled MCR 302 rheometer (Anton Paar) with a stainless-steel cone–plate geometry (cone angle 1°, cone diameter 50 mm) equipped with a solvent trap. Inertial calibration and motor adjustment were performed before each measurement.

Gelation experiments were carried out on a UV-transparent lower glass plate connected by an optical fiber cable to a high pressure 200-W mercury vapor UV source (OmniCure S1500) at an aperture of 25%. The sample was monitored at a constant shearing amplitude and frequency ( $\gamma = 0.05$ ;  $\omega = 1.0 \text{ rad} \cdot \text{s}^{-1}$ ) until the elastic modulus reached a plateau value, but at least for 120 min.

To determine the mechanical properties of the metallo-supramolecular assemblies, each sample was monitored for 30 min at a constant shearing amplitude and frequency ( $\gamma = 0.01$ ;  $\omega = 0.1 \text{ rad} \cdot \text{s}^{-1}$ ) to ensure sample equilibration. Then, an amplitude sweep was carried out to determine the linear viscoelastic regime of each compound. Subsequently, a frequency sweep was recorded at the before determined strain amplitude ( $\gamma = 0.01$ ;  $\omega = 0.01$ ;  $\omega = 0.01$ –20 rad·s<sup>-1</sup>) at 20 °C.

#### 3.3.3. Results and discussion

### 3.3.3.1. Material platform

The purpose of this study is to investigate the interplay of the polymer chain inherent dynamics and the metallo-supramolecular chain extension that adds upon that in linear telechelic polymeric assemblies in solution, as illustrated in Figure 1. The material platform for this endeavor are terpyridine-terminated pEG chains as the linear chain-extending building blocks. To realize this strategy, a pair of two different functional groups is attached to each end of the pEG chains.<sup>43, 52</sup> For this purpose, commercially available pEG-OH is first deprotonated with sodium hydride and subsequently reacted with epichlorohydrin to yield pEG-epoxide, as illustrated in Scheme 1A. The epoxide rings are then asymmetrically opened by sodium azide, which gives  $\beta$ -hydroxy- $\alpha$ -azide-terminated pEG chains, pEG-TPy (Scheme 1B). These are reacted in a thermally driven, catalyst-free azide–alkyne Huisgen cycloaddition with an alkyne-functionalized terpyridine compound prepared separately by nucleophilic substitution of a pyridone with propargyl bromide (Scheme 1C–D). This synthetic procedure is performed on a multigram scale with 56–78% yields.

The functionalization of the pEG chain-termini with terpyridine groups occurs with degrees between 92–99%, as determined by <sup>1</sup>H-NMR and UV spectroscopies. This synthesis is carried out with pEG precursors with molar masses of M = 4, 6, 8, 10, and 12 kg·mol<sup>-1</sup>, from here on be named pEG-4K, Peg-6K, pEG-8K, pEG-10K, and pEG-12K. Poly(ethylene glycol) is an ideal model polymer for dynamical investigations because of its high chain flexibility, as assessed by its low characteristic ratio of  $C_{\infty} = 4.1 \pm 0.4^{53, 54}$  and its short persistence length of  $\lambda = 3.8$  Å.<sup>55, 56</sup> For our solution-focused investigation, we chose an isochoric mixture of chloroform and methanol (denoted CHCl<sub>3</sub>/MeOH from here on) as the solvent. This is done for three reasons. First, the Hildebrandt solubility parameter of this solvent mixture  $\delta_{CHCl3/MeOH} = 11.9$  (cal·cm<sup>-3</sup>)<sup>0.5</sup>, calculated from the arithmetic average of the pure compounds  $\delta_{CHCl3} = 9.3$  (cal·cm<sup>-3</sup>)<sup>0.5</sup>. and  $\delta_{CHCl3/MeOH} = 14.5$  (cal·cm<sup>-3</sup>)<sup>0.5</sup>, for is close to that of pure pEG  $\delta_{pEG} = 9.9$  (cal·cm<sup>-3</sup>)<sup>0.5</sup>. This indicates that CHCl<sub>3</sub>/MeOH provides good solvent conditions for the pEG chains. Second, a competing association of the solvent mixture to terpyridine can be ruled out, as CHCl<sub>3</sub>/MeOH was found to not interfere with the metallo-supramolecular bond.<sup>59</sup> Third, whereas the former two criteria would also be met by pure chloroform as the solvent, only the chloroform– methanol 1:1 mixture fully dissolves the metal ions that are needed for the terpyridine complexing.

The strength of the transient metal-terpyridine complex can be tuned by the choice of the complexing metal ion, which we select from the d-row of the periodic table. We pick  $Mn(NO_3)_2$ ,  $Zn(NO_3)_2$ ,  $Co(NO_3)_2$ , and  $Ni(NO_3)_2$ , because these salts are known to form complexes of markedly varying strength with pyridines.<sup>47-49</sup>



**Scheme 1.** (A) Preparation of linear pEG that carries a terpyridine motif at each chain end. For this purpose, commercially available pEG-OH is functionalized to form pEG-epoxide, and (B) further converted to pEG- $\theta$ -hydroxy-azide. (C) In a separate reaction, propargyl-terpyridine is prepared by nucleophilic substitution of a pyridone with propargyl bromide and (D) subsequently reacted with the pEG- $\theta$ -hydroxy- $\alpha$ -azide in a thermally-driven, catalyst-free azide–alkyne Huisgen cycloaddition to yield pEG- $\theta$ -hydroxy- $\alpha$ -terpyridine.

A quantity that expresses the coordinative binding affinity of these metal ions to terpyridine is the association equilibrium constant, K, which relates the equilibrium concentration of associated complexes to that of the non-associated binding motifs. Terpyridine complexes to metal(II) ions in a 2:1 ratio (M + 2L  $\rightarrow$  ML<sub>2</sub>), leading to an equilibrium constant of  $K = [ML_2]/([M][L]^2)$ .

Table 2. Equilibrium constants, $K$ , and dissociation rate constants, $k_{dis}$	ss, for the complexation and decomplexation of metal
ions with terpyridine, estimated by ITC <sup>10</sup> and UV spectroscopy. <sup>47-49</sup>	

Metal ion	κ (L²mol <sup>-2</sup> ) <sup>α</sup>	<i>k</i> <sub>diss</sub> (s <sup>-1</sup> )
Mn <sup>2+</sup>	3.5 x 10 <sup>9</sup>	4.0
Zn <sup>2+</sup>	1.3 x 10 <sup>12</sup>	1.2
Co <sup>2+</sup>	2.1 x 10 <sup>10</sup>	1.0 x 10 <sup>-4</sup>
Ni <sup>2+</sup>	1.3 x 10 <sup>11</sup>	1.6 x 10 <sup>-6</sup>

pEG precursor	<i>R</i> н (nm)	<i>с</i> * (g·L <sup>−1</sup> ) <sup>а</sup>	<i>c</i> (g·L <sup>−1</sup> )	
pEG-4K	1.8	56.6	250	
pEG-6K	2.2	44.4	200	
pEG-8K	2.7	32.2	150	
pEG-10K	3.0	26.9	120	
pEG-12K	4.4	22.2	100	

**Table 3.** Hydrodynamic radii *R*<sub>H</sub>, calculated from dynamic light scattering as well as overlap and absolute polymer concentrations utilized during oscillatory shear rheology experiments.

°: calculated by  $c^* = 3M/(4\pi R_g^3 N_A)^{62}$ 

The *K*-values in a CHCl<sub>3</sub>/MeOH-mixture (1:1) have been determined by isothermal titration calorimetry (ITC) in the context of an earlier work.<sup>10</sup> In addition to this equilibrium constant, an additional quantity that represents the metal–ligand binding–unbinding *kinetics* of these complexes are their dissociation rate constants,  $k_{diss.}$ . Literature values of these parameters are available for aqueous solutions, as compiled in Table 2. These data show that the binding affinity gets larger from Mn<sup>2+</sup> to Co<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>, whereas the kinetic stability of the association is enhanced from Mn<sup>2+</sup> to Zn<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>.

Two aspects need to be considered in view of linear telechelically associating polymer chains. First, they do not inherently create networks, as would be the case for side-chain associating or star-shaped polymers, but instead, form extended linear chain assemblies. These longer chains then might at least form entanglement networks, whereas only in special cases, lateral stacking or clustering of the binding motifs may also act as a means of higher-order non-covalent cross-linking.<sup>60, 61</sup> Second, linear chain association is accompanied by an entropy penalty: the order of the system increases when two chains bind two each other and form an extension. This effect is further pronounced for each additional chain that participates in the assembly. We therefore expect the linear telechelic chain-interlinking to be less marked than it could be in side-chain associating or star-shaped polymers carrying the same binding motif.

We account for these conditions by probing our material at absolute concentrations 4–5 times higher than their precursor's overlap concentrations,  $c^*$ , as compiled in Table 3. That way, the polymer is always kept in the semi-dilute concentration regime in which the chains, and thus also their active ends, are in reasonably close proximity to each other. Additionally, because of the good solvency conditions provided by the CHCl<sub>3</sub>/MeOH mixture, the polymer coils are expected to be expanded.

# 3.3.3.2. Covalent chain extension via photolinking

To gauge the upper efficiency boundary for the metallo-supramolecular chain extension of the pEG-TPy chains, we first investigate a pEG model compound that can chain-extend via covalent permanent bonds rather than transient bonds. For this purpose, we synthesize pEG chains that carry a photoactive dimethylmaleimide (DMMI) motif at each chain end (pEG-DMMI), as displayed in Figure 2A and B. These DMMI units undergo a [2+2] cycloaddition dimerization when irradiated by UV light ( $\lambda = 320-500$  nm) in an organic solvent in the presence of a suitable triplet sensitizer such as thioxanthone.<sup>63</sup>



**Figure 2** (**A**, **B**) Preparation of a pEG compound that carries a photoactive dimethylmaleimide (DMMI) motif at each chain end. Upon triplet-sensitized UV irradiation, the DMMI units undergo [2+2]-cycloaddition dimerization, thereby covalently jointing the pEG chains. (**C**) Time-dependent evolution of the shear and loss moduli (*G*': full purple symbols, *G*'': open purple symbols) of a semi-dilute solution of such pEG-dimethylmaleimide chains during UV-induced photodimerization in the presence of a suitable photosensitizer, as well as reaction conversion as a function of the reaction time (full black symbols). The precursor chains have a molar mass of  $M_w = 6$  kg·mol<sup>-1</sup> and are probed at 5 times their overlap-concentration ( $5 \cdot c^* = 200 \text{ g·L}^{-1}$ ) in an isochoric mixture of chloroform and methanol. The conversion is calculated from the decrease of the UV absorbance of the DMMI moieties at a wavelength of 245 nm. (**D**) This is valid, because the UV absorbance of the DMMI unit disappears after the photodimerization, as was checked with a low molar mass model compound (dimerization reaction shown in inset).

As such, this pEG-DMMI model compound is able to undergo chain extension just as the analogous supramolecular telechelic compounds, albeit pEG-DMMI does so *irreversibly*, thereby allowing us to estimate the maximum possible degree of chain extension at otherwise same experimental conditions.

We probe the pEG-DMMI during the UV photoreaction by oscillatory shear rheology at a constant shearing amplitude of  $\gamma = 5\%$  and a constant angular frequency of  $\omega = 1 \text{ rad} \cdot \text{s}^{-1}$  as a function of the reaction time to follow the evolution of the elastic and viscous moduli, *G*' and *G*'', as shown in Figure 2C.

Upon completion of the covalent chain extension, the moduli of all compounds investigated have increased by at least three orders of magnitude for the short chains of pEG-4K-DMMI and pEG-6K-DMMI and about two orders of magnitude for the other pEG-DMMI compounds (8K–12K). At several intervals during the photoreaction, UV spectra are recorded to follow the consumption of the DMMI units by the weakening of their absorption signal at 245 nm.<sup>64</sup> From the relative differences of this absorption, an approximate conversion of 67–75% can be calculated. This means that about 25– 33% of the chain ends do not participate in the chain extension, which is most likely caused by topological constraints that increase during the course of the reaction: as the aggregates become longer, their mobility is lowered, and at some point, the remaining reactive chain ends cannot find each other, especially as they are located in the interior of increasingly large coils. To check for the validity of this interpretation, a low molar mass model compound is dimerized under the same conditions. In that case, completion of the photoreaction is evident by complete disappearance of the DMMI absorption signal at 245 nm, as shown in Figure 2D. From the conversion of the pEG-DMMI system, the number and weight average degree of polymerization (DOP) of the pEG-DMMI building blocks can be calculated with the Carothers equation for polyaddition, yielding  $X_n \approx 3-4$  and  $X_w$ ,  $\approx 5-6$ . Following this, the polydispersity  $\mathcal{D} = X_w/X_n$  is estimated to be around  $\mathcal{D} = 1.7$  for all extended chains. This is reasonably close to the expected value of D = 2.0 for a Schulz–Flory distribution. These results of the covalently extended precursor chains will serve as a benchmark when examining the data of the metallo-supramolecular chain extension.

# 3.3.3.3. Oscillatory shear rheology

To investigate the mechanical properties of our compounds after coordinative chain extension by metal(II) ions, we probe them by frequency-dependent oscillatory shear rheology in the linear viscoelastic regime to determine their frequency-dependent elastic and viscous shear moduli,  $G'(\omega)$ and  $G''(\omega)$ . For the purpose of the metallo-supramolecular chain extension, solutions of the polymer and the interlinking metal ions are prepared in an isochoric mixture of CHCl<sub>3</sub>/MeOH. They are then mixed on the rheometer, whereby stoichiometric amounts of metal nitrate relative to the concentration of linkable terpyridine moieties are used. In this assessment, we also check for the impact of possible secondary means of association, such as micro phase separation,  $\pi$ - $\pi$  stacking, or hydrogen bonding. The latter is of specific relevance, because the pEG-TPy precursors carry one additional hydroxyl group close to each of their terpyridine functionalities as a remnant of the synthetic pathway. These groups might establish hydrogen bonds to a neighboring precursor chain, which could lead to a faulty interpretation of the rheological data. However, a single hydroxyl functionality can be considered a weak hydrogen-bonding group, in fact, the weakest. Anthamatten and co-workers have shown that such weak hydrogen-bonding groups do not influence the frequency-dependent viscoelastic spectrum in a polymer melt.<sup>65</sup> We are confident that, if this is true even in a crowded melt environment, it will even more hold true for a semi-dilute polymer solution, in which the binding motifs are comparably far apart. Nevertheless, we check for the influence of possible secondary associations by comparing the frequency-dependent viscoelastic data of our native pEG-OH precursor compounds before any further functionalization to those of their length-corresponding pEG-TPy samples in the absence of coordinatively linking metal ions. Both datasets are found to superimpose for all molar masses, so we conclude that any potential secondary associations that might be present in the system are weaker in energy than the primary one mediated by the metal-ligand complexation.



**Figure 3 (A)** Concentration-dependent complex viscosity  $\eta^*$  of semi-dilute solutions of pEG-*B*-hydroxy- $\alpha$ -terpyridine precursor chains (blue symbols), the metallo-supramolecular compound chain-extended by Zn<sup>2+</sup> ions (orange symbols), representative of a weak transient bond, and Ni<sup>2+</sup> ions (green symbols), representative of a strong transient bond, as the linking agent, as well as the covalently chain-extended compound (purple symbols). The precursor chains have a molar mass of  $M_w = 6 \text{ kg} \cdot \text{mol}^{-1}$  in an isochoric mixture of chloroform and methanol. Red trend lines visualize apparent power-law scaling of  $\eta^*$  as a function of *c*. **(B)** Frequency-dependent storage and loss moduli,  $G'(\omega)$  and  $G''(\omega)$ , of semi-dilute solutions of the same samples. The color scheme of Panel (A) is retained. The storage moduli  $G'(\omega)$  are denoted by full symbols, whereas the loss moduli  $G''(\omega)$  are denoted by open symbols. Note that all the rheology curves in Panel (B) show a low-frequency plateau in the storage modulus  $G'(\omega)$ . This is due to an instrument effect caused by a faulty recording of the phase angle, which is particularly severe for low-viscous samples.<sup>17</sup>

Before frequency-resolved mechanical characterization of the metallo-supramolecular assemblies is conducted, concentration-dependent viscosity measurements are carried out to identify the relaxational regime of the assembly. For this pretest, we select the pEG-6K-TPy sample. Further testing with other molar masses is deemed unnecessary, as all absolute concentrations are the same factor of their corresponding overlap concentrations (see Table 3) and therefore in the same relaxational regime. Thus, the result for pEG-TPy-6K is considered representative for all other samples. The goal of the experiment is to ascertain whether or not the assemblies are long enough to entangle. If they are, the viscosity should scale with the concentration according to  $\eta \sim c^{3.5}$ , as predicted in Cates' model for solutions of entangled wormlike surfactant micelles that is often applied to interpret experimental data for entangled and "living" linear telechelic polymer chains in solution as well.<sup>66</sup> By contrast, the viscosity of a non-entangled polymer solution should scale according to  $\eta \sim c^{1.0}$ , reflecting Rouse-type dynamics.<sup>67</sup> The latter is expected for the non-extended precursor polymers solution that consists of the terpyridine end-capped pEG compounds without metal ions present. We find that the  $\eta(c)$ -scaling of the non-extended precursor solution is indeed in agreement with this prediction, displaying a  $\eta(c)$ log–log slope of 1.09. Upon metallo-supramolecular chain-extension, the  $\eta(c)$  log–log slope steepens systematically, as shown in Figure 3A. It is raised to 1.17 when Zn<sup>2+</sup> ions are used as the linking species, representative of a weak coordinative bond. Strong association by Ni<sup>2+</sup> ions as the linker further raises it to a value of 1.35. The pEG-6K-DMMI sample that is chain-extended by covalent bonds exhibits a  $\eta(c)$  log-log slope of 1.59. These exponents show that all the linear chain assemblies are much closer to the Rouse regime than to the reptative one, which is an indicator that the assemblies are not entangled. This is a surprising result, because the metallo-supramolecular association of terpyridine with d-row metal ions is the strongest and therefore longest-lived of any supramolecular binding motifs, as indicated by its equilibrium and dissociation rate constant (see Table 2). It was also shown that the stability of this association is further amplified when the binding motif is attached to a pEG backbone in the melt state.<sup>30, 31</sup> As a consequence, we expected chain-extended assemblies long enough to form entanglements. In contrast to that expectation, our experimental results are in agreement with other studies carried out for dilute or semi-dilute supramolecular polymer solutions.<sup>68,</sup> <sup>69</sup> The exact nature of the relaxation mechanism of the supramolecular assemblies, however, is a matter of speculation. Some of the pathways proposed are a phantom crossing mechanism akin to the phantom network model<sup>68</sup>, as well as ligand<sup>31, 66</sup> or bond exchange<sup>70</sup> mechanisms. Richter and coworkers encountered a similar structure-dynamics discrepancy during their study of telechelic pEGs in the melt state that associate via triple hydrogen bonding. They proved through small angle light scattering (SANS) that their assemblies surpassed the entanglement length up to a factor of 10, but still observed Rouse-type dynamics.<sup>36</sup> Rather than hypothesizing on an alternative relaxation process, they concluded that the association lifetime of the hydrogen-bonding motif must be short enough that the chain aggregates do not experience any entanglement constraints because they are in the fast breaking regime. In light of the high stability of the metallo-supramolecular associations used for this study, however, fast breaking bonds seem an unlikely explanation for our experimental results. In a theoretical work, Dormidontova et al. showed by molecular dynamics simulations that the viscosities of solutions containing head-to-tail associating polymers of various lengths and association energies all obey a power-law scaling dependence on the volume fraction with an exponent of 1.5.44 This was attributed to the polydispersity of the metallo-supramolecular assemblies, which obey Schulz-Flory statistics due to their polyaddition-analog association pathway. Consequently, only a fraction of the assemblies is long enough to form entanglements at any given time. This reasoning is supported by our data: we determine a polydispersity index D of 1.7 for the covalently linked pEG-DMMI model compound, and the polydispersity is expected to be not markedly different for the coordinatively linked chains (as later confirmed in Table 6). Indeed, our data support the argument raised by Dormidontova et al.: as the metallo-supramolecular association gets stronger, the transient bonds have a longer lifetime than before, and the percentage of chain assemblies that entangle increases. As a result, the  $\eta(c)$  log-log slope steepens. Due to the inherent polydispersity of the samples, however, the amount of entangled chains is never significant enough for the entire sample to relax via reptation.

The main part of this study focuses on the mechanical characterization of the metallo-supramolecular chain assemblies. For this purpose, we probe them by frequency-dependent oscillatory shear rheology, as shown in Figure 3B, again exemplarily displaying the pEG–6K compounds. In the probed frequency domain ( $\omega = 0.01-20$  Hz), the terminal flow regime according to the Maxwell model is assessed. The frequency-dependent loss moduli  $G''(\omega)$  of all samples exhibit a  $G''(\omega)$  log–log slope of 1 in this regime; this is a further confirmation that we are investigating the flow properties of the chain-extended compounds. The frequency-dependent storage moduli  $G'(\omega)$  of the non-extended chains, that is, our precursor chains without a metal ion present, also exhibit relaxation according to the Maxwell model with a  $G'(\omega)$  log–log slope of 2 in agreement with predictions for the terminal regime. Upon metallosupramolecular chain-extension, this scaling deviates from predicted values in a systematic fashion. (i) For any given pEG–TPy precursor, the  $G'(\omega)$  log–log slope increasingly shallows as the stability of the TPy-metal association increases. For example, a pEG-6K-TPy precursor chain exhibits a  $G'(\omega)$  log-log slope of 2.05. When the precursor chain is extended by Zn<sup>2+</sup> ions, representative of a weak association, the G'( $\omega$ ) log-log slope drops to 1.76. It further decreases to 1.57 when Ni<sup>2+</sup> ions that form a strong terpyridine–metal association are utilized. (ii) For any given metal ion, the  $G'(\omega)$  log–log slope increasingly shallows when the precursor polymer chain becomes shorter. For example, a pEG-12K-TPy precursor chain that is extended by Ni<sup>2+</sup> ions exhibits a  $G'(\omega)$  log-log slope of 1.58. When the same ion is used to extend shorter pEG-4K-TPy precursor chains, this value is lowered to 1.44. All determined  $G'(\omega)$  log–log slopes are compiled in Table 4.

	рЕG- <b>4К</b> -ТРу	рЕG- <b>6К</b> -ТРу	pEG- <b>8K</b> -TPy	рЕG- <b>10К</b> -ТРу	рЕG- <b>12К</b> -ТРу
no metal	1.89	2.05	2.06	1.99	2.00
Mn <sup>2+</sup>	1.75	1.77	1.90	1.84	1.90
Zn <sup>2+</sup>	1.79	1.76	1.71	1.78	1.79
Co <sup>2+</sup>	1.69	1.61	1.60	1.71	1.74
Ni <sup>2+</sup>	1.44	1.57	1.43	1.63	1.58
<i>c</i> (g·L <sup>−1</sup> )	250	200	150	120	100

**Table 4.** G'( $\omega$ ) log-log slopes in the frequency regime of  $\omega = 1-20$  rad s-1 for all measured systems sorted by increasing stability of the metal-ligand association (top to bottom) and precursor chain molar mass (left to right). Corresponding absolute concentrations of the measurements are shown in the last line.

We argue that two factors that work in conjunction are the reason for the shallowing of the scaling exponent. First, as demonstrated for the covalently extended pEG-DMMI system, the chain assemblies exhibit a Schulz–Flory distribution with a broad polydispersity  $\mathcal{D}$  and a maximal conversion of approximately 70%. This also applies to the metallo-supramolecular extended chains, since the introduction of end-group dynamics does not change the association pathway of extension, but only introduces reversibility of it. Consequently, the samples consist of unbound precursor chains as well as a variety of differently long chain assemblies.<sup>30</sup> This non-uniformity leads to a wide distribution of corresponding relaxation times for all chains, which is reflected in a shallowing of the  $G'(\omega)$  log–log scaling exponent, and this effect is further amplified when the average lifetime of the transient bond becomes longer.<sup>41</sup> In fact, it qualitatively follows the kinetic stability of the association from Mn<sup>2+</sup> over  $Zn^{2+}$  to  $Co^{2+}$  and  $Ni^{2+}$  (see Table 3.). This observation can be related to recent findings showing that supramolecular inter-chain sticking causes the frequency-dependent power-law scaling of  $G'(\omega)$  to shallow down in the terminal regime,<sup>71, 72</sup> whereby the extent of this flattening is in line with the association strengths of the transient binding motif. An additional factor that can alter the  $G'(\omega)$  log-log slope is the possible formation of loops. Dormidontova and co-workers have shown via Monte Carlo simulations that the concentration-dependent ring fraction of a head-to-tail associating supramolecular polymer system is mainly dependent on the length and flexibility of the precursor polymer.<sup>44, 73</sup> In view of the chain length, they concluded that a longer polymer chain leads to a reduced chance of ring formation, as the reactive chain ends are placed further apart from one another than it would be the case for a shorter chain. The longest chain they investigated, comprised of 64 monomer units, exhibits a ring fraction of less than 10% in the concentration regime we use for our study. The shortest chain we examine is the pEG-4K sample that is comprised of about 90 monomer units. Thus, ring formation is unlikely to be significant for all pEG compounds in the context of chain length. In view of the chain flexibility, they conclude that a flexible polymer backbone like that of pEG inherently promotes ring formation. This promotion is reversed above a specific crossover concentration  $c_{cr}$ , above which the concentration of the ring fraction is smaller than that of the chain fraction. For flexible polymers, it was determined that  $c_{cr} \approx 0.2 c^{*.73}$  At this point, small-ring formation (rings composed of one precursor polymer chain) is saturated, which has been confirmed experimentally.<sup>74</sup> The saturation level of larger-sized rings is higher than c<sub>cr</sub>, but the formation of these higher-order rings is much less likely in general. In our study, we use concentrations of 4–5 times higher than their precursor's overlap concentrations, c\* (see Table 3). We are therefore confident that a ring fraction is negligible in our system.

When the rheology data of a semi-dilute solution of non-extended chains are compared to those of an extended one, the following observations can be made. (i) For any given pEG precursor, both the storage and loss modulus,  $G'(\omega)$  and  $G''(\omega)$ , are shifted to higher values. This upshift is more pronounced for a strong association and, again, qualitatively follows the kinetic stability of the TPy-metal complex from  $Mn^{2+}$  to  $Zn^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$ . As an example, pEG-6K-TPy precursor chains extended by  $Mn^{2+}$  ions as the linking agent exhibit an upshift of G' and G'' of one order of magnitude. When the precursor chain is extended by Zn<sup>2+</sup> or Co<sup>2+</sup> ions, these upshifts become more pronounced to about two orders of magnitude. Finally, a chain extended by Ni<sup>2+</sup> ions exhibits G' and G'' values three orders of magnitude higher than that of the unlinked precursor polymer chain. This is already close to the covalently linked pEG-DMMI assemblies discussed for the covalent chain extension. (ii) For any given metal ion, the upshift becomes more pronounced when the precursor polymer chain gets shorter. For example, the  $G'(\omega)$  and  $G''(\omega)$  values of the pEG-12K-TPy precursor chains that are extended by Ni<sup>2+</sup> ions are one order of magnitude higher than those of the unlinked precursor chains. For the same linking ion, the upshift of G' and G'' of a pEG-10K-TPy precursor polymer is about two orders of magnitude upon chain extension, and three orders of magnitude for the extended pEG-4K-TPy precursor chains.

### 3.3.3.4. Time marching algorithm

A crucial parameter for the quantitative analysis of the investigated metallo-supramolecular assemblies is the apparent relaxation time,  $\tau_{eff}$ . This parameter consist of a contribution of the extended chains' diffusive motion in form their relaxation time,  $\tau_{relax}$ , as well as a contribution by the kinetics of the metallo-supramolecular chain breakage in form of the transient bond breakage time,  $\tau_{break}$ . According to the Maxwell model,  $\tau_{eff}$ , corresponds to the inverse of the low-frequency crossover point of the storage and loss moduli,  $G'(\omega)$  and  $G''(\omega)$ . It can therefore be extrapolated from the rheological spectra. To determine this point, which is not accessible in the frequency range of our rheology experiments, we model our system using the time marching algorithm (TMA) developed by van Ruymbeke *et al.*<sup>50</sup>

In the basic model for the reversible association of telechelic supramolecular polymer systems, a chain consisting of n units ( $L_n$ ) can break from (n - 1) points along its length or combine with other chains from two extremities, all with the same probabilities. This simple picture requires the rate of both association and dissociation processes to be independent of the chain length and uncorrelated. With these assumptions, the following reaction path and concentration balance for  $L_n$  can be derived:

$$L_n + L_m \underset{k_d}{\overset{k_a}{\underset{k_d}{\leftrightarrow}}} L_{n+m} \tag{1}$$

$$\frac{dL_n}{dt} = -k_a L_n \lambda_0 + \frac{1}{2} k_a \sum_{i=1}^{n-1} L_{n-i} L_i - (n-1) k_d L_n + 2k_d \sum_{i=n+1}^{\infty} L_i$$
(2)

where  $\lambda_0 = \sum_{i=1}^{\infty} L_i$  is the number of chains with different lengths from one to infinity and similarly,  $\lambda_1 = \sum_{i=1}^{\infty} iL_i$  is the total number of telechelic polymer precursors distributed among those chains. The first two terms account for the consumption and formation of  $L_n$  during the association reaction, while the second two terms represent similar contributions from the dissociation reaction. The time evolution of the number of chains can be obtained by integration over all chain lengths:

$$\frac{d\lambda_0}{dt} = \sum_n \frac{dL_n}{dt} = -\frac{1}{2}k_a \lambda_0^2 + k_d(\lambda_1 - \lambda_0)$$
(3)

At equilibrium, the number of chains with specific length *n* reaches a steady value, since the probabilities of breakage and formation of supramolecular bonds become equal. Therefore, at high association affinities, which results in high degrees of polymerization ( $\lambda_1 \gg \lambda_0$ ), we can calculate the number-average chain length as:

$$\bar{L} = \frac{\lambda_1}{\lambda_0} = \left(\frac{\lambda_1 k_a}{2k_d}\right)^{0.5} = \left(\frac{\lambda_1 K_{eq}}{2}\right)^{0.5} \tag{4}$$

With this kinetic scheme, we can predict the dynamics of stress relaxation of the supramolecular polymer systems using classical tube-based models. However, such modeling is rather challenging, as the structure of the relaxing polymers changes dynamically in the course of stress relaxation. The attempt to combine such random inter-conversion processes with the tube-based relaxation mechanisms requires a robust stochastic approach that is computationally expensive.<sup>31</sup> In a seminal work, Cates included the random reversible scission of polymeric chains in a one-dimensional diffusion process to predict the rheological properties of a supramolecular system based on linear precursors.<sup>51</sup> However, the considered one-dimensional diffusion process is far different from the quantitative relaxation mechanisms that are nowadays established for linear chains.<sup>75</sup> In most of the recent modeling efforts, the dynamic breakage and formation of supramolecular bonds are neglected, and their effect on the topology of the system is replaced by an equivalent average number of permanent bonds (Eq. 4).<sup>40, 76, 77</sup> Following this approach, van Ruymbeke and coworkers considered a standard Schultz–Flory distribution for linear telechelic supramolecular assemblies, and inversely used a tube-based model to determine their number-average degree of polymerization based on experimental rheological data.<sup>40</sup>

In this work, we reconstruct the distribution of the number of assemblies using a general log-normal distribution, as shown in Figure 4. A classical TMA tube-based model for linear chains is used to predict the rheological properties of the metallo-supramolecular polymers. Details of that model can be found elsewhere.<sup>50, 78</sup> To keep consistency with former publications, we use model parameters including the plateau modulus, the entanglement molar mass, and the Rouse time of an entanglement segment from Ref. [59], i.e.,  $G_N^0 = 1.45$  MPa,  $M_e = 2 \text{ kg} \cdot \text{mol}^{-1}$ , and  $\tau_e = 5 \cdot 10^{-8}$  s, respectively. The number-average molar mass,  $M_n$ , the number-average degree of polymerization,  $\overline{L}$ , and the polydispersity,  $\mathcal{D}$ , are determined by minimizing the mismatch between the measured and the calculated dynamic moduli, using the Nelder–Mead optimization algorithm.

Modelling of the rheological data enables us to extend the assessable frequency regime from the experimental boundary of 20 Hz up to 10<sup>10</sup> Hz, as shown in Figure 4 for the pEG-6K samples. For all compounds, the model is in good agreement with the experimentally determined loss moduli, but less so for the storage moduli, where the best-fit modeling results still show a notable discrepancy, specifically in the terminal region. The main reason for this discrepancy is probably that not all of the considered assumptions are valid. Namely, the dynamic association–dissociation process, which is prone to reduce the log–log slopes of the loss and storage moduli, respectively from 1 and 2, is still influential.<sup>41, 71, 72, 79</sup> Moreover, due to the low number of associations compared to a real polymerization, the assumptions made in the described kinetic scheme are not definite.



**Figure 4.** Frequency-dependent storage and loss moduli,  $G'(\omega)$  and  $G''(\omega)$ , of semi-dilute solutions of pEG-B-hydroxy- $\alpha$ -terpyridine precursor chains (blue symbols/lines), the metallo-supramolecular chain-extended compound with Zn<sup>2+</sup> ions (orange symbols/lines), representative of a weak transient bond, and Ni<sup>2+</sup> ions (green symbols/lines), representative of a strong transient bond, as the linking agent, as well as the covalently chain-extended compound (purple symbols/lines). The precursor chains have a molar mass of  $M_w = 6 \text{ kg} \cdot \text{mol}^{-1}$  and were probed at 5x their overlap-concentration  $5 \cdot c^* = 200 \text{ g} \cdot \text{L}^{-1}$  in an isochoric mixture of chloroform and methanol. The experimentally determined storage moduli  $G'(\omega)$  are denoted by open symbols, whereas values calculated by the TMA model are denoted by solid lines for the storage moduli  $G'(\omega)$  and dashed lines for the loss moduli  $G''(\omega)$ . An alternate version of Figure 4 that displays all four compounds separately is provided in the electronic supplementary information.

Therefore, a Schultz–Flory distribution might not be a good representative for the real distribution of the number of assemblies. Finally, the real number of assemblies should be higher than the one calculated using the explained method. The observed rheological spectrum is the result of not only the polymeric relaxation mechanisms but also the reversible breakage of assemblies, while the model accounts for the relaxation of an equivalent average number of assemblies that are permanently bonded. In fact, though, despite the dynamic association–dissociation processes that keep the average length of assemblies constant, the breakage process accelerates the relaxation of metallo-supramolecular chains compared to covalently linked polymer chains with the same length.

All calculated curves exhibit the same upshift also observed during the frequency-dependent oscillatory shear rheology measurements, and thereby confirm its relation to the kinetic stability of the terpyridine–metal complex. They also all coincide in the high-frequency regime ( $10^5$  Hz– $10^{10}$  Hz), independent of the type of association (covalent, transient, or none) or association stability; this is reliable, because this regime features Rouse modes of (precursor) chain sub segments and the dynamic glass transition, which are the same for all systems, extended and unextended, because they are all based on the same polymer backbone, pEG. In contrast to the high frequency domain, the modeled curves differ from one another in the mid- and low-frequency regime  $(10^{-2} \text{ Hz}-10^5 \text{ Hz})$ . Here, we find the same system-dependent differences as also determined by the rheology experiments. Particularly interesting is the mid-frequency domain (10<sup>1</sup> Hz–10<sup>5</sup> Hz), wherein some samples exhibit an elastic plateau. We have concluded from the concentration-dependent viscosity measurements that only small amounts of the extended chains are long enough to form entanglements due to the inherent polydispersity of the assemblies caused by the polyaddition-analog reaction pathway. We propose that it is this particular fraction that causes the plateau in this frequency regime. Indeed, the trends that we find are in line with the observations from the viscosity measurements: the samples that display the most distinct mid-frequency plateau are the ones with  $Ni^{2+}$  ions building up the chain aggregates. These are also the samples where the  $\eta(c)$  log-log slope deviates most from pure Rouse-type dynamics.

	pEG- <b>4K</b> -TPy		рE	pEG- <b>6K</b> -TPy pEG- <b>8K</b> -TPy		pEG- <b>10K</b> -TPy		pEG- <b>12K</b> -TPy		
	Ī	relaxation mode	Ī	relaxation mode	Ī	relaxation mode	Ī	relaxation mode	Ī	relaxation mode
no metal	-	Rouse	-	Rouse	-	Rouse	-	Rouse	-	Rouse
Mn <sup>2+</sup>	2.4	reptation	1.2	Rouse	1.0	Rouse	1.1	Rouse	1.1	Rouse
Zn <sup>2+</sup>	2.7	reptation	2.0	reptation	1.4	reptation	1.2	Rouse	1.1	Rouse
Co <sup>2+</sup>	3.1	reptation	1.8	reptation	1.8	reptation	1.1	Rouse	1.3	Rouse
Ni <sup>2+</sup>	10.3	reptation	7.4	reptation	4.4	reptation	1.6	reptation	2.1	reptation

**Table 5.** Number-average degree of polymerization,  $\overline{L}$ , and mode of relaxation as determined by the time marching algorithm (TMA) for metallo-supramolecular chain assemblies.

Following the kinetic stability of the terpyridine–metal complex from strong to weak (Ni<sup>2+</sup> to Co<sup>2+</sup>, Zn<sup>2+</sup>, and Mn<sup>2+</sup>), the mid-frequency plateau becomes less pronounced or disappears entirely. The TMA calculations show that this is based on the length of the precursor chain: whereas a chain assembly extended by Ni<sup>2+</sup> ions displays a  $G'(\omega)-G''(\omega)$  crossover point and an elastic plateau for all precursors, all other metal ions switch their mode of relaxation in relation to the precursor chain length. Assemblies built from a pEG-4K-TPy precursor all show a  $G'(\omega)-G''(\omega)$  crossover point and an elastic plateau, meaning they all contain a fraction of entangled assemblies. For samples made from a pEG-12K-TPy precursor, however, the plateau is absent for chains extended by Mn<sup>2+</sup>, Zn<sup>2+</sup> or Co<sup>2+</sup> ions as a linker. They have switched to Rouse-type dynamics, indicating that they are fully unentangled. The unextended precursor chain expectedly exhibits no crossover point between the  $G'(\omega)$  and  $G''(\omega)$  curves, and consequently no elastic plateau either. A full overview of the relaxation mode as well as the calculated number-average degree of polymerization  $\overline{L}$  for each compound is compiled in Table 5.

The number-average degree of polymerization,  $\overline{L}$ , follows the same trends that we have observed for the viscosity and frequency-dependent oscillatory shear rheology measurements: (i) Assemblies connected through metal ions that create a weak associative bond are shorter, meaning that they are composed of less precursor chain units, than assemblies connected by strong transient bonds.  $\overline{L}$  gualitatively follows the kinetic stability of the terpyridine–metal complex from Mn<sup>2+</sup> to Zn<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>, akin to the G'( $\omega$ ) log-log slope and the upshift in absolute values of both G'( $\omega$ ) and G''( $\omega$ ) encountered during the rheology measurements. For example, a pEG-8K-TPy precursor chain that is extended by Zn<sup>2+</sup> ions, with a weak metallo-supramolecular bond, exhibits a number-average degree of polymerization of only 1.4. When the transient bond for the same precursor polymer is formed by Ni<sup>2+</sup>, the linker that creates the strongest transient bond,  $\overline{L}$  rises to a value of 4.4. (ii) For any given metal ion,  $\overline{L}$  is highest for the shortest precursor chain and drops significantly with increasing precursor chain length. In the exemplary case of a Ni<sup>2+</sup>-mediated chain extension, an assembly composed of pEG-4K-TPy precursor chains contains an average of about 10 precursor units, whereas when a longer pEG-12K-TPy precursor chain is extended by the same ions, this value drops to only 2.1. Overall, the values obtained for the number-average degree of polymerization  $\overline{L}$  are quite low, given how strong the metal ion-terpyridine metallo-supramolecular bond is supposed to be when judged by either its high equilibrium or its low dissociation rate constant (see Table 2). This finding indicates some sort of destabilization of the associative bond that is of particular relevance in the case at hand of a linear telechelic metallo-supramolecular polymer system in semi-dilute solution state, as it is contrary to the result of other recent studies that report a prolonged lifetime of the transient bonding in the case of side-chain associating associative polymer systems or linear telechelic systems in the melt.<sup>10, 30, 31, 35</sup> This discrepancy will be discussed in more detail in the next subchapter.

From the number-average degree of polymerization and the precursor chains' molar mass, the number-average molar mass of the assemblies, Mn, is calculated. These values, trivially, again confirm that stronger transient bonds yield longer chain aggregates, following the kinetic stability of the terpyridine-metal complex. However, the molar masses also show that assemblies built from shorter precursor chains yield higher overall molar masses than ones made from longer precursor chains. This is counterintuitive, because it means that the longest chain aggregates also incorporate the highest number of dynamic bonds, which can be considered as predetermined braking points in a simplistic view. As such, this effect can be interpreted as another indicator of the aforementioned destabilization of the transient bond, and that it is possibly connected to the precursor chain length. Another argument might be an entropic one, as the chains naturally assume the shape of a random coil. This shape causes the associative chain ends to be buried inside the coil rather than being available on its surface for further linkages, an effect that is exacerbated as the length of the precursor chain is increased. This penalty is somewhat moderated by the good solvency condition provided by the isochoric solvent mixture of chloroform and methanol, which causes the polymer chain to extend to a certain degree, but it will not remove it entirely. An additional factor are the absolute concentrations of our samples, that are adjusted to always have the same multiple of their corresponding precursor chain overlap concentration c\*. This condition results in much lower total concentrations of terpyridine chain ends and metal ions for telechelic chains built from long precursors than for those made from short ones.

Another parameter that can be determined by the TMA modeling are the polydispersities,  $\mathcal{P}$ , for each metallo-supramolecular chain assembly. They range from 1.66–1.84 and do not exhibit any noticeable relation to neither the metal ion employed nor the precursor chain used. This independence confirms that the association pathway is the same for all assemblies. It is also in agreement with the covalently linked pEG-DMMI reference for which we determined a polydispersity  $\mathcal{P}$  of 1.7. On average, the calculated  $\mathcal{P}$ -values for the dynamic chain assemblies are slightly higher than those obtained for the covalent ones. We argue that this is caused by the introduction of dynamic bonds: on top of the inherent polydispersity of the supramolecular polyaddition reaction pathway, chains now break and reform reversibly. This, in turn, further broadens the spectrum of existing aggregate molar masses. Both the calculated number-average molar masses,  $M_n$ , and polydispersities  $\mathcal{P}$  are compiled in Table 6 for all samples investigated.

	pEG- <b>4K</b> -TPy		pEG- <b>6K</b> -	ТРу	pEG- <b>8K</b> -TPy pEG- <b>10K</b> -TPy		-TPy	pEG- <b>12K</b> -TPy		
	<i>M</i> n (kg∙mol <sup>−</sup> ¹)	Ð	<i>M</i> n (kg·mol⁻ ¹)	Ð	<i>M</i> n (kg∙mol <sup>−</sup> ¹)	Ð	<i>M</i> n (kg∙mol <sup>−</sup> ¹)	Ð	<i>M</i> n (kg·mol⁻ ¹)	Ð
Mn <sup>2+</sup>	9.5	1.78	7.1	1.69	8.0	1.66	10.6	1.73	12.8	1.73
Zn <sup>2+</sup>	10.7	1.82	11.9	1.79	11.3	1.76	11.5	1.74	13.5	1.73
Co <sup>2+</sup>	12.5	1.81	10.6	1.78	14.4	1.78	11.2	1.72	15.4	1.76
Ni <sup>2+</sup>	41.0	1.78	44.4	1.80	35.4	1.84	16.4	1.80	25.4	1.82

**Table 6.** Number-average molar masses,  $M_n$ , and polydispersities, D, as determined by the time marching algorithm (TMA) for the metallo-supramolecular chain assemblies.

#### 3.3.3.5. Quantitative determination of the influence of the metallo-supramolecular association

The effective relaxation time of the chain assemblies,  $\tau_{eff.}$ , is determined from the calculated rheological spectra, depending on the mode of relaxation of the assembly. Whereas entangled chain aggregates exhibit a characteristic low-frequency  $G'(\omega)-G''(\omega)$  crossover (see Figure 4, orange, green and blue lines), whose inverse corresponds to their effective reptation time,  $\tau_{eff-rep}$ , unentangled samples do not display this crossover, but instead, a characteristic point where both the  $G'(\omega)$  and  $G''(\omega) \log$ -log slopes change to 0.5 (see Figure 4, blue line), and the inverse of that frequency corresponds to their effective relaxation times determined along these lines are compiled in Table 7.

The times obtained for the precursor polymer without any metal ions are the elementary relaxation times of the chain building blocks and will be denoted  $\tau_0$  from here on. As expected, they become longer with increasing precursor chain length. Chain assemblies composed of these long building blocks, however, show a shorter effective relaxation than their counterparts made from short precursors, provided the metal ion connecting them is the same. This difference might seem strange at first, but it is in line with the argumentation we have raised when discussing the number-average degree of polymerization,  $\overline{L}$ , and the number-average molar mass,  $M_n$ . Both are higher for the telechelic chains built from short precursors than for those built from long precursors for the reasons discussed above. That causes the relaxation of chains built from the shorter building blocks, which are overall longer than those built from long precursors, to be slower. This effect is more pronounced the stronger the association is. When viewed for any single precursor chain length, the effective relaxation times, again, qualitatively follow the kinetic stability of the association: the weakest association yields the shortest effective relaxation times, whereas the strongest association yields the longest ones.

The effective relaxation times themselves have two contributions,  $\tau_{relax}$  and  $\tau_{break}$ . As mentioned in the description of the TMA,  $\tau_{relax}$  corresponds to diffusive motion of the chain aggregates, whereas  $\tau_{break}$  quantifies the contribution by the kinetics of the metallo-supramolecular chain breakage. We assume geometric averaging of these two, as commonly done for data on log-scales.<sup>3, 31, 51</sup> This yields the following relation:

$$\tau_{eff} = (\tau_{relax} \cdot \tau_{break})^{0.5}$$
 (5)

τ <sub>eff</sub> (ms)	рЕG- <b>4К</b> -ТРу	рЕG- <b>6К</b> -ТРу	рЕG- <b>8К</b> -ТРу	pEG- <b>10K</b> -TPy	рЕG- <b>12К</b> -ТРу
no metal <sup>a</sup>	$1.58\cdot 10^{-4}$	$2.50\cdot 10^{\scriptscriptstyle -3}$	$4.99\cdot10^{\scriptscriptstyle -3}$	$9.96 \cdot 10^{-3}$	$1.58 \cdot 10^{-2}$
Mn <sup>2+</sup>	$7.14 \cdot 10^{-2}$	$8.81 \cdot 10^{-2}$	$9.92 \cdot 10^{-2}$	$1.10 \cdot 10^{-1}$	$1.25 \cdot 10^{-1}$
Zn <sup>2+</sup>	$1.38\cdot10^{-1}$	$1.59\cdot 10^{-1}$	$7.23 \cdot 10^{-2}$	$1.57 \cdot 10^{-1}$	$1.57 \cdot 10^{-1}$
Co <sup>2+</sup>	$2.63 \cdot 10^{-1}$	$2.49\cdot 10^{1}$	$2.45\cdot10^{-1}$	$1.98 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$
Ni <sup>2+</sup>	16.0	18.2	7.15	1.25	1.39

**Table 7.** Effective relaxation times,  $\tau_{eff}$ , assessed from the frequency-dependent storage and loss moduli,  $G'(\omega)$  and  $G''(\omega)$ , calculated by the time marching algorithm (TMA).

The Rouse time of the unentangled telechelically extended chains is

$$\tau_{\rm R} = \tau_0 N^{1+2\nu} \tag{6}$$

where  $\tau_0$  is the relaxation time of the chain building blocks, which can be determined from the lowfrequency crossover of  $G'(\omega)$  and  $G''(\omega)$  in the rheological spectra of those, along with a Flory-exponent of v = 3/5, representative of good solvent conditions. Similarly, in the case of entangled telechelically extended chains, the reptation time is appraised as

$$\tau_{\rm rep} = \tau_0 N^3 \phi^{3 - 3\nu/3\nu - 1}$$
(7)

Rearrangement of Equation (5) yields the following expression to calculate the contribution of the kinetics of the transient bond:

$$\tau_{\rm break} = \frac{(\tau_{\rm eff})^2}{\tau_{\rm relax}} \tag{8}$$

in which  $\tau_{relax}$  is either attributed as  $\tau_R$  for unentangled aggregates or as  $\tau_{rep}$  for entangled ones. The breakage time can then be further converted into the corresponding dissociation rate constants,  $k_{diss}$ , which are compiled in Table 8.

The dissociation rate constants that we calculate from the contribution of transient bond breakages of the chain assembly,  $\tau_{break}$ , reflect the relative kinetic stability from Mn<sup>2+</sup> (weakest) to Zn<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> (strongest) as described in literature,<sup>47-49</sup> but they are, in all cases, much faster than these known values. The speed-up of the dissociation is directly connected to the length of the polymer backbone that the terpyridine motif is attached to: we determine the longest dissociation times for those assemblies built from the shortest precursor chains (pEG-4K-TPy), and the shortest ones for those assemblies made up of the longest precursor chains (pEG-12K-TPy). For further discussion of this result, we subdivide the aggregates into two groups: (1) chains that are extended by either Mn<sup>2+</sup> or Zn<sup>2+</sup> ions as a linker, representative of a weak coordinative bond; and (2) chains that are extended by either Co<sup>2+</sup> or Ni<sup>2+</sup> ions as a linker, representative of a strong coordinative bond. Group (1), the weakly coordinating chain assemblies, have a dissociation time that is close to the literature value for the shortest precursor chains. They are roughly three orders of magnitude higher compared to their literature counterpart for an extended pEG-12K-TPy precursor.

Table 8. Dissociation rate constants, $k_{diss}$ , calculated from the effective relaxation time, $\tau_{eff}$ , according to $\tau_{break} = (k_{diss})^{-1} = (k_{diss})^{-1}$
$\frac{(\tau_{eff})^2}{r}$ . Relaxation times, $\tau_{relax}$ , are determined depending on their mode of relaxation, which is assessed to be either Rouse of
reptation type.

k <sub>diss</sub> (s⁻ ¹)	рЕG- <b>4К</b> -ТРу	рЕG- <b>6К</b> -ТРу	рЕG- <b>8К</b> -ТРу	рЕG- <b>10К</b> -ТРу	pEG- <b>12K</b> -TPy	Literature value <sup>47, 49</sup>
Mn <sup>2+</sup>	51.8	$4.67\cdot 10^2$	$5.08\cdot10^2$	$9.31\cdot 10^2$	$1.18\cdot10^3$	4.0
Zn <sup>2+</sup>	19.9	68.8	$1.56\cdot 10^2$	$5.48 \cdot 10^{2}$	$8.28\cdot 10^2$	1.2
Co <sup>2+</sup>	8.73	19.9	28.2	$3.26\cdot 10^2$	$9.09\cdot 10^2$	1.0 x 10 <sup>-4</sup>
Ni <sup>2+</sup>	$8.25 \cdot 10^{-2}$	$2.73 \cdot 10^{-1}$	$4.91 \cdot 10^{-1}$	1.64	2.43	1.6 x 10 <sup>-6</sup>

For group (2), the strongly coordinating chain assemblies, we determine dissociation times that deviate even more from the literature values. The extended chains made up of the short pEG-4K-TPy precursor already dissociate four orders of magnitude faster. The gap increases to a staggering six orders of magnitude faster dissociation for an extended pEG-12K-TPy precursor. We conclude from these findings that the complexes might be significantly weakened in the linear semi-dilute-solution polymer environment compared to the free state. The linear polymer segments attached to the terpyridine motifs seem to destabilize their metal-coordinative bond by the dynamic activity of the polymer chain, making the complexes open more often per time than without a polymer backbone attached. This is in stark contrast to opposite findings in melt<sup>30, 31, 36</sup> and solution-based systems with complexes that are not localized at linear-chain ends but at either star-polymer termini<sup>10, 35</sup> or as side-chain pendants along linear backbone chains;<sup>32-34</sup> in these systems, the bond lifetime is renormalized to be effectively longer, because the polymer chains are constrained due to topological crowding and any broken complex often re-associates with its old close-by binding partner rather than with a new remote one. Only Craig et al. reported on side-chain associating metal-ligand transient networks in solution, in which the dynamics of low molar mass model complexes is quantitatively unaltered in the polymersystem's relaxation, so that no bond lifetime renormalization is operative.<sup>80, 81</sup> In the present case of a linear telechelic system in solution, by contrast, the polymer chains can create enough spatial separation after occasional dissociation to allow for association with a new binding partner, which renders renormalization to longer complex lifetimes void. On top of that, by contrast, the polymer backbone exerts a dragging force on the transient bonds, thereby causing renormalization to shorter lifetimes. This effect is more pronounced for longer than for shorter polymer chains, as the longer chains pull stronger than the shorter.

# 3.3.4. Conclusions

Attaching a supramolecular binding motif to a polymer backbone is commonly believed to lead to a restricted activity of its non-covalent bond due to topological constraints in a polymeric environment, which causes renormalization of its bond lifetime to longer times.<sup>28, 29</sup> In the present study, we reveal that this effect could also be inverse. We show that attaching a supramolecular binding motif, in our case terpyridine groups that can form metallo-supramolecular bonds, to the ends of linear polymer chains in semi-dilute solution actually enhances the complex dissociation kinetics. Dissociation rate constants are found to be as much as six orders of magnitude higher than described for the free complexes, underlining the scale of the instability of the transient bond in the polymer system. The acceleration of the dissociation process depends on the length of the polymeric chain segment attached to the associative end groups, with longer chain segments yielding faster dissociation times, indicating that it is the dynamic activity of the polymer chain itself that causes the complex destabilization. We therefore conclude that bond lifetime renormalization needs to be considered as an important parameter in the endeavor of rational design of (metallo-)supramolecular polymer materials, but this requires careful distinction of the case at hand. Specifically, whether the transient bond lifetimes have to be renormalized to shorter or longer times depends on the structural architecture and dynamic agility or freedom of the polymeric building blocks they are attached to.

As a follow-up study, it would be enlightening to investigate the influence of both temperature, concentration and chain-stoppers in reference to the work of Cohen-Stuart,<sup>3, 4</sup> to widen the scope of this investigation and to further support the results and hypotheses presented herein. In particular, it would be beneficial to understand whether the metal–ligand complex destabilization proposed is

concentration-dependent. Following comparable studies in the melt-state, we can imagine a crossover concentration, after which the transient bond lifetime is prolonged instead of shortened. Additionally, it would be informative to determine whether the proposed destabilization is specific to the metal–ligand bond, or if it also holds true for lesser-energy transient bonds such as hydrogen bonds in an analogous system.

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# 3.3.7. Supporting Information

# Chemicals:

Compound	CAS number	Supplier	Purity
pEG-4K pEG-6K pEG-8K pEG-10K	25322-68-3	Sigma Aldrich	not provided <sup>1</sup>
Sodium hydride (60% in mineral oil)	7646-69-7	Sigma Aldrich	60%
Epichlorohydrin	106-89-8	Acros Organics	99%
Sodium azide	26628-22-8	Sigma Aldrich	99%
Ammonium chloride	12125-02-9	Acros Organics	99.5%
Potassium carbonate	584-08-7	Acros Organics	≥ 99%
2,6-Bis(2-pyridyl)-4(1H)-pyridone	128143-88-4	TCI Chemicals	> 98%
Propargyl bromide (80 wt% in toluene)	106-96-7	Acros Organics	79–87% (propargyl bromide) 13–27% (toluene)
Diaminoethane	107-15-3	Sigma Aldrich	≥ 99%
Di-tert-butyl dicarbonate	24424-99-5	Sigma Aldrich	≥ 98%
Dimethyl maleic anhydride	766-39-2	Alfa Aesar	≥ 97%
Trifluoroacetic acid	76-05-1	Alfa Aesar	99 %
4-Nitrophenyl chloroformate	7693-46-1	Alfa Aesar	97%

<sup>1</sup>: Purity information is not provided by the manufacturer. According to the specification sheet, all pEG compounds contain  $\leq 1\%$  of water and  $\leq 0.2\%$  of sulphated ash. An IR spectrum confirms the chemical structure. Coloured impurities were quantified via UV spectroscopy at  $\lambda = 260$  nm (absorption  $\leq 0.1$ ) and  $\lambda = 280$  nm (absorption  $\leq 0.04$ ).



#### **Alternative Figure 4:**

Alternative representation of the frequency-dependent storage and loss moduli,  $G'(\omega)$  and  $G''(\omega)$ , of semi-dilute solutions of pEG- $\theta$ -hydroxy- $\alpha$ -terpyridine precursor chains (blue symbols/lines), the metallo-supramolecular chain-extended compound with Zn<sup>2+</sup> ions (orange symbols/lines), representative of a weak transient bond, and Ni<sup>2+</sup> ions (green symbols/lines), representative of a strong transient bond, as the linking agent, as well as the covalently chain-extended compound (purple symbols/lines). The precursor chains have a molar mass of  $M_w = 6 \text{ kg} \cdot \text{mol}^{-1}$  and were probed at 5x their overlap-concentration  $5 \cdot c^* = 200 \text{ g} \cdot \text{L}^{-1}$  in an isochoric mixture of chloroform and methanol. The experimentally determined storage moduli  $G'(\omega)$  are denoted by full symbols, the loss moduli  $G''(\omega)$  are denoted by open symbols, whereas values calculated by the TMA model are denoted by solid lines for the storage moduli  $G'(\omega)$ .

### <sup>1</sup>H-NMR Spectra:



Full <sup>1</sup>H-NMR spectrum of pEG-epoxide, 4000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-epoxide, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-epoxide, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-epoxide, 10000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.


Full <sup>1</sup>H-NMR spectrum of pEG-epoxide, 12000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-azide, 4000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-azide, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-azide, 8000 g⋅mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-azide, 10000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-azide, 12000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of propargyl-terpyridine. The solvent is CDCl<sub>3</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-terpyridine, 4000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-terpyridine, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-terpyridine, 8000 g⋅mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-terpyridine, 10000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-hydroxy-terpyridine, 12000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of Tert-butyl (2-aminoethyl)carbamate. The solvent is CDCl<sub>3</sub>.



Full <sup>1</sup>H-NMR spectrum of Tert-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)carbamate. The solvent is CDCl<sub>3</sub>.



Full <sup>1</sup>H-NMR spectrum of 1-(2-Aminoethyl)-3,4-dimethyl-1H-pyrrole-2,5-dione trifluoroacetate. The solvent is CDCl<sub>3</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-p-nitrophenylcarbonate, 4000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-p-nitrophenylcarbonate, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-p-nitrophenylcarbonate, 8000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-p-nitrophenylcarbonate, 10000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-p-nitrophenylcarbonate, 12000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-DMMI, 4000 g⋅mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-DMMI, 6000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-DMMI, 8000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-DMMI, 10000 g·mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.



Full <sup>1</sup>H-NMR spectrum of pEG-DMMI, 12000 g⋅mol<sup>-1</sup>. The solvent is DMSO-d<sub>6</sub>.

## 4. Summary and Conclusion

In this thesis, three separate investigations were presented that aim to achieve a better understanding of the structure–property relationship in stimuli-responsive and dynamic polymer materials.

In a first investigation, the dynamic covalently cross-linked polymethylsiloxane (PDMS) networks were studied. Dynamically cross-linked PDMS networks were prepared by anionic ring-opening polymerization of octamethylcyclotetrasiloxane (D<sub>4</sub>) and its dimeric form bis(hepta-methylcyclotetrasiloxanyl)ethane (bis-D<sub>4</sub>). These compounds are known to display molecular rearrangement in the presence of anionic end groups. Thermal degradation of dibenzoyl peroxide (DBPO) creates free radicals that react with D<sub>4</sub> to form a dimeric siloxane species, bis-D<sub>4</sub>, which is used as a cross-linker in the subsequent anionic polymerization of  $D_4$ . In a second step, tetramethylammonium hydroxide (TMAH) is added to the reaction mixture to initiate the anionic anionic ring-opening polymerization. TMAH resides within the PDMS polymer as a counter-ion to the anionic end groups of the obtained material. Mechanical properties were probed by frequency-dependent oscillatory shear rheology to show that the amount of DBPO and TMAH employed directly correlates to the mechanical strength. Stress relaxation and self-healing properties were probed on a purpose-built piercing device equipped with a pressure sensor to monitor shear and tensile forces as a brass pin is driven into and retracted from the dynamic PDMS network. The networks showed promising self-healing rates at ambient temperature after optimization of the synthesis protocol. Piercing test force measurements revealed a force-relaxation plateau value, indicating significant elastic energy storage within the material under piercing. It can be suggested that this is a prerequisite to the self-healing properties, as the release of this stored energy at the moment of pin retraction brings the surfaces into contact again. However, evaporation of persistent monomeric D<sub>4</sub> and toxicity of the tetramethylammonium ion limit potential applications of these materials in sealed environments.

In a second investigation, the change in interfacial interactions of poly(N-isopropy)acrylamide)(pNIPAAm) hydrogels that accompanies the deswelling during their volume phase transition was decoupled from one another. This was achieved by incorporating a thermosensitive pNIPAAm core inside a non-thermosensitive polyacrylamide (pAAm) shell to create core-shell microgels with independently tunable elasticity. The pNIPAAm cores were templated using droplet-based microfluidics and, in a second microfluidic experiment, wrapped with a pre-polymerized AAm shell carrying the photo-reactive 2-(dimethylmaleimide)-N-ethyl acrylamide. Subsequent UV irradiation produced the final core-shell microgel. Whereas the position of the core inside the shell was not controllable in this process, the distribution of particle sizes resulting from the two consecutive microfluidic experiments was narrow and well-defined. Colloidal probe force mapping by atomic force microscopy was used to determine the core-shell microgels Young's modulus at the microgel's surface at temperatures above and below the volume phase transition temperature (VPT) of pNIPAAm. A pronounced stiffening of the surface's Young's modulus upon deswelling of the pNIPAAm core above the VPT was found. This was accompanied by a small but reproducible size reduction of the pAAmshell. This elasto-thermal effect of the per-se non-responsive pAAm-shell was attributed to an interconnection between the core- and the shell network in the microgels that drags the shell toward the center of the core upon deswelling. Interfacial interactions that usually change drastically during the volume phase transition of pNIPAAm were shown to remain constant under deswelling by analysis of the recorded force-distance curves by the Hertz and Johnson-Kendall-Roberts theory. Decoupling the interfacial interactions parameter from the change in elasticity might open pathways for the

rational design assemblies of microgel layers or aggregate-substrates with the ability to independently regulate their elasticity.

A third investigation aimed at getting a better understanding of the interplay of supramolecular and macromolecular dynamics of linear associating supramolecular polymers in semi-dilute solution, with particular focus on the renormalization of the transient bonds' lifetime. For this purpose, a modular polymer system was designed, comprised of linear poly(ethylene glycol) (PEG) functionalized with terpyridine (tpy) moieties. PEG was chosen for its high chain flexibility, its good solubility in different media, and its well-defined terpyridine-based coordinative polymer chemistry that allowed fine-tuning of the strength of the metallo-supramolecular association by selecting different transition metal ions. Metallo-supramolecular bonds were used, because they are quite strong in terms of their binding energies compared to other supramolecular interactions, and therefore amplify the influence of the transient association. Additionally, they are tunable by mere exchange of the central ion without unsought structural changes on the polymeric level. The mechanical properties of the metallosupramolecular assemblies were determined by frequency-dependent oscillatory shear rheology at concentrations of 4–5 times the overlap concentration of the corresponding tpy–PEG precursor. Rheological data showed a consistent trend depending on the length of the precursor and the kinetic stability of the metallo-supramolecular bond. Shorter precursors and stronger transient bonds formed longer and more stable chain assemblies, whereas longer precursors and weaker transient bonds formed shorter and less stable ones. The upper boundary of this type of supramolecular chain extension was estimated by covalent chain extension following the same mechanism. For this purpose, a photocrosslinkable unit was attached to the PEG backbone and irradiated with UV light. Viscosity calculations revealed that the assemblies display Rouse-type relaxation behavior, with assemblies based on strong metallo-supramolecular bonds deviating more towards reptative motion than those based on weaker transient bonds. To quantify the extent of the chain extension as well as calculate the contributions of the supramolecular and macromolecular dynamics to the effective relaxation time, the data were modelled with the time marching algorithm (TMA) developed by van Ruymbeke et al.. These calculations provided values for the number-average degree of chain extension, the number-average molar mass of each assembly as well as effective relaxation times, from which dissociation constants as much as six orders of magnitude faster than the free metal-ligand complex were calculated. The acceleration of the dissociation process depended on the length of the polymer precursor chain attached to the associative end groups, with longer chain segments yielding faster dissociation times. These findings indicated that the complex destabilization is caused by the dynamic activity of the polymer chain itself. It was concluded that the structural architecture and dynamic agility or freedom of the polymeric building blocks they are attached to is a key factor in determining, whether the lifetime of a transient bonds needs to be renormalized to longer or shorter times. It also suggested the possible presence of a crossover concentration, after which the transient bond lifetime is prolonged instead of shortened.

All three investigations reveal how understanding the way molecular parameters can influence macroscopic properties of polymeric materials is useful, both for theory and for applications. By designing the appropriate polymer system and choosing suitable experiments, structure–property relationships can be used to either validate or challenge established theory. They also allow functional materials to be tailor-made starting from the molecular level with a specific application already in mind.

# 5. References

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### 6. Publications

#### 6.1. Publications with Peer Review Process

- The Non-Effect of Polymer Network Inhomogeneities in Microgel Volume Phase Transitions: Support for the Mean-Field Perspective
   A. Habicht, <u>W. Schmolke</u>, F. Lange, K. Saalwächter, and S. Seiffert, Macromol. Chem. Phys. 2014, 215, 1116–1133.
- Critical Fluctuations and Static Inhomogeneities in Polymer Gel Volume Phase Transitions
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- 3) Dynamically Cross-Linked Polydimethylsiloxane Networks with Ambient-Temperature Self-Healing <u>W. Schmolke</u>, N. Perner, and S. Seiffert, *Macromolecules* **2015**, *48*, 8781–8788.
- 4) Core–Shell Microgels with Switchable Elasticity at Constant Interfacial Interaction
   M. Seuß, <u>W. Schmolke</u>, A. Drechsler, A. Fery, and S. Seiffert, ACS Appl. Mater. Interfaces 2016, 8, 16317–16327.
- 5) Dominance of Chain Entanglement over Transient Sticking on Chain Dynamics in Hydrogen-Bonded Supramolecular Polymer Networks in the Melt
   A. Jangizehi, S. R. Ghaffarian, <u>W. Schmolke</u>, and S. Seiffert, Macromolecules 2018, 51, 2859–2871.
- Enhancement of metallo-supramolecular dissociation kinetics in telechelic terpyridine-capped poly(ethylene glycol) assemblies in the semi-dilute regime <u>W. Schmolke</u>, M. Ahmadi, and S. Seiffert, *Phys. Chem. Chem. Phys.* 2019, 21, 19623–19638.

#### 6.2. Publications without Peer Review Process

Addition to "Dominance of Chain Entanglement over Transient Sticking on Chain Dynamics in Hydrogen-Bonded Supramolecular Polymer Networks in the Melt" A. Jangizehi, S. R. Ghaffarian, <u>W. Schmolke</u>, and S. Seiffert, *Macromolecules* **2020**, *53*, 491–493

# 7. Conference Contributions

## 7.1. Oral Presentations

- Synthesis and Rheology of Terpyridine Endcapped Poly(ethylene glycols)
   <u>W. Schmolke</u> and S. Seiffert, Bilateral workshop of the Freie Universität Berlin, Germany, and
   Université Catholique de Louvain, Belgium, **2015**
- 2) Interplay of Supramolecular and Macromolecular Dynamics in Metallo-Supramolecular Telechelic Polymers

W. Schmolke and S. Seiffert, European Polymer Federation Congress (EPF), Lyon 2017

### 7.2. Poster Presentations

- Sensitive Microgels as Model Materials
   <u>W. Schmolke</u>, A, Habich and S. Seiffert, Makromolekulare Kolloquium, Freiburg 2015
- 2) Smart Soft Matter: Sensitive and Supramolecular Polymer Gels
   <u>W. Schmolke</u>, A. Habicht, R. Rochette and S. Seiffert, 6. Mainzer Arbeitskreis-Symposium der Gesellschaft Deutscher Chemiker, Mainz 2016
- 3) Kinetically Controlled Chain-Extension of Metallo-Supramolecular Telechelic Polymers driven by the Belousov–Zhabotinsky Reaction

D. Rochette, W. Schmolke and S. Seiffert, European Polymer Federation Congress (EPF), Lyon 2017

7. Conference Contributions

# 8. Teaching Contributions

1) Script "Statistical Thermodynamics"

W. Schmolke and S. Seiffert, Bachelor of Chemistry lecture, 41 pages, 2016

2) Script "Physical Chemistry of Polymers Part 1"

W. Schmolke and S. Seiffert, Master of Chemistry lecture, 108 pages, 2018

- 3) Script "Physical Chemistry of Polymers Part 2"
   <u>W. Schmolke</u> and S. Seiffert, Bachelor and Master of Chemistry lecture, 110 pages, 2018
- 4) Script "Physical Chemistry 1"

W. Schmolke and S. Seiffert, Bachelor of Chemistry lecture, 205 pages, 2019