

Aus dem Max-Planck-Institut für Polymerforschung in Mainz

**Synthesis and Application of Stimuli Responsive Tunable
Systems Based on Physical Interactions**

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1. Motivation and Objectives

In the course of time and especially during their development in the 20th and 21st century, adhesives have gained an irreplaceable position in numerous applications and production processes. Despite of their increasing importance, already today there is hardly any product in our surroundings that does not contain at least one adhesive - be it the label on a beverage bottle, protective coatings on automobiles or profiles on window frames.^[1]

The use of adhesives offers many advantages over other binding techniques. These advantages include the ability to bind different materials together, the ability to distribute stress more efficiently across the joint, the cost effectiveness of an easily mechanized process, an improvement in aesthetic design, and increased design flexibility.

The earliest use of adhesives was discovered in Italy. At this site, two stone flakes partially covered with birch-bark-tar and a third uncovered stone from the Middle Pleistocene era (circa 200,000 years ago) were found. This is thought to be the oldest discovered human use of tar hafted stones.^[2]

From the XVII century the industrial production of natural adhesives has intensely developed. The most widespread adhesives being “animal glue”, starch or casein based adhesive materials. While largely replaced by synthetic resins, casein-based glues still have a use in certain niche applications, mostly as labeling adhesive of bottles.

A key step in the development of synthetic plastics was the introduction of a thermoset plastic known as Bakelite phenolic in 1909.^[3] Within two years, phenolic resin was applied to plywood as a coating varnish. In the early 1930s, phenolics gained importance as adhesive resins.^[4] This almost simultaneous development of plastics and adhesives demonstrates the importance of macromolecular chemistry and design for modern adhesive technologies.

Important characteristics of adhesives, such as tack and setting behavior, together with the ability to withstand mechanical loads during service, are in correlation with the chemical composition, as well as with the rheological and mechanical properties. The transition from the initial adhesive fluid state to its final condition, where it can

carry high loads, is strongly influenced by the rate of the cross-linking reactions (for reactive adhesives) or by physical processes, such as polymer chain relaxation, rate of drying, or the rate of physical cross-link formation (for non-reactive adhesives).

During this work a strong emphasis will be laid on water-based, non-reactive polymer systems with tunable cross-linking properties, which for example have strong potential to be used as adhesives in labeling applications.

Adhesive materials for labeling applications mostly represent highly viscous non-reactive systems, able to quickly restore the rheological properties after removal of the applied stress. Tuning of physical interactions in such systems and thus adjusting the thickening and adhesive properties (with corresponding changes of rheological parameters) is of crucial importance for improved performance of such materials.

Fast industrial development in the 20th century led to the development of several different types of materials with similar thickening properties, such as: polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM) and Xanthan gum based thickeners. Expectedly, the next step in the development of water soluble thickeners was the development of associative thickeners, mostly based on the associative force of hydrophobic segments, and thus providing an additional tuning mechanism of the mechanical properties. The systems that bear significant industrial importance are hydrophobically modified polyacrylamide (HMPAM),^[5] ethoxylated polyurethane (HEUR),^[6] and hydroxyethyl cellulose (HMHEC)^[7].

Compared to the above listed and well investigated systems, alkali soluble emulsions (ASE) represent less extensively studied systems. They are good competitors to ionic HEUR polymers for applications as thickeners. One of the first reported alkali soluble acrylic emulsions by Fordyce et al. in 1959 has become a cornerstone for the development of this tremendously important field for the industry.^[8] These systems showed numerous advantages over the existing systems at the time, such as solutions of polymeric acrylic salts with low solid content or dry powders with extremely high hygroscopic nature.

ASE potentially represents a good alternative to casein based labeling adhesives. They represent stable latexes in acidic conditions. Upon increasing the pH slightly

above neutral values the dissolution occurs and highly viscous polyelectrolyte solutions are obtained. This enables a relatively simple VOC-free (volatile organic compound) preparation of adhesive compositions and provides a significant window for the tuning of the desired rheological properties. Rheological and mechanical properties of ASE can further be easily modified via the introduction of hydrophobic moieties, which can lead to the formation of hydrophobic domains. These domains do represent an additional thickening mechanism, because they act as physical cross-linking sites between charged polymer chains and improve the mechanical properties and viscosity of the solutions. Such systems are also referred as hydrophobically modified alkali soluble latexes (HASE). HASE systems show significant advantages over other types of rheology modifiers in a significant number of real-life applications.

The objective of this work is the development of novel HASE systems, which show an exceptionally high degree of control to tailor the physicochemical interactions and the related rheological properties. Based on this goal a novel and facile synthesis procedure for HASE will be introduced, which is based on the miniemulsion polymerization technique but shows certain differentiating distinct features from the ideal case which is mostly described in literature. To demonstrate the high control and adjustability of the novel HASE polymers labeling adhesives where chosen as model systems to specifically tailor the intra- and intermolecular interactions and to modify the related rheological properties. The ultimate goal could be the mimicking of casein based glues, with easily addressable stimuli response tailored into the system.

In general, the systems considered in this study do not represent the classical miniemulsions. The technique, employed here, can rather be referred as a “miniemulsion-analogous” technique. The high shear forces are employed at the initial stage, similarly to the miniemulsion preparation procedure. However, due to the presence of significant amounts of water soluble monomer there is high likelihood of homogenous nucleation during polymerization and, besides, “nanoreactor” principle of miniemulsions cannot be applied.

Targeted tuning of the viscoelastic properties of the obtained systems at neutral pH also represent one of the major scopes of conducted research. Reversible

disturbance of the certain type of physical interactions is used to obtain dilution resistant fast setting systems for adhesive applications.

Thus, the work described below is related to investigation of the influence of different factors on the mentioned miniemulsion-analogous synthesis and the characterization of the obtained alkali soluble latexes. Complex neutralization behavior and the postsynthetic tuning represent also an important part of the overall framework.

2. Theory and Basics

2.1. Radical Polymerization and Copolymerization

During the development of polymer science two main classifications of polymerization came into use. One of them is based on the polymer structure and divides polymers into condensation and addition polymers. The other classification is based on the polymerization mechanism and divides polymerizations into step and chain polymerizations.^[9] Chain growth polymerizations are characterized by high degrees of polymerization at low monomer conversions. These polymerizations proceed through active centers and can be further categorized into radical, cationic, anionic and complex coordination. Similar to other chain growth reactions, free radical polymerization is a rapid process which consists of the characteristic steps of initiation, propagation, and termination.^[10, 11] Since in this work free radical polymerization was used for polymer synthesis, it will be described here in more detail with particular emphasis on heterophase systems. In radical polymerization initiators are employed to generate radicals in several ways, such as: thermal decomposition, redox reactions, photochemical reactions and initiation by ionizing radiation. Besides, pure thermal initiation of monomers is also possible. Other methods of radical polymerization involve electrolysis of monomer solution, plasma polymerization and sonication.^[9] After initiation, the polymerization proceeds via above mentioned propagation and termination steps.

The radical polymerization process can be of both - homogenous and heterogeneous - types. This classification is based on whether the initial system is homogeneous or heterogeneous. Bulk and solution polymerizations are homogeneous processes. Heterogeneous processes include emulsion, suspension, dispersion and precipitation polymerizations.^[9, 12]

Polymerization of a single monomer is relatively limited in terms of the number of the products that can be obtained. Copolymerization of different monomers allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two or more monomer units in the copolymer product. By the structure and distribution of the monomer units the copolymers can be divided into random, alternating, block and graft copolymers.^[11]

It was observed at early stages of development of polymer science that relative copolymerization tendencies of monomers often showed little resemblance to their relative rates of homopolymerization. Some monomers are more reactive in copolymerization than indicated by their rates of homopolymerization, while the opposite can also be true as well. The most extreme example is the copolymerization of maleic anhydride and stilbene, which have very little or no tendency to undergo homopolymerization, but they copolymerize easily with radical initiators.

The determining factors of copolymer composition have been intensively studied based on the assumption that the chemical reactivity of the propagating chain in a copolymerization is dependent only on the identity of the monomer unit at the growing chain end and is independent of the chain composition preceding the last monomer unit. This assumption is referred to as the first order Markov or terminal model of copolymerization. Based on these studies the copolymerization equation (also referred as the copolymer composition equation) has been derived.^[9]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (1)$$

According to the equation, the copolymer composition, $d[M_1] / d[M_2]$, is the molar ratio of the two monomer unit in the copolymer, which is related to the concentration of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2 . The parameters r_1 and r_2 are termed as monomer reactivity ratios and are defined as the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant for its addition of the other monomer (2):

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21} \quad (2)$$

The copolymerization equation is even more complicated for terpolymerization^[13, 14] [equation (3)], which is more important for the present work:

$$\begin{aligned}
 d[M_1]:d[M_2]:d[M_3] &= \\
 &= [M_1] \left\{ [M_1] + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right\} : [M_2] \frac{r_{21}}{r_{12}} \left\{ \frac{[M_1]}{r_{21}} + [M_2] \right. \\
 &\quad \left. + \frac{M_3}{r_{23}} \right\} : [M_3] \frac{r_{21}}{r_{12}} \left\{ \frac{[M_1]}{r_{31}} + \frac{M_2}{r_{32}} + [M_3] \right\}
 \end{aligned} \tag{3}$$

Equation (3) clearly shows that the monomer ratio in terpolymers is a function of the reactivities and concentrations of all three monomers and any change of these parameters can significantly alter the overall monomer distribution, as it will be shown throughout this work.

2.2. Emulsions

Emulsions are an indivisible part of our everyday life from food products, such as milk or butter to cosmetic products and adhesives. Emulsions are the dispersions of two liquids into another where the two considered liquids are immiscible or have at least only limited miscibility. In such systems one of the liquids represents the dispersion medium (continuous phase) in which the other liquid is dispersed as small droplets (disperse phase). Most emulsions are composed of water and (hydrophobic) oil. Based on the composition and the phase behavior, one can distinguish between oil-in-water emulsions (O/W, direct emulsions) and water-in-oil emulsions (W/O, inverse emulsions).

Upon the formation of emulsions droplets, the surface area between continuous and dispersed phases is drastically increasing. This leads to a corresponding increase of the surface tension (contractive tendency of the surface of a liquid that allows it to resist an external force and is caused by excess energy at the surface of a material compared to the bulk). Surface energy is usually decreased using surfactants, which also account for the emulsion stabilization against coalescence (chapter 2.2.1). The latter can basically be understood as the merging of the emulsion droplets through collision.

2.2.1. Colloidal Stabilization

Except for some special cases (e.g. microemulsions) colloidal dispersions are not thermodynamically stable but by virtue of energy barriers much greater than $k_B T$

they are kinetically stable. Similar surface charge of colloidal particles can impart stability to colloidal systems via repulsion forces. These forces exceed inherent van der Waals forces. The thermal energy must overcome this repulsion for the two particles to flocculate. However, this balance is very strongly affected by the presence of salt. By increasing the salt concentration the electrostatic repulsion is easily reduced, so that the total potential becomes attractive. In this situation and in the case of non-polar solvents, where the electrostatic stabilization is difficult, another mechanism is required to stabilize the dispersion and this is often provided by an adsorbed polymer layer. The effectiveness of this layer depends very much on the conformation of the chains involved.^[15] These mechanisms are shortly discussed below.

2.2.1.1. Charge Stabilization

DLVO theory, developed around the 1940s by Russian scientists (Derjaguin and Landau) and approximately at the same time independently by two Dutch scientists (Verwey and Overbeek), considers the total energy of interaction of colloidal particles as the linear sum of the attractive and repulsive interactions:^[15-20]

$$V_T = V_A + V_R \quad (4)$$

where V_T represents the total potential energy of interaction, V_A is the potential energy of attractive interactions and V_R represents the energy of repulsion.

The attractive potential energy is directly proportional to a particle radius (a), a material constant – the Hamaker constant (A) and is inversely proportional to the distance of separation (H). For small separation ($H \ll 2a$) the reduced form of the attractive potential energy is expressed as:

$$V_A = -\frac{Aa}{12H} \quad (5)$$

When the particles are immersed into the medium the combined or the composite Hamaker constant (A) can be estimated as the geometric mean of that of the particle ($A_{particle}$) and that of the medium (A_{medium}) with respect to their values in vacuum. It is more precise to use this mean value in the calculation of the attractive potential.

$$A = (\sqrt{A_{particle}} - \sqrt{A_{medium}})^2 \quad (6)$$

On the other hand, electrostatic repulsion (V_R) is an important stabilizing mechanism for particles dispersed in aqueous solutions or moderate polarity liquids. Repulsion forces arise due to charged particle surfaces and the distribution of counterions, and can be expressed as:

$$V_R = \frac{\epsilon_r a^2 \psi^2}{2a + H} e^{-\kappa H} \quad (7)$$

Where ϵ_r is the dielectric constant of the medium. ψ is the surface potential of the charged particles and κ is the inverse of the Debye length (see chapter 2.6). The Debye length corresponds to the distance to which the surface potential of the charged particle falls to its $1/exp$ value.

Typical plots of V_A and V_R as a function of the distance between particles are shown in the Figure 1.

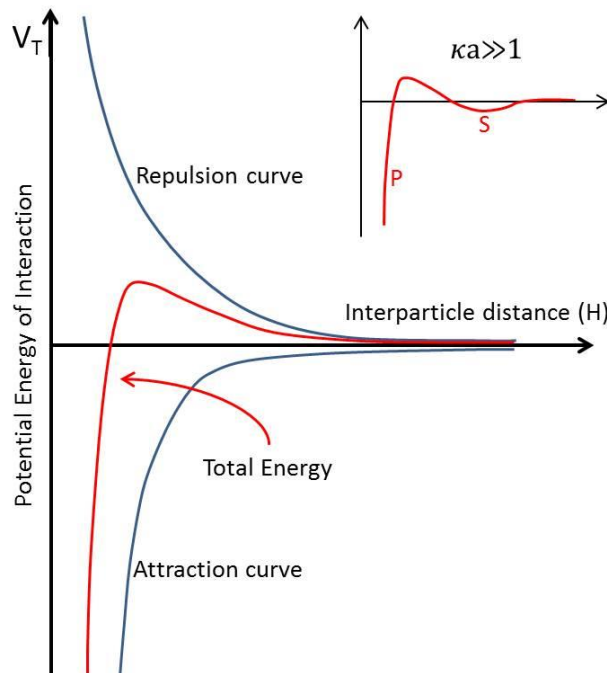


Figure 1: Total interaction energy curve obtained by summation of attraction and repulsion curves.

For the case when $\kappa a \gg 1$ (i.e. when the ratio of particle size to thickness of the electrical double layer is very large), the curve for the total energy shows a secondary minimum (S) at relatively large distance of separation between the

particles in addition to the primary minimum (P), as shown in the inset of Figure 1. Particles may therefore aggregate at a relatively large distance between each-other. This type of aggregation is referred as flocculation and is distinguished from irreversible aggregation in the primary minimum which is called coagulation. Since the depth of the secondary minimum is rather shallow, flocculation of this type is easily reversible and the particles can be freed by agitation.^[21]

2.2.1.2. Steric Stabilization

Another important mechanism for providing colloidal stability is steric stabilization, which is achieved via covering colloidal particles with a dense polymer layer. when the continuous phase is a good solvent for the stabilizing polymer, this layer gives rise to steep repulsions between the particles.^[15]

When two particles approach, the polymer layers will touch as soon as the particle surface distance H becomes less than twice the layer thickness. Two possible scenarios now arise (Figure 2): (a) interpenetration, in which the two polymer layers gradually intermingle as the surfaces approach, locally doubling the polymer segment concentration, or (b) compression, in which the concentration of polymer segments between the surfaces gradually increases from its initial value but is at the same value across the gap between the surfaces.

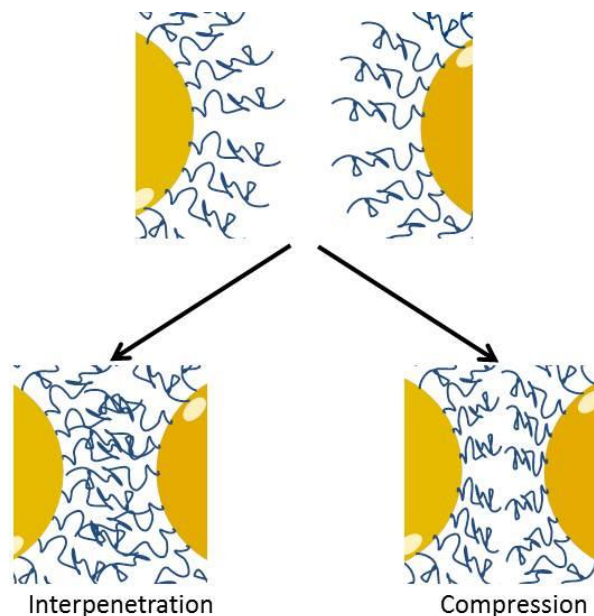


Figure 2: Principle of steric stabilization.

In a good solvent for the polymer the local increase in polymer concentration carries a free energy penalty and this gives rise to a repulsive steric interaction between the

particles. An increase of the Gibbs free energy is caused by the restriction of the movement of polymer chains and corresponding reduction of entropy. Besides, increasing the concentration of the stabilizing polymers in the interparticle region leads to an increased osmotic pressure, which is counterbalanced by dragging the solvent molecules in the considered region and leads to the separation of the particles.

The repulsion forces will arise as soon as the surface separation H becomes less than twice the unperturbed thickness of polymer layer L_0 , $H < 2L_0$ and it will increase steeply as soon as $H < L_0$, when compression of the polymer layers is inevitable. This steep repulsion provides the steric stabilization of suspensions. Whereas van der Waals attraction still operate between the colloidal particles, effective stability may ensue, provided the attractions are weak (compared to $k_B T$) at separations $D \approx L_0$, where the steric repulsion sharply increases.^[15]

2.3. Micellation of Surfactants

Surfactants are amphiphilic molecules consisting of two parts with different solubilities in particular solvents, e.g. lyophilic and lyophobic parts. When the solvent is water, one usually talks about the hydrophilic and hydrophobic parts. The hydrophilic part is usually referred as a head group, while the hydrophobic part is referred as tail.

Besides their characteristic tendency to adsorb at interfaces, another fundamental property of the surfactants is that unimers in solutions tend to aggregate.

At low concentrations surfactants show behavior like simple electrolytes. One notable exception is the surface tension which decreases rapidly with surfactant concentration. At higher concentration, which is different for different surfactants, unusual behavior is observed. For example, the surface tension, as well as the osmotic pressure takes on an approximately constant value, while light scattering starts to increase and the self-diffusion starts to decrease. All the observations suggest and are consistent with a change-over from a solution containing single surfactant molecules or ions, i.e. unimers, to a situation where the surfactant occurs more and more in a self-assembled or self-associated state. The first-formed

aggregates, micelles, are approximately spherical in shape, and the concentration where they start to form, is referred as critical micelle concentration (CMC). CMC depends on the chemical structure of the surfactant molecule and is highly sensitive to the hydrophobicity of the hydrophobic chain, valency of the counterion or the structure (branching) of hydrophobic alkyl chain. An increased hydrophobicity of the hydrocarbon chain leads to the decrease of the CMC and increase of the aggregation number (the number of surfactant molecules in a micelle once the CMC has been reached).^[22-24]

CMC is in most cases less sensitive towards temperature, but strongly affected by cosolutes. The presence of the salt can lower the CMC to an order of magnitude. This effect is more pronounced for long chain surfactants.

Other lower molecular weight cosolutes produce changes in the CMC to a very different extent depending on the cosolute polarity. Both, increases and decreases of CMC are possible. More common and more investigated cases are the decrease of the CMC, observed for most uncharged cosolutes. The effect depends on the cosolute polarity and any amphiphilic character it might have.^[22]

As it will be described throughout the work, the micellation of surfactants shows strong similarity to the physical cross-linking of here considered systems (see chapter 2.6.2.1). This similarity can also be employed for selective disturbance of the hydrophobic domains with amphiphilic additives.

2.3.1. Hydrophobic Effect as an Entropic Force

In order to understand the mechanism of the micelle formation, it is important to understand the origin of the hydrophobic interactions. The hydrophobic interaction is mostly an entropic effect that is caused by disruption of the dynamic hydrogen bonds between the molecules of water by the nonpolar solute. The hydrogen bonds are reoriented tangentially to such surface to minimize disruption of the hydrogen bonded 3D network of water molecules and thus leads to a structured water "cage" around the nonpolar surface. The water molecules that form the "cage" (or solvation shell) have restricted mobility. This leads to the loss of translation and rotational entropy of the water molecules. By aggregating together, nonpolar molecules reduce the surface area exposed to water and minimize the mentioned effect.^[25]

The hydrophobic effect is found to be only slightly dependent on temperature and becomes smaller at low temperatures, which is observed in case of “cold denaturation” of proteins.^[26]

2.3.2. Driving Forces of Micelle Formation

As described in the chapter 2.3.1, water does not interact favorably with hydrophobic groups and there is a driving force for expelling them from the aqueous environment. This may be achieved by a macroscopic phase separation or by “hiding” non-polar groups in some other way.

When a polar group is attached to a hydrophobic group, an opposing force is created, which counteracts phase separation. If the opposing force is weak, phase separation will still result. If it is very strong compared to the hydrophobic effect, on the other hand, the amphiphile will occur as single molecules or as small aggregates, like dimers. Micellization (and surfactant self-assembly in general) is somewhere intermediate between phase separation and simple complex formation.

The hydrophobic interaction increases with increasing alkyl chain length of an alkane or the hydrophobic group of a surfactant. Indeed, the decrease in solubility of an alkane with the number of carbons very much parallels the change in the CMC.^[22]

The hydrophilic-lipophilic balance is a convenient measure for the characterization of surfactant to which degree it is hydrophilic or lipophilic. The concept was first introduced by Griffin who characterized a number of surfactants, and derived an empirical equation for non-ionic alkyl polyglycol ethers (C_iE_j) based on the surfactant chemical composition:^[15]

$$HLB = \frac{E_j \text{ wt\%} + OH \text{ wt\%}}{5} \quad (8)$$

where $E_j \text{ wt\%}$ and $OH \text{ wt\%}$ are the weight percent of ethylene oxide and hydroxide groups respectively.

Davies proposed a more general empirical equation that associates a constant to the different hydrophilic and hydrophobic groups:^[15]

$$HLB = [(n_H \times H) - (n_L \times L)] + 7 \quad (9)$$

where H and L are constants assigned to hydrophilic and hydrophobic groups respectively, and n_H and n_L the number of these groups per surfactant molecule.

2.4. Classification of Emulsions

Besides their type, e.g. oil/water (O/W) or water/oil (W/O), emulsions can also be classified according to their size as micro-, mini-, and macroemulsions. However, this size classification is only a guide and not rigorous. It is more appropriate to attribute the systems to these classes based on their thermodynamic characteristics. Microemulsions are thermodynamically stable systems, while macro- and miniemulsions are only metastable (i.e. kinetically stable).^[15]

Macromulsions are usually produced by applying relatively mild shear forces (such as stirring or shaking) to a mixture of two non-miscible liquid phases. The free energy of formation of such systems can be expressed as:

$$\Delta G = \Delta A\gamma_{12} - T\Delta S_{conf} \quad (10)$$

where ΔA is the change in interfacial area A , γ_{12} is the interfacial tension between phases 1 and 2 at the temperature T and ΔS_{conf} is the configurational entropy change. For classical macroemulsions formed by comminution, the corresponding ΔG is positive, while ΔS_{conf} is small in magnitude and negligible. Therefore, increasing the concentration of surfactant at around the CMC in the continuous phase and corresponding decrease of the γ_{12} is the most efficient way to aid the liquid/liquid interface formation. However, as mentioned, the systems are thermodynamically unstable and in relatively short time phase separation occurs.^[15]

On the other hand, microemulsions represent thermodynamically stable systems and corresponding ΔG values are negative. This is achieved by extremely high surfactant concentrations and in most cases by the application of cosurfactants, such as alcohols. The droplet size for microemulsions is less than 100 nm and quite often is in the range of 5 – 50 nm, leading to optical transparency of the systems. However, it should be noted that microemulsions are kinetically unstable, e.g. internal contents of the microemulsion droplets are known to exchange, typically on the millisecond time scale.^[27] They diffuse and undergo collisions. If collisions are sufficiently violent, then the surfactant film may rupture thereby facilitating droplet exchange. Therefore

the droplets are kinetically unstable. However, if one disperses emulsions as sufficiently small droplets (<500 Å), the tendency to coalesce will be counteracted by an energy barrier. Then the system will remain dispersed and transparent for a long period of time (months).^[28] Such an emulsion is said to be kinetically stable.^[15, 29]

As opposed to microemulsions, miniemulsions do not represent thermodynamically stable systems. They are rather critically stabilized emulsions with smaller droplet sizes.^[30-32] They are stabilized against different degradation mechanisms. The stability of miniemulsions will be discussed below in more detail.

2.4.1. Stability of Miniemulsions

To create a stable miniemulsion, the droplets must be stabilized against molecular diffusion degradation (Ostwald ripening, a monomolecular process or τ_1 mechanism) and against coalescence by collisions (a bimolecular process or τ_2 mechanism).^[32] The above described stabilization mechanisms for emulsions are efficient to avoid droplet coalescence, but cannot prevent diffusion degradation.

The driving force for the diffusion degradation is the Laplace pressure which is calculated as follows:

$$P_{laplace} = \frac{2\gamma_{12}}{a} \quad (11)$$

Where γ_{12} is the surface tension between liquid phases 1 and 2 and a is the droplet radius.^[33] Laplace pressure is the pressure difference between inside and outside of the droplet surface and as it is seen from the equation (11) its value is higher for smaller droplets. In order to balance for this pressure difference, the molecules from the smaller droplets can diffuse through the continuous phase to the bigger droplets until they disappear completely.

In order to suppress the monomer diffusion according to the described process, osmotic pressure agents are commonly used as additional stabilizers for miniemulsions. Osmotic pressure agents are highly hydrophobic (ultrahydrophobic) substances for direct miniemulsions and lipophobic substances for inverse miniemulsions. Davis et al. described that the added material reduces the total vapor pressure as defined by Raoult's law.^[34] These additional components build the osmotic pressure inside the droplets:

$$\Pi_{osmotic} = RTc \quad (12)$$

where R is the gas constant, T is the temperature in Kelvin and c is the molar concentration of the employed osmotic pressure agent. The presence of the osmotic pressure counteracts Laplace pressure, thus suppressing the diffusion degradation.^[32]

2.4.2. Formation of Miniemulsions

The formation of miniemulsions is schematically represented in Figure 3 on the example of direct miniemulsions. It is usually conducted in two steps. Initially a pre-emulsion is formed via simple stirring of the organic phase, containing the osmotic agent and the water phase, containing the dissolved surfactant. Subsequently high shear forces are applied to the pre-emulsion. Application of high shear forces is usually achieved via ultrasonication or the use of high pressure homogenizers.

For the miniemulsion preparation on the small scale the ultrasonication was employed throughout this work and therefore it will be discussed in more detail.

During ultrasonication high frequency (above 20 KHz) ultrawaves are applied to the pre-emulsions, which leads to cavitation processes in the system. Cavitation is understood as the formation of vapor bubbles due to applied force (transferred energy from high frequency waves). The formed vapor bubbles implode and cause strong shockwaves that leads to further disruption of emulsion droplets.^[35] However, the exact process of droplet disruption due to ultrasound as a result of cavitation is not yet fully understood. At constant energy density, the droplet size decreases when adding stabilizers, whereas the viscosity of the continuous phase has no effect.^[36] This clearly speaks for strong elongational flow components.

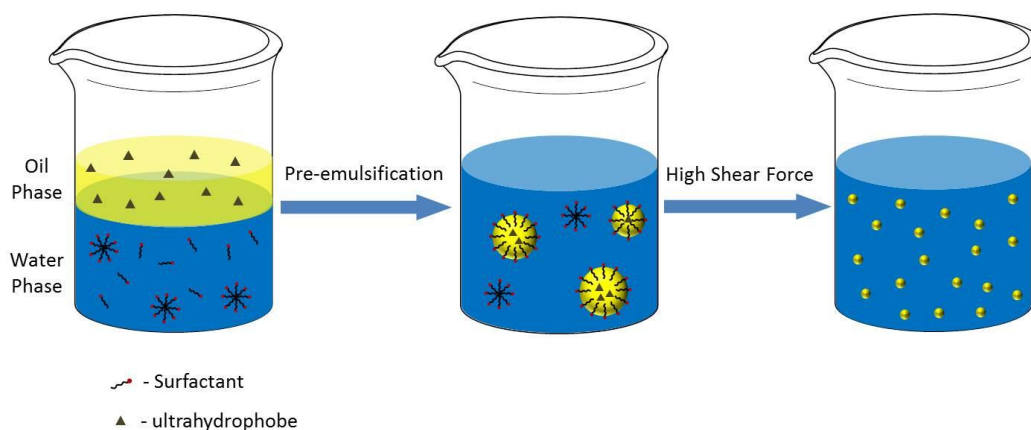


Figure 3: Schematic representation of miniemulsion formation. Pre-emulsification is achieved by simple stirring of the system. On the second step high shear forces, such as ultrasonication or high pressure homogenization are employed to form miniemulsions.

It should be noted that freshly formed miniemulsion droplets have to be stabilized via (partial) surface coverage with surfactant molecules. It has been proven that at the initial stages of miniemulsion formation, not sufficiently stabilized droplets can aggregate. Only after a certain time of sonication, a maximal possible coverage of the oil-water surface by the surfactant is achieved. Once this pseudo-steady state is reached, the size of the monomer droplets is no longer a function of the amount of applied mechanical energy, assuming a required minimum is used. In the beginning of homogenization, the polydispersity of the droplets is still high, but by constant fusion and fission processes, the polydispersity decreases, the miniemulsion reaches then a steady state.^[32]

2.5. Polymerization and Copolymerization in Heterophase Systems

In an idealized case the target of miniemulsions polymerization is to initiate the polymerization in each of the small stabilized droplets while avoiding any secondary nucleation processes or mass transport.

To emphasize the importance of the approach a short description of the emulsion polymerization will be given here. Emulsion polymerization is schematically described in Figure 4.

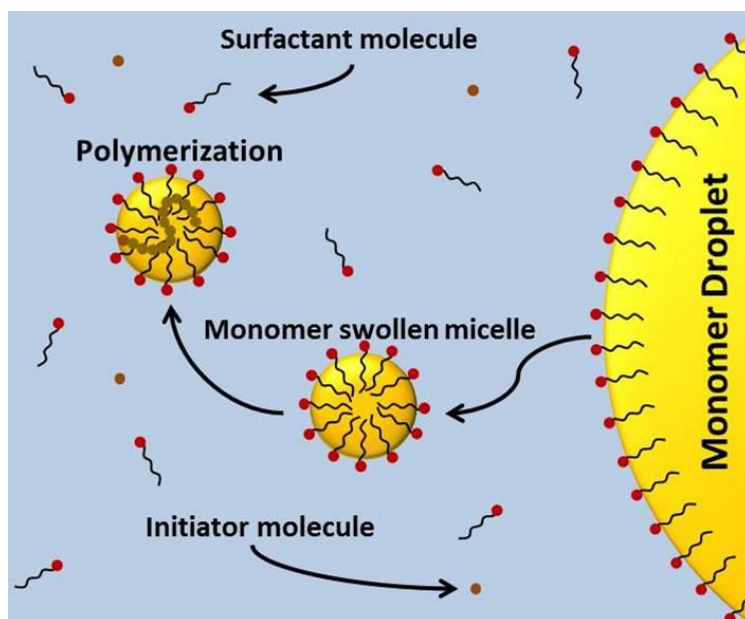


Figure 4: Schematic representation of the emulsion polymerization process.

As shown in Figure 4, the main reaction locus is the monomer swollen micelle and the monomer droplets act as reservoirs for the monomer. As concluded from the kinetic studies of the emulsion polymerization, the rate limiting factor for this type of polymerization is the monomer diffusion rate through the water phase (Figure 5).^[37]

Irrespective of the particular behavior, three intervals can be observed in all emulsion polymerizations based on the particle number and the existence of a separate monomer phase (i.e. monomer droplets) as shown in Figure 5. There is a separate monomer phase in intervals I and II but not in III. The particle number increases with time in interval I and then remains constant during intervals II and III. Particle nucleation occurs in interval I, with the polymerization rate increasing with time as the particle number builds up.

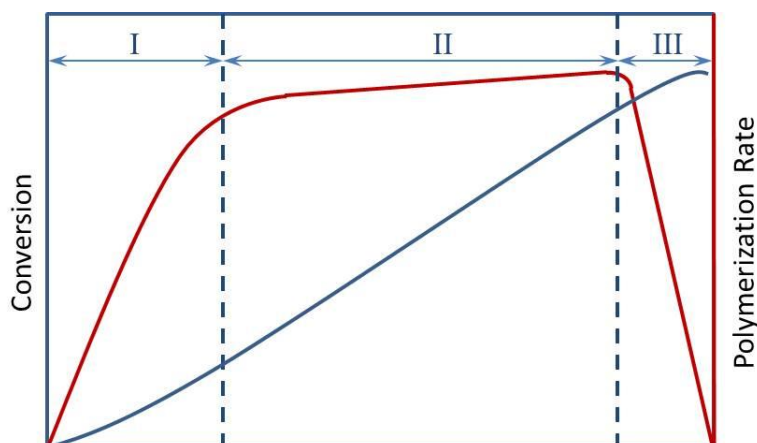


Figure 5: Kinetic of the emulsion polymerization

During interval II (Figure 5) the slight increase of the reaction rate is assigned to the gel effect. In this interval there are no more particles formed and the polymer particles increase, while the size of the monomer droplets decreases. This occurs on the expense of the diffusion of monomer molecules through the water phase. Interval II ends when the monomer droplets disappear.^[9] These observations support the diffusion controlled mechanism described in Figure 4.

Unlike emulsion polymerization, in the miniemulsions systems in an ideal case the particle number and identity is preserved throughout the whole polymerization process and each droplet can be considered as an isolated nanoreactor.^[32] Schematically the process of miniemulsions polymerization is described in Figure 6:

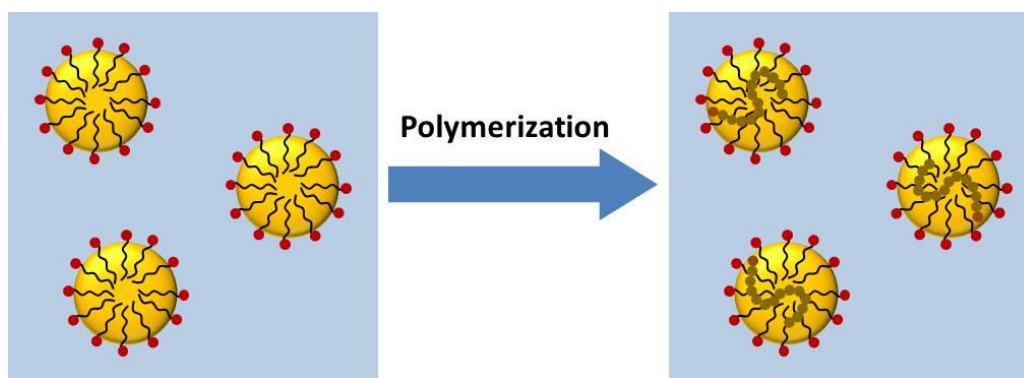


Figure 6: Schematic representation of the miniemulsion polymerization. In an ideal case the particle number and identity is preserved throughout the process. Chain growth occurs within “nanoreactor” droplets without significant extent of diffusion between the particles/droplets.

As it is described in Figure 6, unlike emulsion polymerization, during the miniemulsion polymerization the nucleation occurs in the monomer droplet and therefore the above mentioned nanoreactor principle can be applied. This is of particular importance for the work described here, since it enables a direct introduction of highly hydrophobic monomers without the necessity of the mass transport through the water phase.

2.6. Polyelectrolytes

Polyelectrolytes are polymers that develop substantial charge when dissolved or swollen in a high polar solvent. These polymers are also commonly termed as polyions because their charge arises from many ionized functional groups positioned along the chain. Electrostatic interactions between the ionized groups, as well as the

presence of small electrolyte ions in the nearby solution, provide polyelectrolyte solutions with the properties distinct from those of neutral polymers.

The presence of covalently attached ionic groups fundamentally distinguishes polyelectrolytes from neutral polymers, and so a description of polyelectrolyte properties begins with the parameterization of the polyelectrolyte charge. The projected number of elementary charges of magnitude e ($1.602 \cdot 10^{-19}$ C) per unit backbone length defines a polyelectrolyte's linear charge density. The inverse of this quantity, given the symbol b , represents the average axial spacing between charges.

Current industrial applications and academic interests mainly focus on polyelectrolyte behavior in solutions, gels, adsorbed layers and grafted brushes. In this work the viscoelastic properties of the polyelectrolyte solutions is addressed and investigated.

At this stage the main assumptions should be brought in, which are employed in the polyelectrolyte investigation.^[38] The first is that the charges, which are physically positioned at some radial distance from the polymer backbone, are treated as the hypothetical charges positioned along the polymer chain. Second, the discrete axial spacing of charges is smeared along the chain contour, eliminating local charge correlations. Finally, the radial mispositioning of the charge implies that the dielectric properties of the backbone are irrelevant to the polymer's electrostatic properties. These assumptions imply that general properties of polyelectrolyte solutions should be investigated on a big enough scale so that no local structural effects contribute to their behavior. Our investigations are based on these assumptions and meet all requirements in terms of experimental design or data treatment. The exceptions to this implication usually are the cases where the local structure is rather important, such as in DNA. In this case one can consider surface charge density instead of linear charge density, or even more complex placement of charged groups relative to finite dielectric constant backbone.^[38] However, these complex scenarios do not apply to systems investigated here.

The electrolyte environment also needs to be described to characterize a polyelectrolyte system. Polyelectrolytes dissolved or swollen in a solvent are bathed in a dielectric medium that typically includes, in addition to other polymer chains and liberated counterions, some level of added or ambient low molar mass electrolyte. A

full system description therefore includes information about the solvent medium and any added electrolyte. In the current work we avoid the presence of any added electrolyte in the system and mainly concentrate the efforts and attention on the added amphiphilic additives, that also have a significant effect on the dielectric constant and consequently on the solution behavior.

The interaction of thermally equilibrated charges across a medium of dielectric constant ε introduces to electrolyte solutions a fundamental length scale l_b , the Bjerrum length.^[38] This length characterizes the distance over which two bare charges of magnitude e experience an electrostatic interaction energy equal to the medium's thermal energy kT , i.e.:

$$l_b = \frac{e^2}{4\pi\varepsilon\varepsilon_0kT} \quad (13)$$

where ε_0 is the permittivity of vacuum ($8.854 \cdot 10^{-12} \text{ (A}^2 \cdot \text{S}^4)/(\text{kg} \cdot \text{m}^3)$). At 25 °C, l_b in water ($\varepsilon=78$) is about 0.71 nm.

The introduction of counterions and added electrolyte introduces yet another length scale to electrolyte solutions, one that manifests the enhanced decay of electrostatic interactions in the presence of screening charges. When electrostatic effects are treated within the standard Poisson–Boltzmann approximation, the Debye length κ^{-1} governs the screening length of electrostatic interactions by these ions:

$$\kappa^{-1} = \left(\frac{\varepsilon\varepsilon_0kT}{\sum_i c_{0,i}(ez_i)^2} \right)^{1/2} \quad (14)$$

where $c_{0,i}$ is the bulk concentration (number per volume) of the i th ion species of valence z_i . Introducing the ionic strength of the solution ($I = 1/2 \sum_i c_i z_i^2$), the Debye length can be expressed as:

$$\kappa^{-1} = \left(\frac{\varepsilon\varepsilon_0kT}{2N_a e^2 I} \right)^{1/2} = (8\pi N_a l_b)^{-1/2} \quad (15)$$

The largest experimentally obtainable values of κ^{-1} are in the range of tens to hundreds of nanometers, values characteristic of dilute, essentially salt-free polyelectrolyte solutions. For these extreme cases, I is dominated by the bulk

concentration of counterions dissociated as the polymer dissolves. For highly charged polyelectrolytes, not all dissociated counterions contribute to I .

Thus, a basic description of the solvent medium provides two additional length scales, l_b and κ^{-1} . The former one characterizes the spatial attenuation of electrostatic interactions according to the medium's dielectric constant, while the latter one characterizes the spatial attenuation of electrostatic interactions according to the medium's concentration of thermally equilibrated small ions.^[38]

2.6.1. Polyelectrolyte Solution Viscosity

The solution viscosity of polyelectrolytes, which is one of the main focuses of this work, follows significantly different trends than that of neutral polymer solutions. For dilute solutions of neutral polymers the concentration dependency of the specific viscosity obeys the standard Huggins formula:^[38]

$$\frac{\eta_s}{c} = [\eta] + k_H[\eta]^2c \quad (16)$$

where $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient. The contribution to η_s/c due to isolated polymer chains is captured in $[\eta]$, while the contribution due to binary chain–chain interactions is captured in k_H . Contributions from higher order chain–chain interactions are neglected in the Huggins formula. Molecular theories show that there is a general proportionality between intrinsic viscosity and the molecular weight of the polymer ($[\eta] \sim M^{3\nu-1}$). At large M , the excluded volume parameter ν provides an indication of chain conformation: for a dense spherical globule, $\nu = 1/3$; for a flexible chain in a theta solvent, $\nu = 1/2$; for a flexible chain in a good solvent, $\nu \approx 3/5$; and for a rod-like chain, $\nu = 1$.^[38]

Polyelectrolyte solutions with high or medium salt contents, where the electrostatic interactions of polymer chain segments are highly screened, still follow Huggins' formula. However, at low or no extra salt content, significant deviations occur. Configuration-based models for trends in η_s/c attribute the anomalous polyelectrolyte viscosity behavior to electrostatically driven chain expansion. Therefore, it has been suggested that in infinite dilutions the chains of salt-free polyelectrolytes become rod-like.^[39, 40]

To model the anomalous behavior of η_s/c at low concentrations of added electrolyte (c_s), Fouss and Strauss proposed an empirical relationship to replace the Huggins formula^[41-43]:

$$\frac{\eta_s}{c} = \frac{A}{1 + Bc^{1/2}} \quad (17)$$

where A and B are constants. The rod-like behavior of salt-free polyelectrolytes at infinitely small c is supported by observed proportionality of A with the second power of M , a feature, consistent with a solution containing rods. However, obvious flows in this model, most significant one being that it does not explain the presence of maximum on the plots η_s/c vs. c , led to development of other configuration-based and nonconfiguration-based models.

Little effort has been expended for polyelectrolytes to measure rheological properties other than η at values of c near and below c^* (critical overlap concentration, where closely packed but non-overlapped chains fully occupy a polymer solution). Several measurements of the storage and loss modulus for dilute flexible polyelectrolyte solutions have been interpreted in terms of shifts in the longest chain relaxation time as the polyelectrolyte expands and contracts.^[44] The c dependence of η reflects the onset of chain entanglement well above c^* through a sharp upward transition in slope. In the semidilute but unentangled region, measured linear viscoelastic properties can be interpreted via a modified Rouse theory, and at the higher concentrations associated with chain entanglement, these properties can be interpreted via a modified reptation theory.^[45] Conditions that govern polyelectrolyte entanglement, however, are not understood.^[38]

2.6.2. Alkali Soluble Latexes

Alkali soluble emulsions (ASE) have been reported as early as 1950's as copolymers of unsaturated organic acids and acrylic monomers.^[8] Neutralization of acid groups in such polymers leads to a strong viscosity increase of the systems as described for polyelectrolytes, where the chain entanglement plays a major role. Owing to their unique properties they were found of high industrial importance for a vast variety of applications, ranging from coatings, adhesives and rheology modifiers to sieving media for DNA sequencing.^[46-48] The alkali-swelling and dissolving behavior of carboxylated latexes have been correlated to the glass transition temperature (T_g),

hydrophilicity and molecular weight of the polymers, carboxyl content and their distribution within the latex particles and other characteristics variables.^[46, 49-52] These investigations have shown that the changes which occur upon neutralization are caused by swelling of the latex particles with accompanying solubilization of polymer molecules upon sufficient hydrophilicity.

When hydrophobic macromonomers, also referred as associative monomers (AM), are embedded into the polymer backbone, the hydrophobic moieties are able to interact with each other. Alkali soluble emulsions with such modification are referred as hydrophobically-modified alkali soluble emulsions (HASE), which will be described below.

2.6.2.1. Hydrophobically Modified Alkali Soluble Latexes

The introduction of hydrophobic groups into the ASE systems has been found to be a convenient method for tuning the rheological and mechanical properties.^[47] The origin and the driving force for the formation of hydrophobic associates are described in the chapter 2.3.1.

As described above for the ASE systems, HASE latexes dissolve upon neutralization at a pH values above ≈ 7 . The increase of viscosity occurs through repulsion of carboxylate anions, positioned along the polymer backbone. However, HASE systems exhibit enhanced viscosity compared to conventional ASE because the hydrophobic groups aggregate together in the water phase in a manner similar to the way in which surfactants form micelles.^[53, 54] e.g. hydrophobic interaction provides systems with additional thickening mechanism.^[54] These associations can be considered as non-permanent physical cross-linking sites between polymer chains. The associative mechanism in HASE systems is presented in Figure 7. Thus, neutralized HASE solutions represent physically cross-linked networks of polyelectrolytes in the water solution.

Despite the micellation-analogous association of HASE polymers, strong differences should also be pointed out. Owing to the higher degree of freedom, self-assembly of surfactants leads to the formation of regular shaped structures, such as spherical or cylindrical micelles, lamellar phase, vesicles etc. On the other hand the hydrophobic domains formed in HASE solutions are less regular and in some cases involve the hydrophobic segments of the polymer backbone. Also, unlike the micellar

assemblies there is no strict characteristic aggregation number (as opposed to the defined number of the surfactant molecules in the micelle) for the hydrophobic domains in HASE systems. Due to the described deviations, along with the structural complexity and polydispersity of the polymers, it is more reasonable that instead of the local character of the hydrophobic associations one considers their influence on the rheological and mechanical behavior instead. As it is presented throughout the work this approach allows correlating the macroscopic properties of the systems to the described microscopic associations.

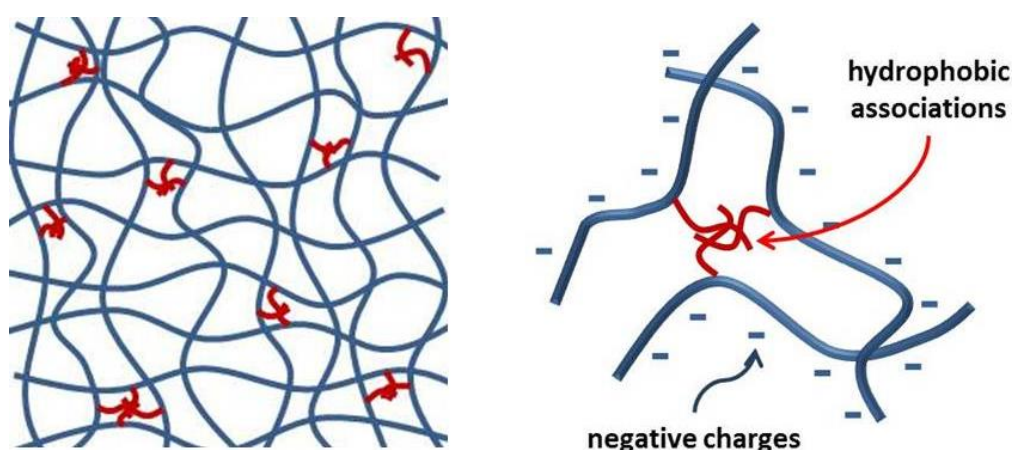


Figure 7: Schematic representation of hydrophobically-modified alkali soluble latexes (physically cross-linked network).

HASE systems have attracted significant interest not only because of their technical performance, but also because of the ease and low cost of manufacturing. A variety of systems with similar general behavior can be synthesized employing different methods, such as solution polymerization in organic solvent, polymer-analogous reactions or micellar polymerization, but they all suffer from certain drawbacks, such as the use of organic solvents, high content of surfactant *etc.*^[55-58] The HASE synthesis on the other hand has its own main disadvantage. The incorporation of the moieties with strongly divergent hydrophobicities requires specifically designed and relatively high cost macromonomers. In classical HASE systems the hydrophobic moieties are separated from polymer backbone with an oligo(ethylene oxide) chain.^[59-61] This requires a corresponding complex structure of the macromonomer. The structure of such a typical macromonomer is provided in Figure 8. Owing to their structure, these macromonomers also act as surfactants for emulsion polymerization. However, the complexity and high cost of such monomers limit the range of rheological properties, covered by final HASE systems.

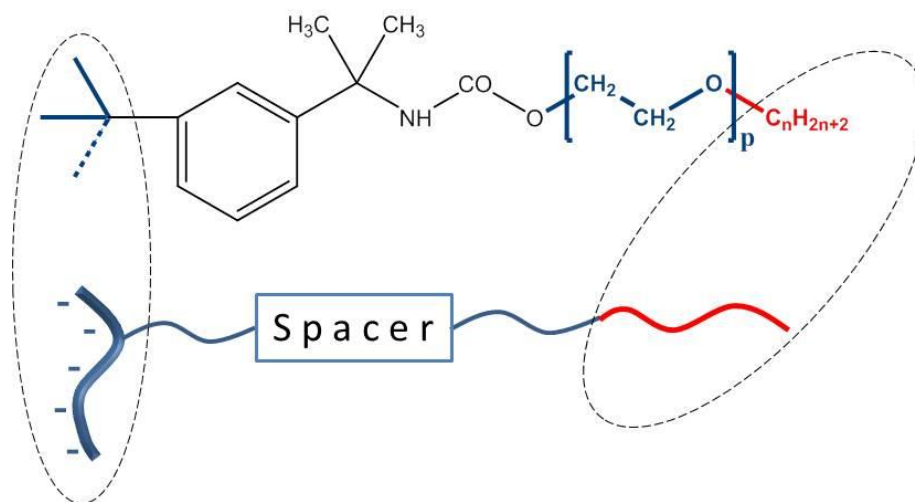


Figure 8: Typical structure of macromonomers used in classical HASE synthesis with unsaturated reactive end-group and hydrophobic group (red colour) separated with PEO chain.

As it will be presented throughout the work, a novel approach is based on the use of the miniemulsion nanoreactor principle and reactive costabilizers.^[62] It simplifies the synthesis of the HASE systems via overcoming the limitations regarding the used hydrophobic modifiers in non-classical miniemulsion-analogous systems. This broadens the choice of the hydrophobic modifiers and enables to cover a range of rheological properties.

Analogous to the surfactant aggregation behavior into micelles, the strength of the hydrophobic domains and their tendency to aggregate, with corresponding changes in mechanical properties can be tuned in various ways. This aggregation behavior is schematically depicted in Figure 9 and will be described in more detail in chapter 5.

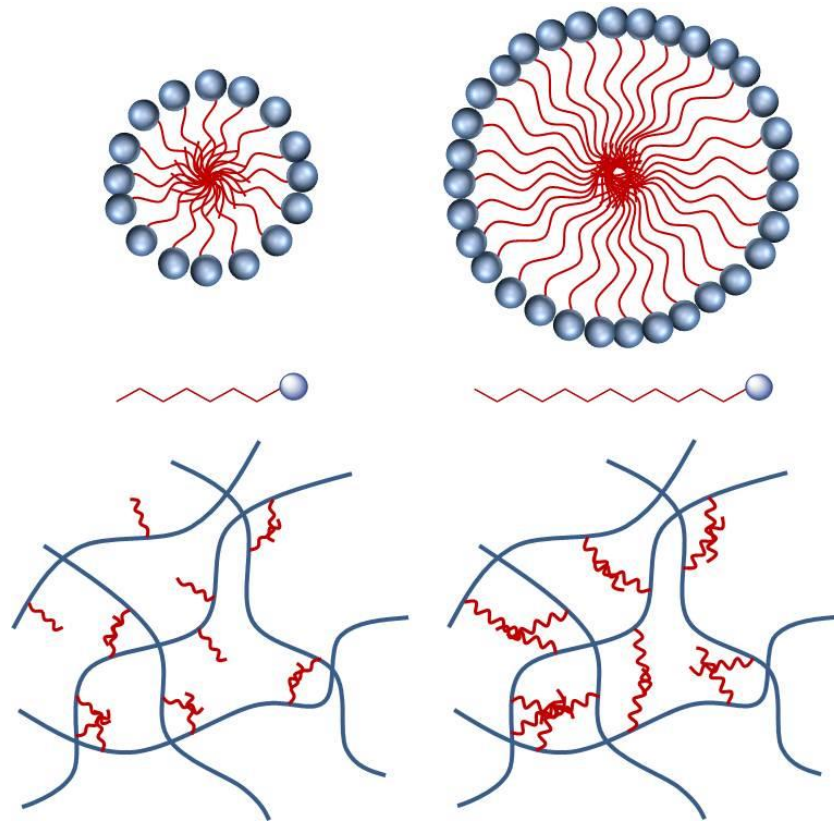


Figure 9: Micelle analogous aggregation of hydrophobic domains in hydrophobically modified polyelectrolyte systems can affect the cross-linking density and aggregation number, with corresponding effects on rheological and mechanical behavior.

As it was mentioned in the chapter 2.3, the surfactant behavior, particularly their critical micelle concentration, is highly sensitive towards different types of additives. Considering the described analogy between HASE systems and surfactant micellation and the influence of the alcohols (amphiphilic additives) on the hydrophobic association, throughout the work we observe and investigate the influence of the alcohols on the rheological behavior of the HASE systems and possibility of their application oriented adjustment.

2.7. Rheological Behavior – Overview

2.7.1. Stress and Strain

The *stress* is simply defined as the force divided by the area over which it is applied. *Shear stress* is defined as the component of the stress coplanar with the material cross section. On the other hand, *normal stress* arises when the force is applied perpendicular to the material cross section. The former one will be described here in

details since all the rheological investigations were conducted in this format. Shear stress is assigned by letter σ and is defined as:

$$\sigma = \frac{F}{A} \quad (18)$$

where the A is the area over which the force F is applied. The unit of stress is Pascal.

When the stress is applied to the material, a deformation will be the result. The strain (γ) is defined as the relative deformation, that is, the deformation per unit length.^[63]

The interdependence of stress and strain is the main subject for the rheological investigations. The corresponding theoretical background is given below.

2.7.2. Viscoelasticity

Many materials can be readily classified as solid or fluids, displaying elastic or viscous behavior respectively. However, for a significant number of materials the timescale of the measurement relative to characteristic time of the material should be considered. The ratio of these times is given by Deborah number, D_e .

2.7.2.1. Deborah Number

Maxwell introduced the idea that viscous flow is the manifestation of the decay of elastically stored energy. Following this concept, the dimensionless group, the Deborah number, D_e , arises naturally. In the relaxed state it can be considered that the material has achieved a certain condition, in which the molecules or particles are in some low energy state which was achieved via their relative movement and diffusion. If at this point the material is instantaneously strained, molecules or particles will shift to a higher energy state and the energy will be stored. For a characteristic time the molecules will diffuse until an original low-energy state equivalent to the initial one has been achieved, although the original shape has been lost, *i.e.* viscous flow occur. This characteristic time can be defined as *stress relaxation time*, τ , of the material. Consequently the Deborah number can be defined as:

$$D_e = \frac{\tau}{t} \quad (19)$$

From here it is obvious that the classifications of materials depend on the observation time t , and the materials can be classified in three different types:

$D_e \gg 1$	$D_e \approx 1$	$D_e \ll 1$
Solid-like	viscoelastic	Liquid-like

2.7.2.2. Other Dimensionless Groups

The above described Deborah number is purely based on experimental measurements, *i.e.* an observation of bulk material behavior. On the other hand the Péclet number, P_e , is determined by the diffusivity of microstructural elements, and is the dimensionless group given by the timescale for diffusive motion relative to that for convective flow.

Several other dimensionless groups, such as the reduced stress (σ_r), the Taylor number (T_a) and the Reynolds number (R_e) are employed in basic characterization of the material flow behavior. However, they are not relevant to the conducted research and will not be discussed here.

2.7.3. Viscoelasticity – Phenomenological Approach

The viscoelastic response of materials can be presented in two ways. From the macroscopic viewpoint the material is considered as a continuum. Its properties are considered to be dynamic, but not explicitly linked to its microstructure. The properties are determined by overall energy storage and loss processes. This approach is also referred as a phenomenological approach and will be shortly discussed in this sub-chapter.

Mechanical spectroscopy has a certain similarity to well-known infrared or ultraviolet spectroscopy, where the response of a sample to various electromagnetic frequencies is used to judge about the sample structure. However, the major difference is that the mechanical response is very difficult to isolate as a single structural process. Besides, very similar mechanical characteristics may be due to completely different structural causes. These features lead to the *phenomenological treatment* of the rheological behavior. In this approach the molecular or colloidal interactions are neglected and the behavior of the system is explained in terms of Hookean springs and Newtonian dashpots.

As mentioned above, applying stress to a sample leads to a corresponding strain. The same is true for the oscillatory stress. In the linear viscoelastic region if the stress is doubled the corresponding strain will also double. This behavior is also characteristic for the Hookean spring or the dashpot containing Newtonian oil (Figure 10).

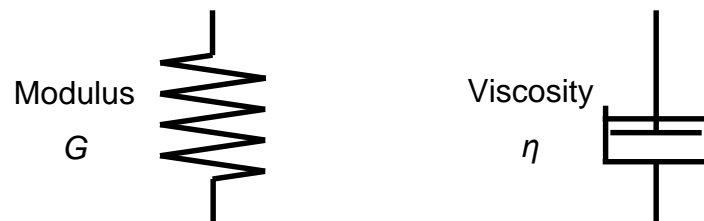


Figure 10: A spring with the modulus G (left) and a dashpot with an oil of viscosity η (right).

The combination of these two models in different ways allows us to describe even very complex rheological behaviors. The stress/strain relationship for Hookean spring and Newtonian dashpot models is given by equation (20) and equation (21) respectively.

$$\sigma = G\gamma \quad (20)$$

$$\sigma = \eta\dot{\gamma} \quad (21)$$

Where $\dot{\gamma}$ is the time derivative of the strain.

The two basic models of serial and parallel combination of these models are Maxwell model and Kelvin-Voigt model respectively (Figure 11).

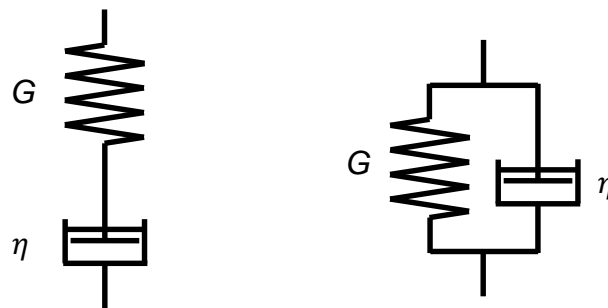


Figure 11: Maxwell model (serial combination – left) and Kelvin-Voigt model (parallel combination – right).

For the Maxwell model strain rates add linearly. Consequently from equations (10) and (11) following equation can be derived:

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \quad (22)$$

Both of these models show viscous and elastic contributions, and so both show viscoelastic behavior. One can visualize a more complex combination of models possessing more complex constitutive equations, which are thus able to describe even more complex rheological profiles.

2.7.3.1. Oscillatory Response

Throughout this work oscillatory experiments were the main investigation method for the rheological behavior studies and therefore some theoretical descriptions will be given in this sub-chapter.

When an oscillating strain is applied to a sample, the oscillatory stress develops in direct response to the applied strain. The corresponding waveforms are represented in Figure 12.

It should be noted that for any given frequency two main characteristic parameters are constant. The first is the ratio of maximum stress (σ_0) to maximum strain (γ_0) (the peak values of the sinusoidal functions on the Figure 12). This ratio is called complex modulus G^* .

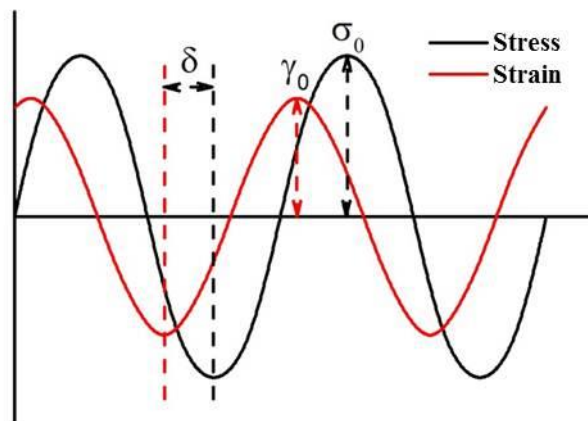


Figure 12: Oscillating strain and corresponding stress for the viscoelastic material. Phase difference (δ) for purely elastic materials equals to 0, while for Newtonian fluids it equals to $\pi/2$ rad.

$$|G^*(\omega)| = \frac{\sigma_0}{\gamma_0} \quad (23)$$

Here the ω is the radial frequency, which is equal to $2\pi f$, where f is the frequency measured in Hertz.

The second feature, which is constant for a given frequency is the phase difference (δ) in radians between the peak value of the stress and the peak value of the strain.

These two values are characteristic for a given material. For purely elastic materials the strain and the corresponding stress are in phase, while for Newtonian liquids the phase difference is $\pi/2$ rad (90°), as the peak stress is proportional to the *rate of strain*. In viscoelastic material some energy is stored and some becomes dissipated. Correspondingly, the stored energy contribution will be in phase while the dissipated energy (energy *loss*) contribution will be out of phase with the applied strain, as is the case with the systems investigated throughout this work.

As it will be shown below, the complex modulus can be divided into two: storage (G') and loss (G'') moduli.

In order to describe the material properties as a function of frequency for a body that behaves as a Maxwell model we need to use the constitutive equation. It is most convenient to express the applied sinusoidal wave in the exponential form of complex number notation:

$$\gamma^* = \gamma_0 e^{i\omega t}; \quad \dot{\gamma}^* = i\omega\gamma_0 e^{i\omega t} = i\omega\gamma^* \quad (24)$$

Now the stress response lags by the phase angle δ :

$$\sigma^* = \sigma_0 e^{i(\omega t + \delta)}; \quad \dot{\sigma}^* = i\omega\sigma_0 e^{i(\omega t + \delta)} = i\omega\sigma^* \quad (25)$$

So, when we substitute the complex stress and strains into the constitutive equation for a Maxwell fluid the resulting relationship is given by equation (26).

$$\dot{\gamma}^* = \frac{\dot{\sigma}^*}{G} + \frac{\sigma^*}{\eta} \quad (26)$$

and using equations (24) and (25):

$$i\omega\dot{\gamma}^* = \frac{i\omega\dot{\sigma}^*}{G} + \frac{\sigma^*}{\eta} \quad (27)$$

or rearranging:

$$\frac{\gamma^*}{G\sigma^*} = 1 + \frac{G}{i\omega\eta} \quad (28)$$

The ratio of stress to the strain is the complex modulus $G^*(\omega)$, therefore:

$$\frac{G}{G^*(\omega)} = 1 + \frac{1}{i\omega\tau_m} \quad (29)$$

which can further be rearranged into:

$$G^*(\omega) = G \frac{i\omega\tau_m}{1 + i\omega\tau_m} \quad (30)$$

This expression describes the variation of the complex modulus with frequency for a Maxwell model. It is normal to separate the real and imaginary components of this expression. This is achieved by multiplying through by $(1 - i\omega\tau_m)$:

$$G^*(\omega) = G'(\omega) + iG''(\omega) = G \frac{(\omega\tau_m)^2}{1 + (\omega\tau_m)^2} + iG \frac{\omega\tau_m}{1 + (\omega\tau_m)^2} \quad (31)$$

where $G'(\omega)$ is called the storage modulus and $G''(\omega)$ the loss modulus:

$$G'(\omega) = G \frac{(\omega\tau_m)^2}{1 + (\omega\tau_m)^2} \quad (32)$$

$$G''(\omega) = G \frac{\omega\tau_m}{1 + (\omega\tau_m)^2} \quad (33)$$

and τ_m is the characteristic decay time of the stress when the rapid strain is applied to the sample and is given by the ratio of viscosity (η) to the shear modulus:

$$\tau_m = G/\eta \quad (34)$$

It should be noted that storage and loss moduli do not represent directly the energy that is stored or dissipated. They simply represent the functions of the applied frequency and represent an alternative description for the system:

$$G'(\omega) = G^*(\omega)\cos(\delta) \quad (35)$$

$$G''(\omega) = G^*(\omega)\sin(\delta) \quad (36)$$

Schematically storage and loss moduli can be represented as shown on Figure 13.

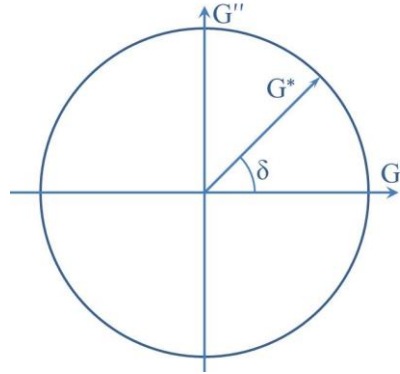


Figure 13: Schematic representation of storage (G') and loss (G'') moduli and phase angle (δ)

As for the energy, stored and dissipated (lost) energies can be calculated as follows:

$$E^s = \frac{G'(\omega)\gamma_0^2}{4} \quad (37)$$

$$E^l = \pi G''(\omega)\gamma_0^2 \quad (38)$$

Correspondingly:

$$\frac{E^l}{E^s} = \frac{4\pi}{\omega\tau_m} \quad (39)$$

Consequently at the crossover point, where G' and G'' are equal and $\omega\tau_m = 1$ only 8% of the work done per unit volume is recoverable as elastically stored energy, the remaining 92% being dissipated.^[63]

The described formulae are derived based on the Maxwell model, which is most appropriate for describing the response of materials to an applied strain as is the case in this work. However, basically the same ideas apply to a sum of Kelvin models that are more appropriately used in controlled-stress experiments.

2.7.4. Viscoelasticity - Microstructural Approach

The microstructural approach to linear viscoelasticity will be only shortly described here, due to its limited significance for the considered work.

If the experiments are conducted at sufficiently low stress or strain values and the microstructure is not perturbed, it can be assumed that the response is characteristic

for the microstructure in quiescent conditions. In this case the convective motion is less than Brownian motion. The ratio of these terms, as mentioned above, is the Péclet number and in this case is less than unity. ($P_e < 1$)

To observe the linear viscoelasticity $De \approx 1$ condition should also be met.

Such experiments allow the comparison and prediction of the response of the material to a wide range of linear viscoelastic experiments, thus allowing us to obtain information on the various properties of the materials. Secondly, it is an indication of the state of matter in quiescent conditions as it can identify whether a material is solid- or liquid-like in nature and provide subtle distinction in the phase behavior. The microstructural approach, which describes the rheological properties in terms of the spatial arrangement of particles and molecules, is complementary to the phenomenological approach.

3. Measurement Methods

3.1. Dynamic Light Scattering

Dynamic light scattering (DLS), also referred as photon correlation spectroscopy relies on measuring scattered light fluctuations over time, caused by Brownian motion of particles, as a result of thermal fluctuations of the solvent molecules.^[64] According to the approximations in Rayleigh scattering, the intensity of the scattering light is proportional to d^6 (particle diameter) and inversely proportional to λ^4 (wavelength of incident light).^[65] Fluctuations in the scattered light frequency may be seen as a result of the Doppler Effect whether the moving particle is approaching or receding from the detector.^[66] Alternatively, fluctuations can be viewed as the result of constructive and destructive interference of scattered light, as the particles move over time.^[65] An autocorrelation function is then used to analyze the intensity fluctuations over short time intervals and determine the translational diffusion coefficient D . Particle diameter is determined by Stokes-Einstein equation:

$$R_h = \frac{k_B T}{6\pi\eta D}$$

where k_B is the Boltzmann constant, T is the temperature and η is viscosity of the solvent.

3.2. Gas-Chromatography

Gas chromatography represents a method for the separation and qualitative and quantitative analysis of volatile substances. The mobile phase is a gas, while the stationary phase is a solid or gel-like polymeric material. A gas-chromatograph is composed of the following basic units: the injector, carrier gas supply, the separation column which is placed in a temperature controlled oven, the detector and the evaluation system (e.g. computer).

The sample is usually injected into an evaporation chamber using an injector. In here fast evaporation occurs at high temperature. The vapor is further transported by a carrier gas, usually helium, through the separation column, filled with stationary phase. Based on the physical and chemical properties and their interactions with the stationary phase the different substances travel at different rates and correspondingly their retention times in the column are different. As they exit the

column, they are detected by a detector. The retention times are not only dependent on the physical and chemical properties of the analyte and the stationary phase, but also on the temperature, the rate of the carrier gas and other parameters.

After exiting the column, the substance detection is often performed using a flame ionization detector (FID), which is particularly convenient for the detection of organic substances. In such systems the compounds are burned in a hydrogen flame, which causes the formation of ions. The generation of ions is proportional to the concentration of organic compounds in the gas stream. Hydrocarbons generally have molar response factors that are equal to the number of carbon atoms in their molecular structure, while oxygenates and other species that contain heteroatoms tend to have a lower response factor. The formed ions cause an electric current flow between the two electrodes above the flame, which can be measured and used for data evaluation.

Figure 14 represents a typical chromatogram for an acrylate copolymerization reaction mixture. The above mentioned retention time (R_t) represent the time given on the x axis and it is the time that is necessary for the particular component to travel through the column from injector to detector. The concentrations of the substances are calculated using the peak areas.

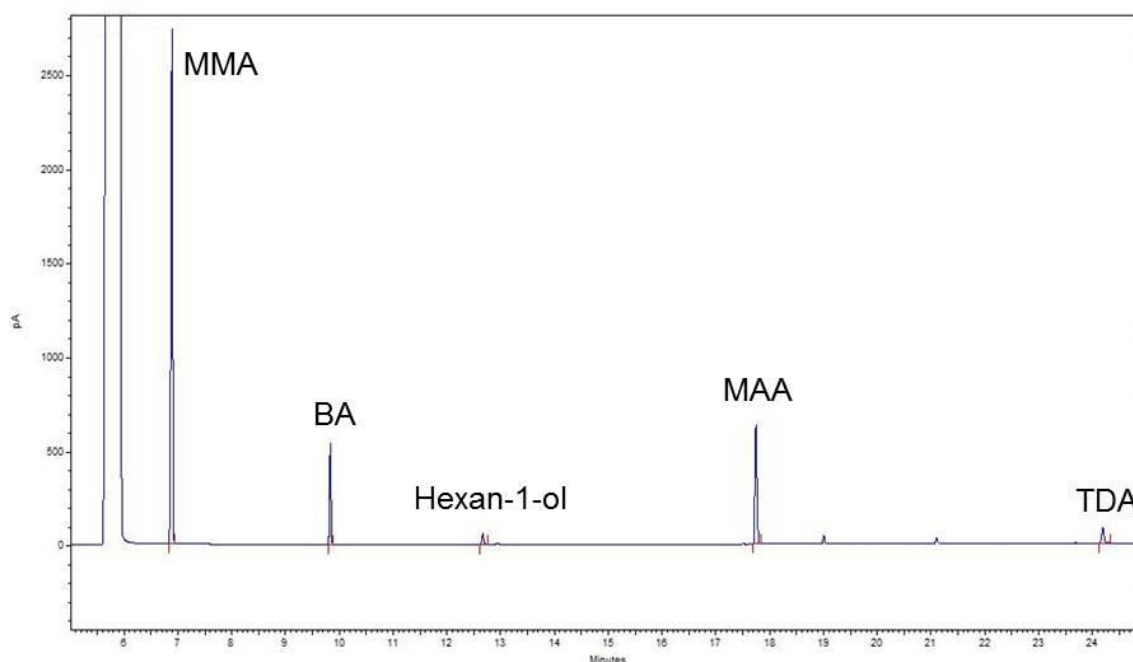


Figure 14: Sample chromatogram for an acrylate copolymerization reaction mixture.

In order to avoid systematic errors (mostly due to errors in the injection and evaporation systems) the internal standard method is frequently used. In this approach a defined amount of a nonreactive substance is added to the reaction mixture and is used as a reference for calculations. If the signal from the internal standard is changed, corresponding recalculations can be done to determine the concentration of other compounds in the system.

As it is described in the experimental section, in our experiments hexan-1-ol was used as an internal standard. Calibration was also performed employing hexan-1-ol as an internal standard. The correction factor is calculated according to equation (40):

$$f = \frac{Area_{IS} \times c_{analyte}}{Area_{Analyte} \times c_{IS}} \quad (40)$$

which allows the calculation of monomers in the analyzed mixture according to equation (41):

$$c_{analyte} = \frac{Area_{analyte} \times c_{IS}}{f \times Area_{IS}} \quad (41)$$

3.3. Rheological Investigations

For the investigation of the rheological behavior, oscillatory experiments were employed predominantly throughout this work. The theoretical background for these investigations is given in the chapter 2.7. Different geometries of the measuring systems are available; however the cone plate configuration (Figure 15) of the measuring system was used in all experiments, since this configuration fulfills the following basic requirements:

- Shear stress and shear rate are constant throughout the fluid sample.
- The layer of the liquid in the measuring gap is thin, which allows constant temperatures and rapid temperature stabilization.
- Small sample amounts (usually less than 1 ml) are sufficient for the observation.

The cone plate configuration of the measuring system is schematically presented in Figure 15. Shear stress and shear rate are constant due to the fact that both the gap width between the cone and plate and the linear velocity at any point on the cone are proportional to the radial distance in such setup. For the experimental setup employed throughout this work oscillatory strain is applied on the cone, while the plate is the passive element of the system. Furthermore, the controlled deformation mode was used as opposed to controlled stress mode, i.e. the amplitude of the oscillations were defined instead of the maximum stress.

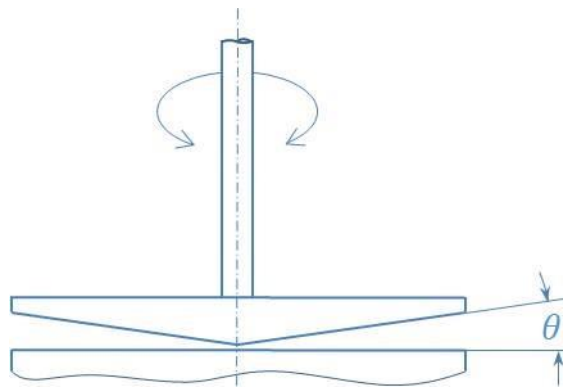


Figure 15: schematic representation of cone-plate measuring system for rheological investigations.

It is extremely important, especially for the physically cross-linked systems investigated throughout these work, to observe the rheological properties without damaging their structure, e.g. maintaining the integrity of the physically cross-linked network throughout the measurement. Amplitude sweep experiments were conducted to determine the linear viscoelasticity region (LVR) for the investigated samples. In these experiments the frequency of oscillation is fixed to a constant value and the amplitude of deformation is gradually increased. Storage and loss moduli of the sample are constant in the LVR and deviation from these values occurs only above a certain deformation, characteristic for the particular sample. Within the LVR the applied strain is below the value at which the destruction of the structure of the sample occurs. If this strain values are exceeded, the elastic structure is destroyed. The graphs, representing the storage and loss moduli within the linear viscoelasticity region and the deviation from the corresponding behavior are shown in Figure 16.

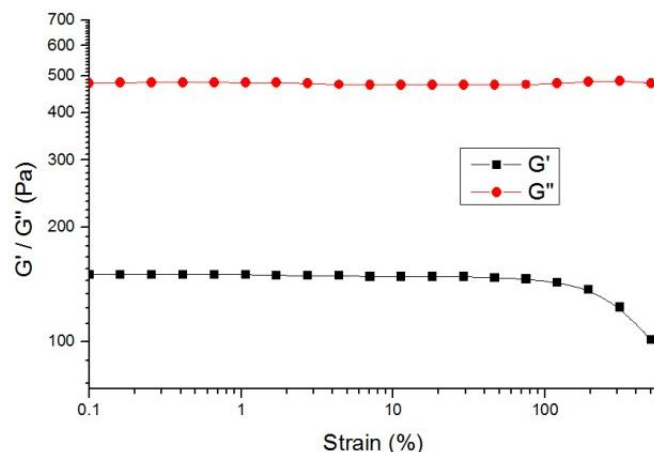


Figure 16: Typical example for amplitude-sweep experiments, employed to determine the linear viscoelasticity region for the systems. As shown in the graph, above certain strain values deviations from linear behavior occurs.

Frequency sweep experiments are usually conducted at amplitudes of applied strain within the LVR. These experiments reveal the frequency dependency of the mechanical properties of a given sample (e.g. storage (G') and loss (G'') moduli and damping factor, $\tan \delta = G''/G'$). These experiments are also employed to determine the crossover frequency, e.g. the frequency at which the G' and G'' are equal and the damping factor equals to 1 ($\tan \delta = 1$). These experiments are used to assess the ability of the material to relax from the stress, caused by applied strain. Stress relaxation is directly related to the freedom of molecular rearrangement of the system.^[63] An example of the frequency-sweep experiment is shown in Figure 17.

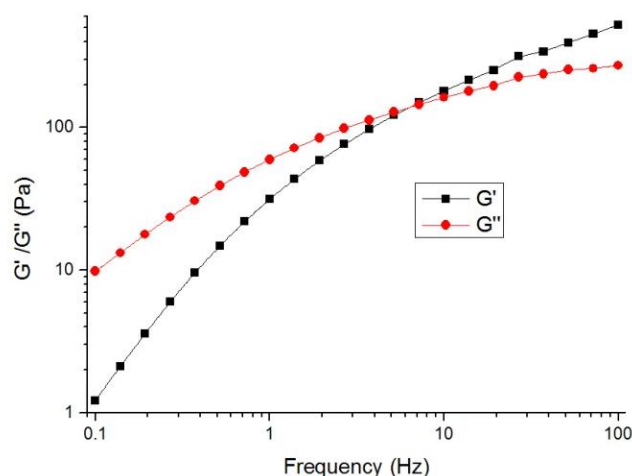


Figure 17: Typical example of frequency-sweep measurements for the investigated HASE solutions. Frequency response and crossover frequency values enable the evaluation of the relaxation behavior of the systems.

3.4. Wet Tack Behavior of the Adhesives

The wet tack of the HASE based labelling adhesives were investigated according to the procedure described in chapter 8.11. The schematic representation of the measuring systems is provided in Figure 18.

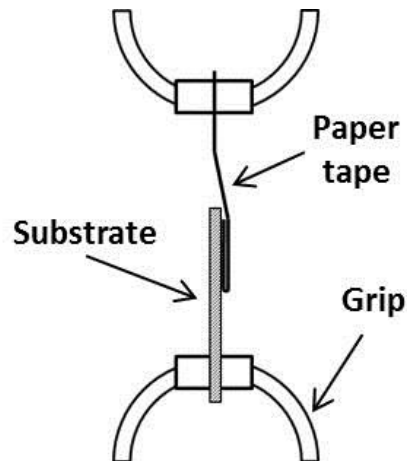


Figure 18: Schematic representation of the measuring system for the wet-tack behavior of the HASE based labelling adhesive.

The tensile strength test machine (Zwick Z 2.5) was employed to measure the peel strength at 180° peeling angle. 25 mm wide labelling paper was used for test as described in experimental section.

4. Facile Miniemulsion-analogous Synthesis of Hydrophobically Modified Alkali Soluble Latexes

4.1. Objective

Even though the HASE systems are well known and widely used in a variety of industrial applications, till now classical O/W emulsion polymerization is considered to be the only viable and industrialized method for their preparation.^[55, 59] Despite the enormous industrial relevance of this technique, it does not allow the direct copolymerization of highly hydrophobic monomers due to its diffusion driven latex growth mechanism (chapter 2.5), because significant monomer solubility in the aqueous phase is required.^[37] On the contrary miniemulsion polymerization works best with components of negligible water solubility, which is a consequence of the so-called nanoreactor concept based on suppressed interparticle diffusion.^[32] In this chapter we describe a novel approach to HASE synthesis, demonstrate its versatility and describe the advantages over the existing techniques.

Various factors, influencing the synthetic routes, properties and behavior of the systems at different stages, were investigated and will be presented in detail. Several points have been emphasized throughout the work, which will be stepwise discussed in upcoming chapters. These points, which involve: the synthesis and colloidal stability, neutralization behavior, influence of the composition on the reaction course as well as on the final mechanical properties of the systems, influence of additives on the rheological behavior, adhesive properties *etc.* evaluated in the a systematic manner, will represent and emphasize the advantages of the miniemulsion analogous approach and demonstrate possible applications for the obtained systems. The applicability of the obtained HASE systems as adhesive materials is one of the major targets of the conducted work and corresponding experimental results will be described and correlated with the rheological behavior of the systems.

4.2. Basic Outline

As it is mentioned above, emulsion polymerization represents the widely accepted method for the synthesis of the hydrophobically modified alkali soluble latexes.

Consequently, the obtained suspensions are commonly referred as alkali soluble emulsions. In the chapter 2.6.2.1 we refer the here employed technique as “mini-emulsion-analogous” polymerization. As it will be described in the experimental part, the synthetic procedure used for the latexes is basically the same as in case of mini-emulsion systems.^[30] This avoids above mentioned restrictions in terms of monomer choice. However, due to the high content of highly hydrophilic monomers here investigated systems cannot be considered as classical mini-emulsions. As it will be represented throughout the work (chapter 4.2.1), considered mini-emulsion-analogous approach enables the direct introduction of highly hydrophobic monomers in polyelectrolyte chains in a water-based system, without using organic solvents (volatile organic compounds (VOC)) or employing specially designed complex monomers or phase transfer agents^[67, 68] (such as cyclodextrin), thus enabling an easy tuning of the rheological behavior with a one-step synthetic procedure.

4.2.1. Synthesis of the Alkali Soluble Latexes and Their Stability

Most HASE systems represent random copolymers of ethyl acrylate (EA), methacrylic acid (MAA) and a small amount of hydrophobic modifier.^[59, 69, 70] EA provides a good balance between hydrophobicity and glass transition temperature.^[53] In classical HASE systems the MAA content is usually close to 50 mol%. The structure of the hydrophobic modifier, also referred as the macromonomer is provided in the chapter 2.6.2.1. Besides the complex structure of the described macromonomer, another disadvantage of such systems can be pointed out. Namely, substitution of the widely used EA in HASE systems is highly desirable due to its low odor threshold. Several works have been published searching for the solution for this latter issue. *Verbrugge et al.* have tested various monomers, such as styrene, methyl methacrylate (MMA), butyl acrylate (BA), 2-ethyl hexyl acrylate (2-EHA) and their mixtures with various ratios in emulsion polymerization together with MAA and evaluated the dissolution and viscosity behavior of the obtained alkali soluble latexes.^[51] More recently the synthesis of ASE and HASE systems, employing BA, MMA, 2-EHA and the mixtures thereof as substituents for EA have been investigated by *Moraes et al.* Emulsion and mini-emulsion polymerization techniques were employed in these investigations.^[53] However, the mini-emulsion approach was found to be unsuccessful in these

particular experiments, which was explained by the strong copolymer composition drift during the polymerization.

Since the hydrophobicities and the glass transition temperatures of the employed monomers in HASE systems are important factors, defining its final behavior, in this work it was considered reasonable to substitute EA with a combination of BA and MMA. BA plays a dual role in the described miniemulsion-analogous systems. It is employed to decrease the glass transition temperature and at the same time to maintain the droplet stability due to its relatively high hydrophobicity. The BA content also has a significant effect on the average particle sizes and particle size distribution of the polymers, which will be described below in more detail.

Since here investigated systems do not represent classical miniemulsions due to the high content of water soluble methacrylic acid, the stability of the systems during polymerization is of major significance at the initial stage of the investigations and several parameters should be considered. Some of the important parameters, affecting the stability and particle size distribution of obtained latexes such as influence of the initiator and the ultrahydrophobe, as well as the influence of the content and type of employed surfactant and monomer ratio, are discussed in the upcoming chapters.

4.2.1.1. Choice of Initiator and Ultrahydrophobe

The concept of copolymerizable costabilizers in miniemulsion systems have been reported in several publications.^[62, 71] As already described above, the introduction of copolymerizable ultrahydrophobes in the described systems represents one of the main advantages of the described approach. However, at the initial steps it is important to investigate the stability of the considered heterophase systems in the presence of different copolymerizable, as well as non-polymerizable ultrahydrophobes. The proper choice of the initiator (oil- or water-soluble) has also immense importance for the stability of the systems. Not only the difference at the nucleation stage, but also handling during the synthesis (especially at industrial scale), should be taken into account. Oil-soluble initiators, which are dissolved in the oil phase prior to miniemulsification require better control in terms of heat distribution and transfer upon application of high shear force, while water soluble initiators can be added to the system after miniemulsification.

Different combinations of initiators and ultrahydrophobes were employed for the investigation of stability of the systems. The ratio of other monomers in these experiments were kept constant at MMA/BA/MAA=25/35/40 wt%. The surfactant concentration was also varied and its influence on the system stability and particle sizes was investigated.

The oil-soluble initiators, V-59 and AIBN, were found not suitable for this polymerization and resulted in latexes with a broad and multimodal particle size distribution and high content of coagulate in combination with all types of tested ultrahydrophobes and at any tested surfactant concentration. It can be speculated that an initiation from the inside of the droplet leads to a strong composition drift because the water-soluble monomers predominantly would react at the later stages of the polymerization at the droplet water interface. This process can also lead to particle bridging and colloidal destabilization of the whole system.

On the other hand, water-soluble KPS turned out to be a suitable initiator for the investigated systems. Stable latexes of lower particle size and broad, but monomodal particle size distributions were obtained (see Table 2). It is expected that the dissolved hydrophilic monomers start to polymerize in the water phase first. The accompanied decreased solubility of the growing oligomer/polymer chains can then lead to their precipitation onto the droplets interface accompanied by quick radical entry and continued polymerization inside the forming latex particles. At the same time secondary homogeneous nucleation is also possible, which should lead to the formation of particles representing mostly MAA and MMA copolymers and could explain the broad particle size distribution. However, the complete solubility of the obtained HASE systems at elevated pH in combination with the excellent reproducibility and easy rheology adjustment (as described in the chapter 5) do support the presence and importance of the droplet nucleation mechanism, which is characteristic for miniemulsion system.

Various redox initiators, such as: *tert*-butyl hydroperoxide with ascorbic acid (AsAc) or sodium formaldehyde sulfoxylate (SFS) systems were also tested. However, fast coagulation and low conversion (< 50%) proved these systems to be not suitable for the polymerization.

Different types of ultrahydrophobes showed also noticeable influence on the miniemulsion stability. Hexadecane, despite being a common ultrahydrophobe in classical miniemulsions, turned out to be non-suitable for the system and unstable latexes with large particle size distributions and high contents of coagulate were obtained regardless of which type of initiator was used. However, slightly less hydrophobic TDA, hexadecanoic acid or hexadecyl alcohol produced monomodal latexes with small particle sizes when used in combination with the water soluble KPS initiator (particle sizes vs. surfactant concentration are represented in Figure 19). The plausible explanation could be the incompatibility of the non-polymerizable and extremely hydrophobic hexadecane with the monomers and/or the growing polymer chains, leading to destabilization and destruction of the miniemulsion. The incompatibility is likely to be caused by the high content of polar acid functionalities in the systems. It should be noted that hydrophobes, like TDA, hexadecanoic acid or hexadecyl alcohol can also act as cosurfactants and that the increased stability of the systems in their presence is not based solely on the diffusional stability.^[72, 73] On the other hand the influence of the above suggested possible incompatibility is less pronounced in case of listed ultrahydrophobes due to their higher likelihood of being closer to the droplet/water interface, (due to their slightly amphiphilic nature), and not being completely immersed in the oil phase as it is the case with the highly hydrophobic hexadecane. However, despite their multiple interaction possibilities there were no significant differences in the particle size of the latexes observed in the investigated systems. It should also be noted that colloidally stable dispersions with comparably small particle sizes are obtained at relatively low concentrations of surfactant, as it is characteristic for most miniemulsion systems.

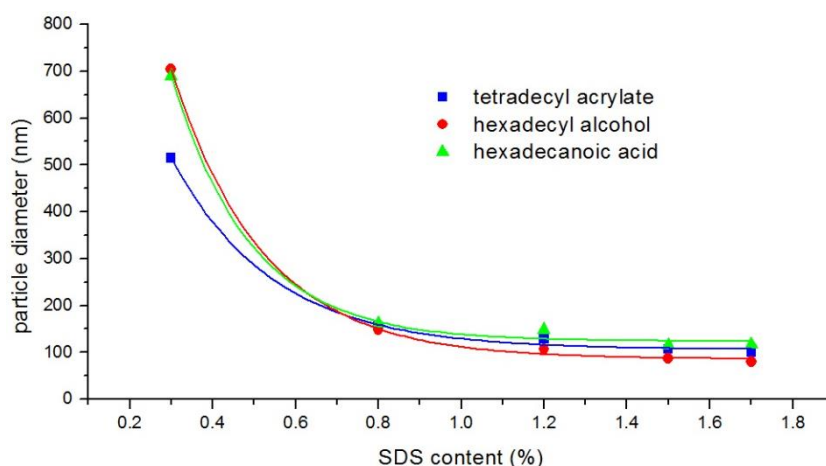


Figure 19: Z-average particle diameter vs. surfactant to total monomer ratio (monomer: MMA/BA/MAA=25/35/40) in the systems with different ultrahydrophobes. 2 wt% ultrahydrophobe used for each sample.

As it can be seen from the Figure 19, above a certain threshold (1.2 wt.% to organic phase) content of the surfactant the particles size dependence on the surfactant concentration becomes less pronounced, e.g. stable droplets are obtained and additional amount of surfactant contributes to reduction of surface tension, which has less influence on the particle size distribution.

A summary of the experimental results for the various combinations of initiators and ultrahydrophobes with different amount of surfactants is provided in Table 1.

Table 1: List of experiments with different ultrahydrophobes, initiators and different concentrations of surfactant (wt% to monomer). The monomer composition was kept constant (MMA/BA/MAA=25/35/40 wt%).

Initiator	Ultrahydrophobe	Surfactant (SDS) conc.	Result (particle size)*
AIBN	Hexadecane	0.3%	Coagulate (\approx 220 nm)
AIBN	Hexadecane	0.6%	Coagulate (\approx 180 nm)
AIBN	Hexadecane	1.2%	Coagulate (\approx 170 nm)
AIBN	Hexadecane	1.5%	Coagulate (\approx 170 nm)
AIBN	Hexadecane	1.7%	Coagulate (\approx 170 nm)
V-59	Hexadecane	0.3%	Coagulate (\approx 300 nm)
V-59	Hexadecane	0.6%	Coagulate (\approx 500 nm)
V-59	Hexadecane	1.2%	Coagulate (\approx 600 nm)
V-59	Hexadecane	1.5%	Coagulate (\approx 500 nm)
V-59	Hexadecane	1.7%	Coagulate (\approx 400 nm)
KPS	Hexadecane	0.3%	Complete coagulation

KPS	Hexadecane	0.6%	Complete coagulation
KPS	Hexadecane	1.2%	Coagulate (≈ 100 nm)
KPS	Hexadecane	1.5%	Coagulate (≈ 100 nm)
KPS	Hexadecane	1.7%	Coagulate (≈ 140 nm)
KPS	Hexadecanoic acid	0.3%	No coagulate (≈ 700 nm)
KPS	Hexadecanoic acid	0.8%	No coagulate (≈ 160 nm)
KPS	Hexadecanoic acid	1.2%	No coagulate (≈ 150 nm)
KPS	Hexadecanoic acid	1.5%	No coagulate (≈ 120 nm)
KPS	Hexadecanoic acid	1.7%	No coagulate (≈ 120 nm)
KPS	Hexadecanol	0.3%	No coagulate (≈ 700 nm)
KPS	Hexadecanol	0.8%	No coagulate (≈ 150 nm)
KPS	Hexadecanol	1.2%	No coagulate (≈ 110 nm)
KPS	Hexadecanol	1.5%	No coagulate (≈ 85 nm)
KPS	Hexadecanol	1.7%	No coagulate (≈ 80 nm)
KPS	Tetradecyl acrylate	0.3%	No coagulate (≈ 600 nm)
KPS	Tetradecyl acrylate	0.8%	No coagulate (≈ 160 nm)
KPS	Tetradecyl acrylate	1.2%	No coagulate (≈ 130 nm)
KPS	Tetradecyl acrylate	1.5%	No coagulate (≈ 110 nm)
KPS	Tetradecyl acrylate	1.7%	No coagulate (≈ 100 nm)
V-59	Tetradecyl acrylate	0.3%	Coagulate (>2500 nm)
V-59	Tetradecyl acrylate	0.8%	Coagulate (>2500 nm)
V-59	Tetradecyl acrylate	1.2%	Coagulate (>2500 nm)
V-59	Tetradecyl acrylate	1.5%	Coagulate (>2500 nm)
V-59	Tetradecyl acrylate	1.7%	Coagulate (>2500 nm)

* - the description "Coagulate" describes systems where the coagulation occurs during or shortly after (several hours) the polymerization reaction

4.2.1.2. Influence of the Composition on the Particle Size Distribution

As already mentioned (chapter 4.2.1), in the investigated systems the BA is not only employed for the adjustment of the glass transition temperature, but is also highly important for maintaining the miniemulsion stability due to its hydrophobicity and hence can influence the average particle diameter. Figure 20 represents the effect of BA and MAA content on the particle size. One can notice that increased hydrophobicity (high BA and low MAA content) leads to the formation of particles with smaller average diameter, reaching plateau values of approximately 100 nm. (Corresponding numerical values of Z-average diameter and polydispersity are

provided in Table 2). It should be noted that the ratio of hydrophobic and hydrophilic monomers also affects the particle size distribution. The latex with the highest content of MAA and the lowest amount of BA (L-5, MAA/BA=40/10 weight ratio) shows a much wider particle size distribution (PDI = 0.141) compared to the samples with the lower amount of MAA and higher content of BA (e.g. sample L-12, MAA/BA=20/30 weight ratio. PDI = 0.046). This can be explained by an increased probability of secondary (homogenous) nucleation in the former case.

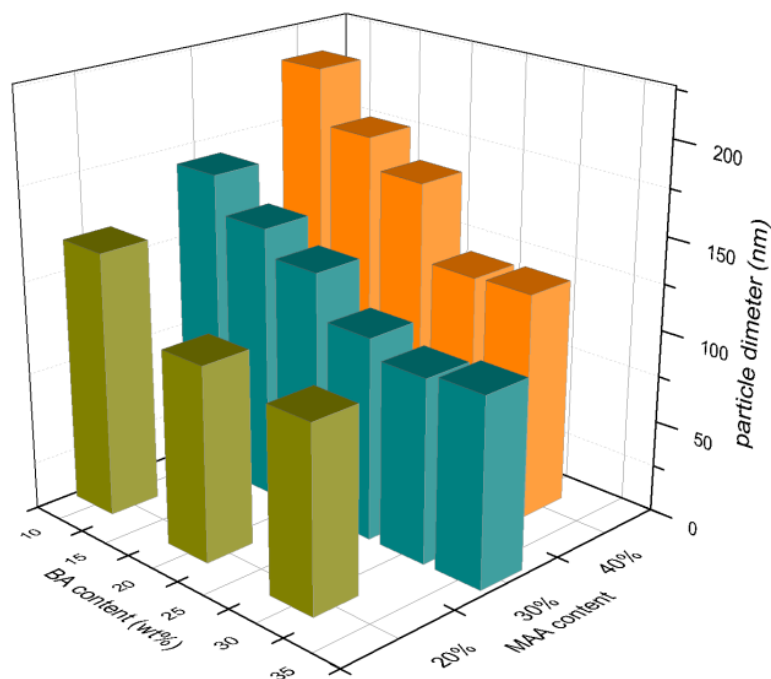


Figure 20: Average particle diameter as a function of BA and MAA content, showing decreasing values upon increased hydrophobicity. Numerical values can also be found in Table 2.

It can be speculated that BA also partially contributes to reduced particle sizes and lower PDI by its high propagation rate. Indeed a slightly higher overall polymerization rate was observed for the BA rich systems according to the monitoring of the solid content. In this context the contribution from the homogenous nucleation of BA is unlikely due to its high partitioning coefficients (chapter 4.2.4). On the other hand, it is long known that the presence of the pre-dissolved polymer in the miniemulsion provides additional stabilization and leads to smaller average particle sizes.^[74] A quick build-up of high molecular weight species within the droplets could therefore lead to an additional stabilizing effect, although the presence or significance of such a contribution is hard (or impossible) to determine.

Table 2: Composition and basic characteristics of the latexes described in the chapter 4.2.1.2.

Sample ID	MMA [wt%]	BA [wt%]	MAA [wt%]	Particle Diameter [nm] (Pdl)	Tg* [°C]
L-1	30	30	40	122 (0.070)	60
L-2	35	25	40	121 (0.063)	71
L-3	40	20	40	163 (0.065)	84
L-4	45	15	40	180 (0.122)	96
L-5	50	10	40	210 (0.141)	111
L-6	35	35	30	102 (0.045)	45
L-7	40	30	30	99 (0.031)	56
L-8	45	25	30	109 (0.045)	67
L-9	50	20	30	133 (0.045)	79
L-10	55	15	30	147 (0.055)	92
L-11	60	10	30	167 (0.029)	106
L-12	50	30	20	100 (0.046)	52
L-13	60	20	20	105 (0.049)	75
L-14	70	10	20	143 (0.021)	101

4.2.1.3. Influence of Solid Content on the Particle Size Distribution

Even though most of investigated latexes have 20% solid content, as the adhesion tests show in the later chapters (see chapter 7) it is crucially important to prepare systems with much higher solid contents. High solid content is generally important for various applications in coating and adhesives. Altered solid content changes the character of intermolecular interactions and has strong influence on the system's rheology. Increased solid contents can be achieved via water removal after polymerization or direct synthesis of high solid content latexes via corresponding changes in the initial recipe.

Low solid content latexes are associated not only with the additional procedures for water removal, but also with destabilization of the systems during these procedures or high shipping costs.^[75]

For the here investigated systems several different approaches were employed for the preparation of latexes with high solid content. Latexes, prepared with standard recipes described in the chapter 8.1 at a solid content of 20% were found unstable upon water removal and coagulation occurred. As an alternative approach, samples with solid content of 25%, 30% and 35% were prepared according to the standard recipe (chapter 8.1) where the content of the employed SDS were maintained constant (1,7 wt.% to organic phase). The results are provided in the Table 3.

Table 3: Influence of solid content on the stability and particle size distribution of the latexes in the presence of the SDS as surfactant.*

Solid Content (%)	Modality	Particle Diameter (nm)	Pdl	Stability
25	Monomodal	159	0.093	Stable
30	Monomodal	177	0.109	Stable
35	Monomodal	207	0.196	Partial coagulation
40	-	-	-	Phase separation

* MMA/BA/MAA=55/15/30. Amount of the SDS = 1.7 wt.% to monomer.

As it is shown in Table 3, increasing the solid content leads to not only to an increased average particle size but also to increased polydispersity index or even unstable systems, e.g. the systems with 35 and 40% solid content partially or completely coagulate during the polymerization.

In order to improve the colloidal stability at 35% solid content, a set of experiments with increased surfactant concentration was performed. Systems with 35% solid content and otherwise same composition have been prepared with several concentrations of the SDS. Results are summarized in the Table 4.

Table 4: Influence of the amount of the surfactant (SDS) on the stability of the latexes (MMA/BA/MAA=55/15/30) with 35% solid content.

SDS content (to monomer, %)	Particle Diameter (nm)	Pdl	Stability
2.5	-	-	Coagulation
3.35	-	-	Coagulation

As shown in the table, higher content of the SDS also led to formation of unstable systems and coagulation occurred.

In another set of experiments the surfactant with a much higher hydrophilic-lipophilic balance (HLB) and low CMC (0.007 g/100g as compared to the CMC of SDS 0.23616 g/100g), Dowfax-2A1 (see chapter 8.12 for exact structure) was employed for the stabilization of the high solid content systems.

Table 5: Influence of solid content on the stability and particle size distribution of the latexes in the presence of Dowfax 2A1 as a surfactant. (MMA/BA/MAA=55/15/30). Content of the Dowfax 2A1 = 1.7 wt.% to monomer.

Solid Content (%)	Modality	Particle Diameter (nm)	Pdl	Stability
30	Monomodal	187	0.049	Stable
35	Monomodal	193	0.165	Stable
40	Bimodal	157 / 496	0.303	Partial coagulation

The obtained results show that increased solid content leads to bigger average particle sizes and wider particle size distributions, which is expected considering the strong deviation from classical miniemulsion systems.

Besides, it is important to note that increasing the surfactant concentration can lead to the destabilization and phase separation of the system (see Table 4) due to possible change of the monomer distribution between the oil and water phases.

Also it should be noted that the surfactant with higher HLB showed slightly improved stability for the systems. As it can be seen from the data provided in Table 3 and Table 5, analogous systems prepared in the presence of the Dowfax 2A1 as a surfactant, showed slightly lower average particle sizes and polydispersities. Besides, despite the bimodality of the particle size distribution of the latexes with 40% solid content, it was found possible to obtain the latexes which do not phase separate or coagulate during synthesis and can be stored without significant coagulations for several weeks.

Throughout the work most samples are prepared with 20% solid content in order to study the factors influencing the rheological behavior. In these cases SDS will be employed as surfactant. Dowfax 2A1 will be used only in specific cases, where the

high solid content is required. This is mostly the case for the preparation of final adhesive materials and their testing as labeling adhesives on different substrates.

4.2.2. Molecular Mass Distributions of the Synthesized Polymers

The molecular masses of the obtained systems have a strong influence on the mechanical properties of the obtained systems after neutralization, enabling the formation of systems ranging from almost solid gels to highly fluid polymer solutions. The dependence of mechanical and rheological properties on the molecular weight of the synthesized polymers will be discussed separately in the chapter 5.1.1.

In our experiments molecular masses of the synthesized polymers were regulated using different amounts of the chain transfer (CTA) agent 1-dodecanthiol. The dependence of the molecular masses on the amount of the employed chain transfer agent is provided in the Table 6.

Table 6: Apparent molecular masses and molecular mass distributions of the samples with different contents of the chain transfer agent (1-dodecanthiol).

Sample	M_w (g/mole)	M_n (g/mole)	Polydispersity
No CTA	$99 \cdot 10^4$	$6.6 \cdot 10^3$	15.1
0.3 wt.% CTA	$59 \cdot 10^3$	$9.9 \cdot 10^3$	6.0
0.5 wt.% CTA	$44 \cdot 10^3$	$8.5 \cdot 10^3$	5.0
0.8 wt.% CTA	$39 \cdot 10^3$	$7.5 \cdot 10^3$	4.0

The corresponding gel permeating chromatography (GPC) curves are provided in Figure 21.

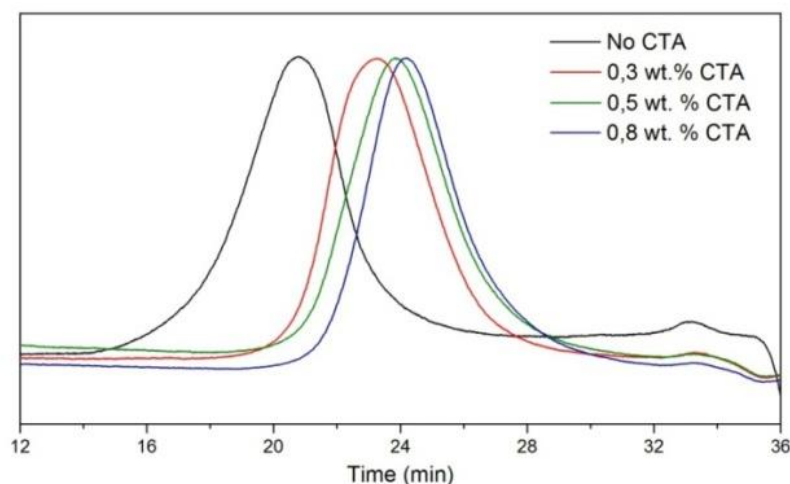


Figure 21: GPC curves of the synthesized polymers with different molecular masses. By increasing amount of CTA the molecular weight can be gradually reduced.

According to the GPC measurements results, the synthesized polymers show broad molecular mass distribution, which can be explained by a pronounced composition drift during the copolymerization reaction related to a strong difference of the propagation rates of the monomers employed in the experiments. Further details regarding the investigation of composition drift and copolymerization behavior are provided in chapter 4.2.4.

As it will be described in the experimental part, 0.8 wt.% chain transfer agent was used in most cases to enable reproducible and reliable rheology measurements. However, it should be noted that the molecular weight affects significantly the mechanical and rheological properties and can be decisive factor for particular applications. Therefore, as mentioned, rheological characterization of the systems with different molecular weights will also be provided.

4.2.3. Neutralization Behavior of the Latexes

As mentioned in the introduction, the viscosity of HASE systems increases drastically when the acid groups become deprotonated upon increasing the pH value. This is caused by the formation of a water-soluble polyelectrolyte system with strong electrostatic repulsion between charged polymer chains, while the hydrophobic moieties act as associative physical cross-linking sites. Due to the presence of this two opposing interactions, a proper hydrophobic/hydrophilic balance and an even distribution of repeating units is of crucial importance. An improper

hydrophobic/hydrophilic balance and a composition drift can lead to poor solubility and phase separation in neutralized polymer solutions (Figure 22). The phase separation is caused by a strong composition drift and high content of hydrophobic moieties, leading to the formation of strong hydrophobic domains. These domains can be strong enough to outweigh the charge repulsion and to prevent dissolution. A composition drift leads to the formation of polymer chains with different hydrophobicity. Consequently, both soluble (transparent) and swellable (translucent) layers are observed in Figure 22. It should also be noted that the described phase separation occurs within several days and in relatively low viscosity systems. Systems with higher viscosities and high dynamic moduli values (G^* is more than approximately 50 Pa) the turbid systems do not form described two layers within several months. The neutralization behavior can reveal additional information about the homogeneity of the monomer distribution along the polymer chains and through the latex particles. A potentiometric titration represents a useful and simple tool to observe the neutralization behavior and was employed in this work. The copolymerization kinetics, as another important parameter affecting the dissolution characteristic of the alkali soluble latexes, will be also discussed in the chapter 4.2.4.

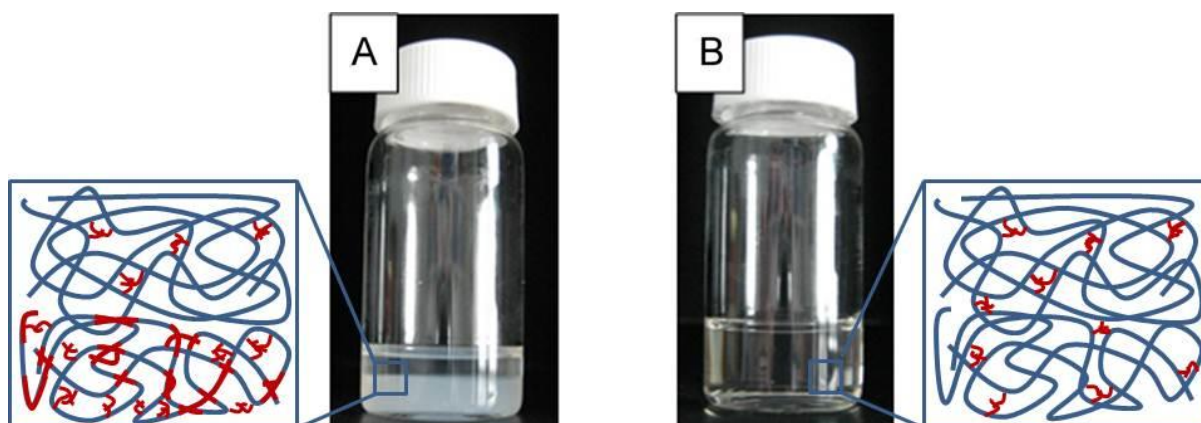


Figure 22: Polymer solutions after neutralization: (A) with strong composition drift and improper hydrophobic/hydrophilic balance (MMA/BA/MAA=20/50/30 wt%, 0.8% 1-dodecanthiol, 2 wt% TDA) and (B) with proper monomer distribution and adjusted composition (MMA/BA/MAA=55/15/30 wt%, 0.8% 1-dodecanthiol, 2 wt% TDA).

4.2.3.1. Potentiometric Titration

The neutralization behavior of polyacids depends largely on the polymer backbone charge distribution and the conformational free energy.^[76] A potentiometric titration was employed to track the electrostatic potential change during the neutralization process and to evaluate the basic structural features of the obtained systems. In

other words, the relationship between the polymer structure and the pK_a value of the acid groups of the considered polymers is employed for the indirect characterization of the system.

In this work potentiometric titration curves are given as they were recorded, pH against the amount of added alkali solution. The recalculation to the ionization degree was not performed due to the ambiguity of defining zero and complete ionization points. Table 2 provides the compositions, together with particle sizes and estimated glass transition temperatures of the synthesized latexes used for potentiometric titration experiments. It should be noted that glass transition temperature, together with hydrophobic attractive forces and hydrogen bonds, defines the above mentioned conformational free energy.

These experiments revealed two general trends: (1) latexes with lower content of acid groups exhibit higher apparent pK_a values and therefore neutralization occurs at higher pH, (2) the pK_a of the acid groups in the samples with higher acid content (40 wt%) is not sensitive to the ratio of nonionogenic monomers, while this parameter becomes clearly noticeable in the latexes with lower acid content (30 wt%). The potentiometric titration curves for these samples are provided in Figure 23(A) and Figure 23(B). Following this trend, samples with an even lower acid content of 20 wt% exhibit distinctive features; the corresponding curves are represented in Figure 23(C). Latex L-13 shows a plateau on the neutralization curve, while latex L-14 exhibits an even more peculiar sigmoidal shape.

All the characteristics of the above provided titration curves can be explained by the delicate balance between repulsive forces and conformation free energy of chains. The gradual increase of pK_a , expressed as slight slope of the titration curves, was observed for most samples and results from the gradually increased electrostatic potential of the polymer chains upon neutralization. Indeed, an increased negative charge density on the polymer chain hinders the dissociation and removal of the positively charged protons from the polymer backbone upon further neutralization.^[38] Furthermore the apparent pK_a can be lowered with a higher content of ionogenic groups, because the rising electrostatic repulsion facilitates the structural reorganization and the neutralization process, while the role of the conformational free energy is diminished. Only when the acid content is below 40 wt% and the

repulsion forces decrease the apparent pK_a values in here investigated samples become sensitive to the ratio of the nonionogenic monomers. In other words the conformational free energy becomes increasingly important, which is strongly influenced by the glass transition temperature and/or hydrophobic attractive interactions. It should also be noted that besides generally described hydrophobic interactions between the reactive ultrahydrophobes, relatively weak hydrophobic interactions arise also due to the presence of the nonionogenic monomer units in the polymer chain, e.g. BA increases the polymer hydrophobicity while the high content of MMA leads to lower hydrophobicity but higher glass transition temperature and the balance of these forces contribute to the overall conformational free energy. Consequently, the copolymerization of monomers of varying nature can be utilized as a convenient tool to adjust the apparent pK_a and the neutralization behavior of the HASE systems.

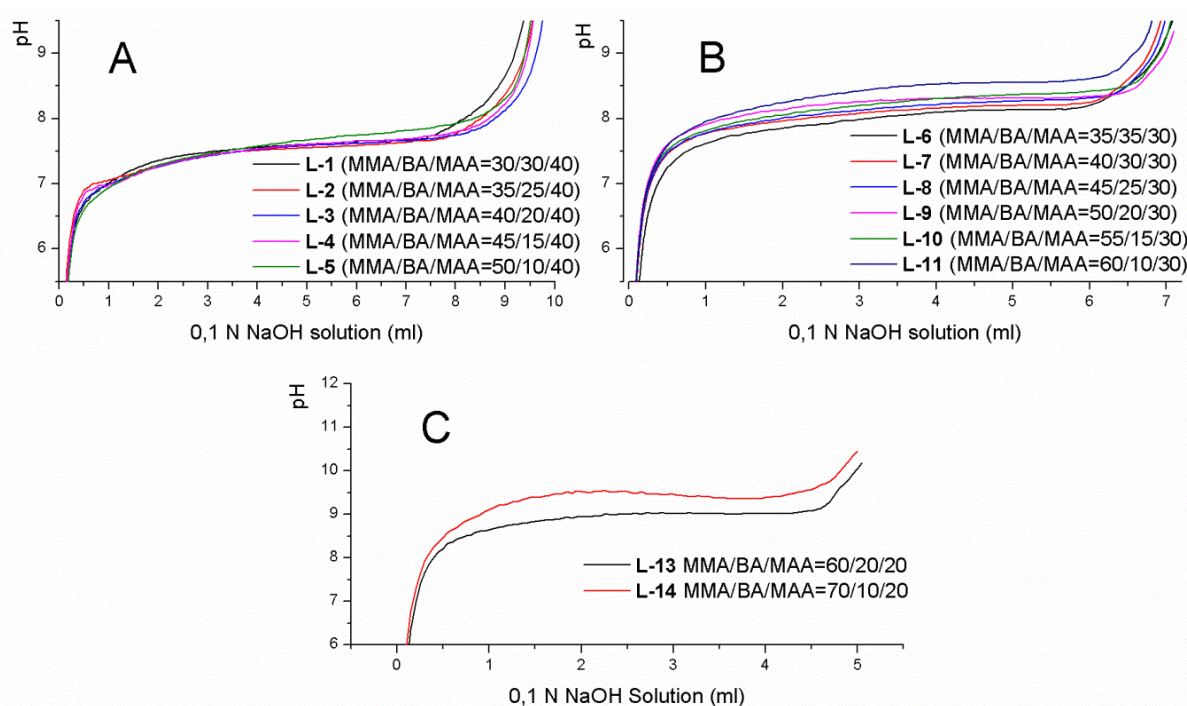


Figure 23: Potentiometric titration curves for the samples L-1 to L-14, showing the sensitivity of pK_a to the content and the ratio of nonionogenic monomers.

The described characteristics are highlighted by the unusual neutralization behavior of the HASE samples with only 20 wt% acid content. At higher MMA/BA ratio (latex L-14) a peculiar sigmoidal character of the titration curve can be observed, whereas for the latex L-13 with increased BA content the neutralization occurs in a significantly narrowed-down window of pH (*plateau in the curve of the latex L-13*),

which is highly desired for various applications. The last two points are the extreme cases of the above described balance between repulsive forces and the conformation free energy of chains, where the sigmoidal shape is probably caused by a coil-to-globule transition similarly to poly(methacrylic acid), which results in a sudden change of the charge density and in the fall of the pK_a value during neutralization.^[76, 77] It should be noted that a similar maximum and minimum on the plots of pK_a against the degree of neutralization was also observed upon neutralization of HASE systems by Wang *et al.*^[78, 79] However, no direct comparison is possible due to the low acid content and the different general composition of the systems here investigated.

The described dissolution process can also be characterized with corresponding rheological features, which is described in more detail in chapter 5.

4.2.4. Copolymerization Behavior Study

In free radical copolymerization a composition drift is often observed due to the different reactivities of monomers. Moreover, in heterophase systems additional parameters, such as the partial monomer solubility in water, the main locus of radical generation (e.g. type of initiator applied), and various diffusion and adsorption phenomena also have a strong influence on the course of copolymerization. In any case, the final properties of HASE systems strongly depend on the monomer distribution along the polymer chains, which significantly affects the neutralization behavior as can be seen by the shapes of the neutralization curves (change from slope to plateau or to sigmoidal). To investigate this phenomena, kinetic observations on the polymerization process of the latexes L-10 (MMA/BA/MAA=55/15/30 wt.%) and L-14 (MMA/BA/MAA=70/10/20 wt.%) were performed. Figure 24 represents the instantaneous molar fractions of the monomers in the resulting copolymer composition as a function of the overall degree of conversion.

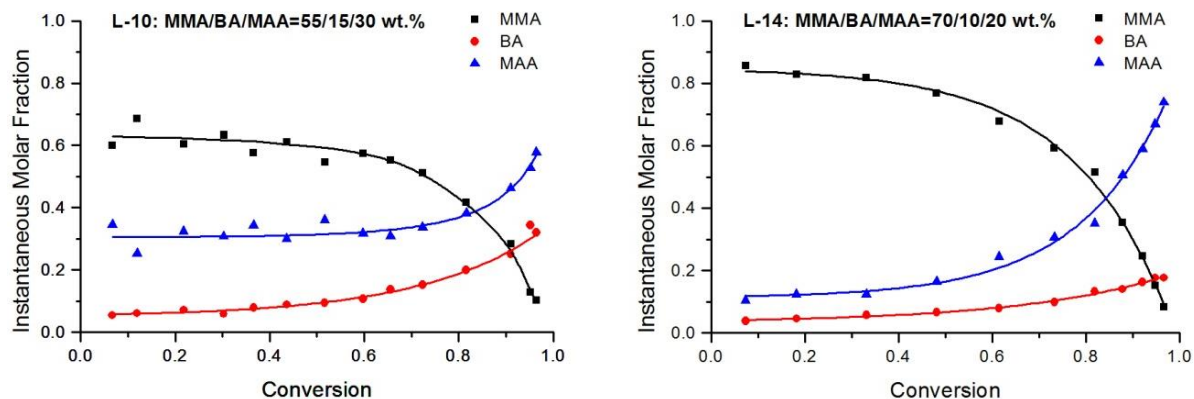


Figure 24: Instantaneous molar fractions of the monomers in the copolymer composition vs. conversion. It can be seen that the initial monomer ratio does have a significant influence on the resulting copolymer composition drift. (Initial molar ratios are L-10: 54.2/11.5/34.3 mol.% and L-14: 69.3/7.7/23 mol.%).

In both experiments it can be observed that the copolymers formed at lower conversions are slightly richer in MMA than the initial composition. On the other hand the BA and MAA content is increased in the copolymers formed at the later stages of the reaction. It should be noted that that the overall hydrophobic/hydrophilic balance determines the HASE properties and that copolymer fractions with a high content of BA could drastically handicap their solubility behavior. In this respect the BA/MAA ratio throughout the polymerization as depicted in Figure 25 is of paramount importance to counterbalance the hydrophobicity from BA-rich copolymer segments by an increased incorporation of acidic functionalities.

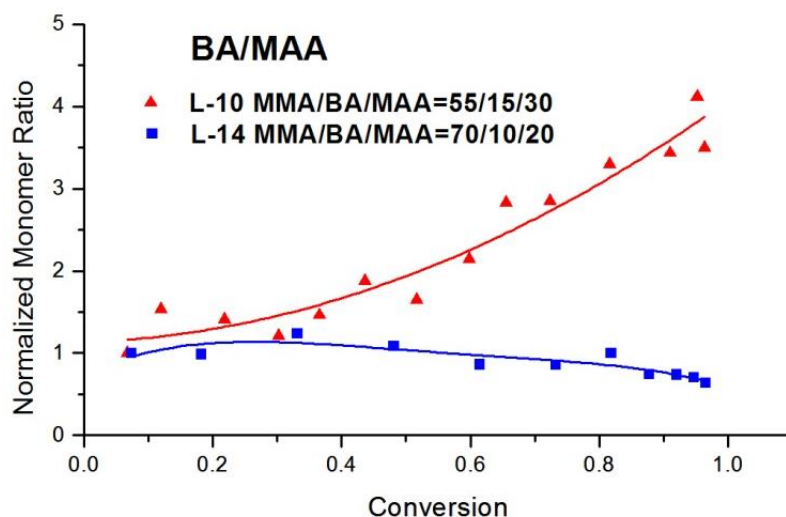


Figure 25: Normalized ratio of instantaneous molar fractions of BA and MAA in the polymer as a function of conversion in different latexes. Strongly altered composition drift is observed for two different samples with strong differences for the HASE behavior.

From Figure 25 it can be seen that the initial composition significantly influences the composition drift. Although both samples have an identical initial BA/MAA ratio, L-10 deviates much stronger compared to L-14, with strong consequences for the HASE behavior. As described in chapter 4.2.3, an improper hydrophobic/hydrophilic balance and a strong composition drift can not only lead to poor solubility, but even result in phase separation after neutralization. Figure 25 shows that upon increasing the MMA content the distribution of BA and MAA units becomes more even, which facilitates the dissolution by a more even distribution of charges. This result is a direct consequence of the terpolymerization equation (3), showing that each monomer acts as a “quasi regulator” for the distribution of other monomers.

In general the described composition drift can be the function of multiple parameters. However, the monomer reactivity ratios and their local concentrations at the reaction site are expected to have the strongest influence on the copolymerization behavior and should be briefly discussed to describe the observed general trends. The partitioning coefficients k_{M_i} , defined as the concentration ratio of a given monomer i between organic and aqueous phase, were determined via GC and reveal only minor differences between the two investigated samples. k_{MMA} is in the range of 28.5 – 30, while k_{MBA} is significantly higher and in the region 235 – 260 due to the much higher hydrophobicity of the BA. As expected the partition coefficient of the water soluble MAA is much lower (k_{MMAA} in the range of 0.95 – 1.01) and shows nearly equal solubility of the monomer in both phases (see Figure 26). However, it should be noted that the investigated systems contain 20 wt.% organic phase and that equal concentration of the MAA in both phases translates into its predominant presence in the aqueous phase. The monomer reactivity ratios reported in the literature for the BA/MMA monomer pair are 0.43 (r_1) and 1.88 (r_2), and for the monomer pair BA/MAA 0.31 (r_1) and 1.25 (r_2).^[80-82] In case of monomer pair MMA/MAA highly ambiguous and in some cases self-contradictory information were reported which can hardly contribute to a meaningful discussion.^[82]

It should also be noted that monomer partitioning studies were carried out for bulk mixtures and slight differences can occur in miniemulsion. However, conducting the same experiments after miniemulsification is impossible and the employed method is widely accepted with reliable approximation.

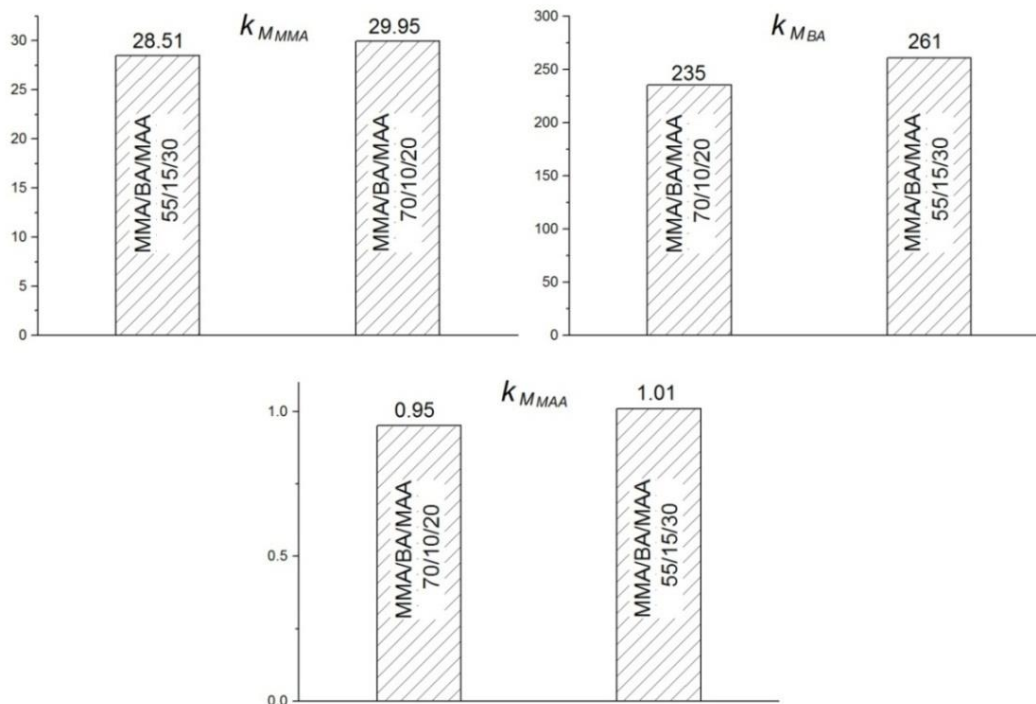


Figure 26: Partitioning coefficients of monomers between oil and water phases in different compositions (latexes L-10 and L-14). No obvious sensitivity of monomer partitioning towards the composition of monomer mixture can be observed.

Considering the monomer reactivity ratios at first, the increase of the BA content at the later stages of the reaction in both experiments is in agreement with theory, because for $r_1 < 1 < r_2$ the respective composition drift can be predicted. Following this argument more BA becomes incorporated into the growing copolymer chain after depletion of the other monomers, with a slightly dominating effect of MMA over MAA. In this respect it should be noted that according to the copolymerization equation the feed composition affects not only the overall composition of the copolymer, but also the copolymer composition drift. The monomer partitioning study between oil and water phases shows that BA is mostly accumulated in the oil phase, while significant amounts of MMA and MAA are present in the water phase (see Figure 26). Due to the very similar partitioning coefficients for both considered systems (L-10 and L-14) a pronounced solvency effect could not be observed, although the slightly increased partitioning values for MMA and MAA for the sample L-14 could principally contribute to a reduced composition drift as shown on the Figure 25.

The described composition drift explains the behavior of the samples upon dissolution as shown in Figure 22, and the suppression of this drift leads to the formation of soluble, visually transparent systems at neutral pH values.

4.2.4.1. Fractional composition of synthesized polymers

As it is expected from the above described observations on the copolymerization, the obtained copolymers should represent a mixture of polymers with different composition.

Fractional precipitation experiments of the obtained polymers from ethanol solution with water and further ^1H NMR investigations of the fractions reveal this trend clearly. Figure 27 provides the overlay of the different fractions of the polymers. For visual representation, proton signals belonging to -O-Me group of MMA units with the chemical shift $\delta = 3.62$ ppm are adjusted to same intensity, while the gradual decrease of the proton signals characteristic for butyl group of BA units in the fractions from 1 to 7 is observed.

This observation is in good correlation with the GC analysis data and confirms the presence of the MMA rich or BA rich polymers in the synthesized latexes. Due to complexity of the spectra it was not possible to observe the distribution of methacrylic acid units via NMR in different fractions. However, it can be assumed that the expected result also in this case is in complete accordance with described GC investigation results.

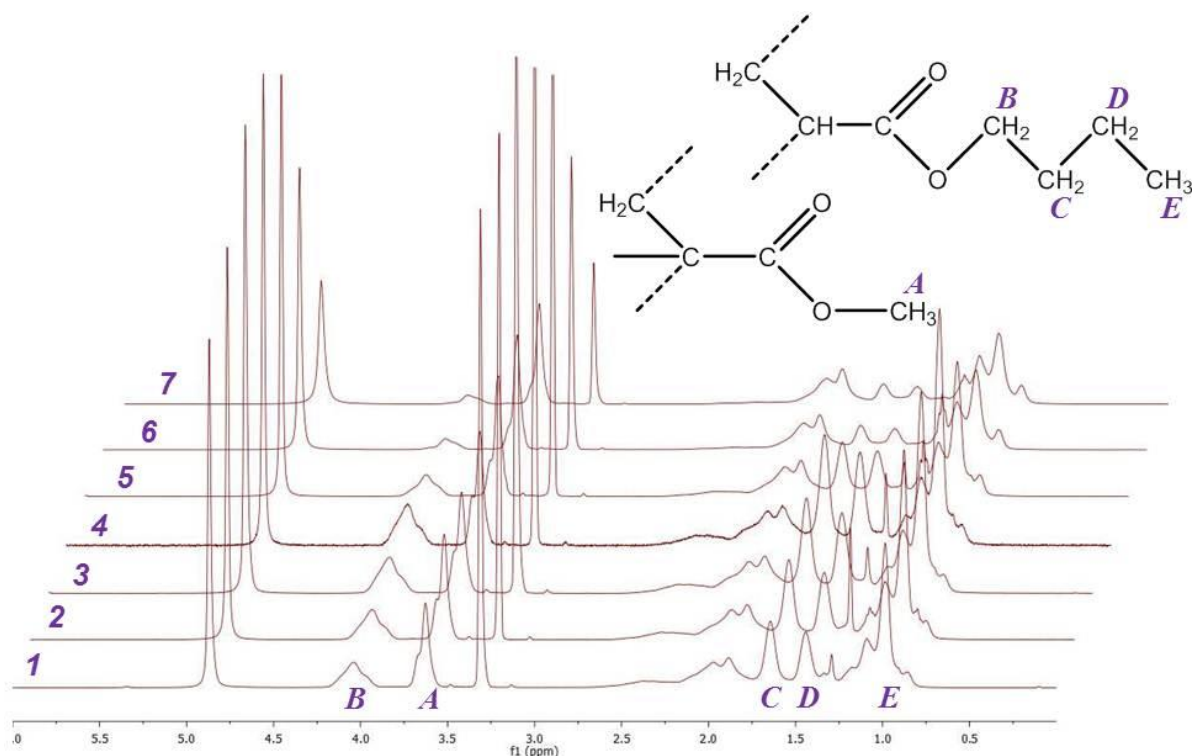


Figure 27: Overlay of ^1H NMR spectra of the different fractions of synthesized polymers, showing the different composition of different fractions caused by composition drift during copolymerization in accordance to GC analyses.

As mentioned in the introduction classical HASE systems based on EA and MAA usually do have much higher acid contents (ca. 50 wt.% MAA), which is unfavorable for many technical applications. It should be noted that the here reported unusually low acid contents for HASE are only possible because of the modified monomer selection and such a defined and adjusted copolymerization behavior.

4.3. Dual Stimuli Responsive Systems

As described above, the miniemulsion-analogous synthetic route enables the preparation of pH responsive (alkali soluble) systems via direct introduction of the molecules with strongly divergent hydrophobicities in the polymer chain. Furthermore, as it will be shown below, this simplified approach towards hydrophobic modification of the polyelectrolytes represents the convenient tuning method of the rheological behavior of the obtained systems upon neutralization (chapter 5). The highly versatile character of the miniemulsion-analogous technique also enables further exploitation of the advantages of the miniemulsion-analogous technique and the introduction of additional response mechanism into the described pH responsive

systems. Increasing the content and the carbon chain length of polymerizable ultrahydrophobes, it was found possible to provide the pH responsive latexes with temperature responsive properties.

It should be noted that in these dual stimuli responsive systems the highly hydrophobic monomer represents the main component of the system and not the copolymerizable miniemulsion costabilizer or hydrophobic modifier for physical cross-linking.

The introduction of additional functionality is accomplished based on the phenomenon known for linear hydrocarbons. Copolymerizable ultrahydrophobes with long linear alkyl groups tend to crystallize leading to the formation of semicrystalline systems. Unlike conventional semicrystalline polymers in which the backbone of the polymer crystalizes, in this case the crystallinity is provided by the alkyl side chain of the polymer.^[83, 84] The minimum length of the alkyl chain and the content of such acrylate in the latex, necessary for the crystallization, depend on the overall composition of the system (e.g. content of other monomers, copolymerization character etc.). Employing the above described approach it was found possible to copolymerize sufficiently high content of octadecyl acrylate (ODA) with the ionogenic MAA, together with other, nonionogenic monomers (BA and MMA), to obtain the dual stimuli (pH and temperature) responsive systems (see chapter 8.1.2).

Stable systems were obtained via the variation of monomer ratio and surfactant content, as well as testing of different surfactants. Due to increased amount of highly hydrophobic ODA (40 wt.%), respective changes were made in general composition of the latexes. To obtain stable systems the MAA content was decreased to 25 wt.%, while the contents of relatively hydrophobic MMA and BA were adjusted to 15 and 20 wt.%.

Systems prepared in the presence of the SDS as surfactant were found unstable, even in case of up to 2.5 wt.% of surfactant to monomer ratio. Using Dowfax 2A1 as surfactant, stable systems were obtained with relatively narrow (PDI < 0.1) and monomodal particle size distribution.

Obtained systems (dispersions, as well as freeze dried samples) show characteristic melting and crystallization peaks upon repeating heating and cooling cycles on DSC

curves. Freeze dried samples also show the characteristics signals on X-ray diffraction patterns.

As it can be observed from the Figure 28 the sample with lower content of the ODA shows lower melting point and lower enthalpy of melting (e.g. lower degree of crystallinity).

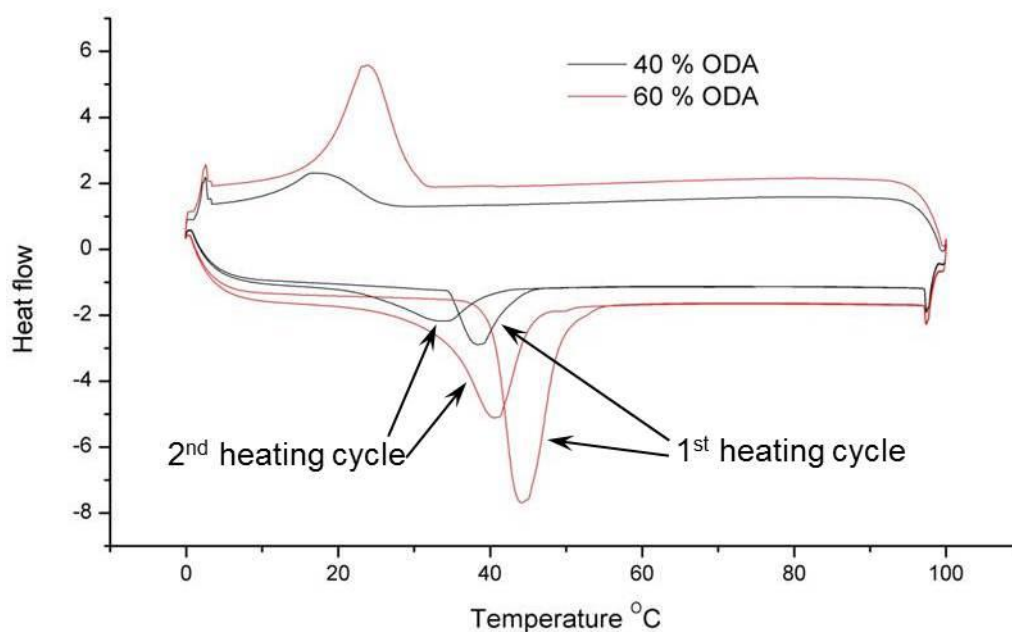


Figure 28: DSC analysis results for freeze dried samples with different content of ODA. Dependence of the melting point and degree of crystallinity (enthalpy of melting) on the content of ODA is observed. 25 wt. % MAA used in both cases. Weight ratio of nonionogenic monomers as described: MMA/BA=3/4

X-ray diffraction experiments also show a higher degree of crystallinity in the samples with higher content of ODA (Figure 29). This observation is in good correlation of the above mentioned shift of melting point in corresponding samples. It should be noted that the degree of crystallinity could not be determined in investigated samples due to absence of the reference with the degree of crystallinity of 100%.

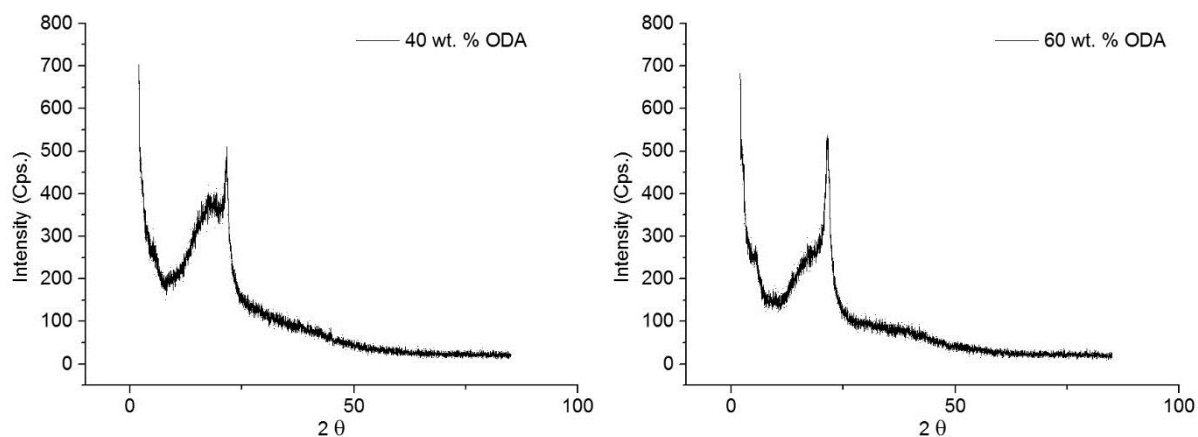


Figure 29: X-ray diffraction pattern for freeze dried samples with different content of ODA. The sample with higher content of ODA exhibits clearly a higher degree of crystallinity.

Similar trends in terms of the melting point shift in crystallisable long chain acrylates have been reported by *Agirre et al.* for pressure sensitive semicrystalline adhesive materials.^[84] For such materials an improved performance of due to the presence of crystalline domains has also been reported. In other words, in the reported cases, as well as in here investigated systems, the presence of crystalline domains can be considered not only as an additional stimuli response mechanism, but also as the type of physical cross-linking point, further enhancing the mechanical and rheological behavior of the systems. Nevertheless, it should be noted that the influence of the crystalline domains in the below investigated systems is of no or minor relevance to the considered work and will not be further elaborated in upcoming chapters.

Molecular weights of the synthesized dual stimuli responsive polymers were found to be noticeably lower ($M_w \approx 5 \cdot 10^5$ and $M_n \approx 5 \cdot 10^4$) as compared to the above considered HASE systems, besides, they are characterized with an extremely high (e.g. up to ≈ 10) polydispersity index. Such wide polydispersity is most likely due to the strong differences in reactivities and monomer partitioning between oil and water phases, which leads to the described strong composition drift during the polymerization.

Investigations on the pH responsiveness of these particles show strong swelling of the particles upon increase of pH (Figure 30). However, no measurable change of the particle size was observed upon increasing the temperature above melting point in alkaline conditions. It can be hypothesized that such behavior is caused by strong attractive hydrophobic interactions between hydrocarbon chains even above melting

point. For the samples with lower content of ultrahydrophobes, a specific neutralization behavior will be described in chapter 5.

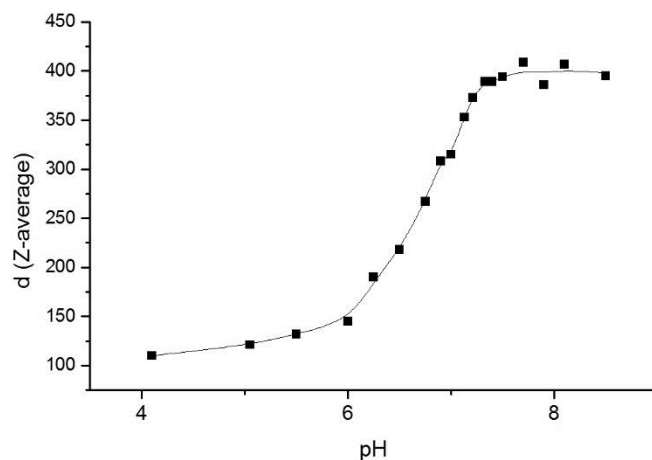


Figure 30: Z-average diameter of dual stimuli responsive systems with 40 % ODA content and as a function of the pH.

Thus, these systems represent the extreme case of the physically cross-linked polyelectrolyte solutions and in spite of the fact that they can be of high significance in pressure sensitive adhesive materials,^[83-87] such materials are out of the main scope of described research. Nevertheless, the described dual stimuli responsive systems strongly emphasize the unique character and the possibilities of the investigated miniemulsion-analogous approach, with potential application in the variety of stimuli responsive systems, ranging from controlled release systems to tunable/switchable materials.

5. Rheological Behavior of Synthesized Hydrophobically Modified Alkali Soluble Latexes

In the following chapters the rheological and mechanical behavior of the synthesized systems upon neutralization are investigated. These characteristics can define the application area of obtained materials, and as it will be described throughout the work, they can easily be tuned to fit particular targets.

The above described synthesized latexes represent fluid systems with a viscosity similar to water. However, as it is well known for ASE systems, upon increasing the pH, neutralization and deprotonation of acid groups occurs, which leads to significant electrostatic repulsion forces between polymer chains. These repulsion forces lead to the chain expansion and entanglement of the macromolecules with corresponding strong increase of viscosity.^[52]

In HASE systems the above described electrostatic repulsion forces are combined with hydrophobic attractive interactions (see chapter 2.6.2.1) and the overall rheological behavior of the systems become much more complex. Rheological parameters are the functions of different variables, such as pH, temperature, hydrophobicity (the content and the type of ultrahydrophobe as well as overall hydrophobicity of non-ionogenic monomers), content and type of additives, *etc.*

Throughout this section we investigate and describe the advantages and simplicity of tuning these parameters via the above described miniemulsion-analogous synthetic method (chapter 4). Significant part of the research is also devoted to the pH dependence of the rheological behavior and characteristic gradual dissolution of the latexes upon neutralization, while most work will be concentrated on the responsive behavior of the obtained systems to additives. It will be shown that different rheological parameters show different trends upon changing pH. This observation can be employed as an indirect method for the characterization of the structure of obtained physically cross-linked polyelectrolyte solutions (Chapters 5.1.3 and 5.1.4).

Oscillatory rheology represents the main tool used in the characterization of the systems. Taking into account that all rheological measurements were conducted in controlled strain mode (strain values were predefined to observe corresponding stress), the Maxwell model is used for the evaluation of the obtained results. For

proper characterization it was considered appropriate to evaluate energy storage and dissipation mechanisms determining the elastic and viscous behavior. Storage (G') and loss (G'') moduli, described in the chapter 2.7.3.1, represent convenient measures for the evaluation of these mechanisms. Several other parameters, such as damping factor (δ) and crossover frequency are also considered as important characteristics for the application of these systems as adhesives or rheology modifiers. Besides, these values along with the storage and loss moduli are useful for the evaluation of the neutralization process and the structure of the investigated systems.

5.1. Dependence of Rheological Parameters on the Intrinsic Properties of HASE Solutions

As described above, the investigated systems undergo sharp transition from low viscosity latexes to highly viscous polyelectrolyte solutions as shown in Figure 31.

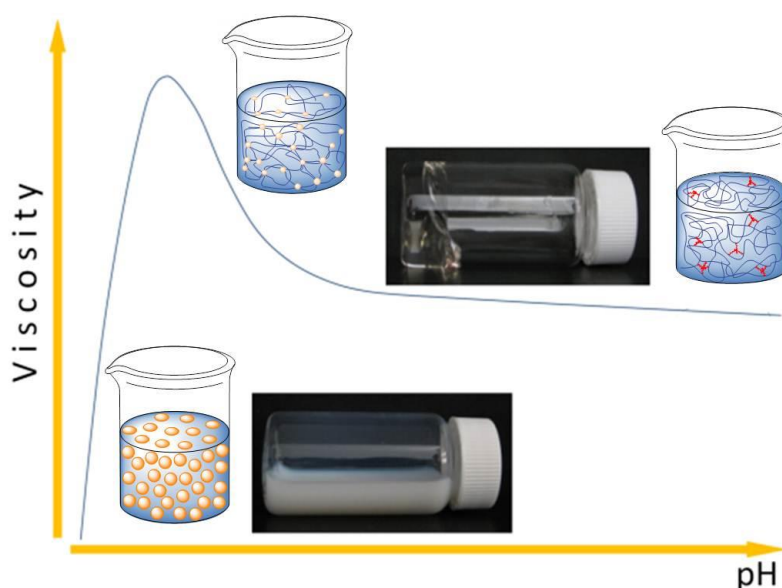


Figure 31: Viscosity, appearance and structure of the HASE systems.

Throughout this work the rheological behavior of the synthesized systems is investigated as a function of different parameters. Some of these parameters are characteristic for the obtained systems themselves. However, the properties of the obtained HASE solutions are also highly sensitive towards different additives and this can be used for fine-tuning and achieving the desired application-specific properties. In this chapter we describe the dependence of the rheological behavior of

the systems on intrinsic “system” variables, such as molecular weight, pH and content and type of ultrahydrophobe (i.e. composition). The influence of additives and the corresponding tuning of the sensitivity towards dilution will be discussed in further chapters.

5.1.1. Dependence of Rheological Parameters on the Molecular Weight

As it was described in chapter 4.2.2, the molecular weight of the synthesized polymers can be controlled using different amounts of the chain transfer agent. As expected, it has a strong influence on the rheological and mechanical properties of the systems upon neutralization and therefore is of high importance for possible application areas.

In this section the rheological behavior of the synthesized systems with different molecular weights is described and a short comparative analysis is provided, showing the importance of its control.

Rheological investigations were performed for the samples described in the chapter 4.2.2, prepared with different contents of chain transfer agents (Table 6). Figure 32(A) provides the frequency sweep experiment results for the samples with 0.3, 0.5 and 0.8 wt.% of 1-dodecanethiol (to monomer), with weight average molecular masses of $59 \cdot 10^3$, $44 \cdot 10^3$ and $39 \cdot 10^3$ g/mol correspondingly. For comparison the frequency sweep experiment curves for the sample without chain transfer ($M_w=99 \cdot 10^4$) agent are provided on Figure 32 (B).

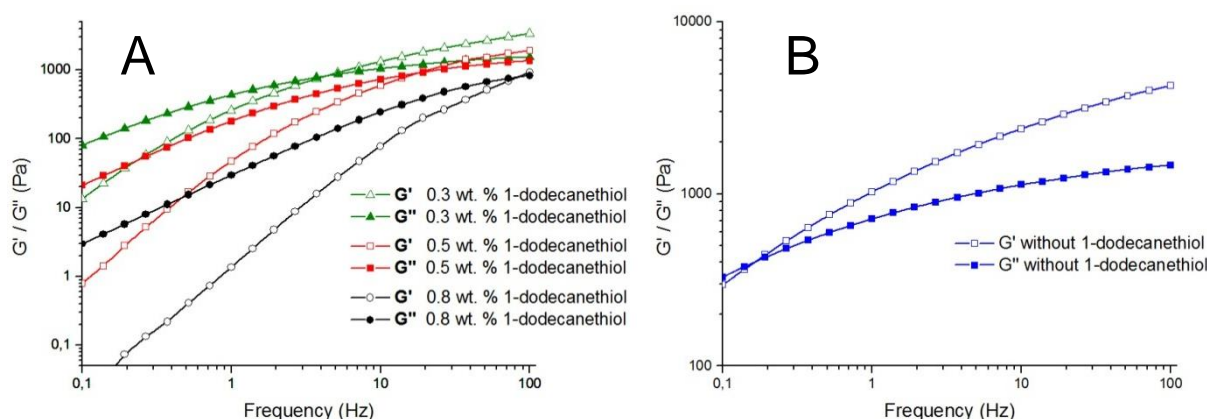


Figure 32: Frequency sweep rheological measurements of the samples with different molecular weights. Differences in the values of the storage and loss moduli, as well as their ratios, are obvious. Note also the different Y scale in figures A and B.

As observed, altered molecular weight strongly changes the behavior of the systems from viscoelastic solids to viscoelastic liquids (or vice versa).

This observation is of high importance for the adjustment of the rheological behavior of the systems for particular applications and is related to the relaxation behavior of polymer chains (as it will be explained later, is also in correlation of polymer structure). For the adhesive systems it is important that at lower frequencies of applied strain G' is lower than the G'' . Such systems represent viscoelastic fluids, able to respond more easily to applied stress and relax quickly after the stress is removed. This property is beneficial for good wet tack behavior at the initial stage of adhesion. Furthermore, an adhesive needs to be able to flow and wet the surface of a given substrate, which is only possible at $G'' > G'$ (or $\tan \delta > 1$)

Besides, low molecular weight polymers enable rheological measurements with a more accurate reproducibility and are convenient for the evaluation of the structure-property relationship. Consequently, in most cases throughout this work 0.8 wt.% 1-dodecanethiol (to monomer) was used. The importance of the interdependence of these two moduli will be discussed further throughout the work (chapter 5.1.1 and 7).

5.1.2. Dependence of Rheological Parameters on the pH of the System

For a comprehensive understanding of the neutralization process and the corresponding structural changes, different rheological parameters were measured at different pH values. These investigations reveal a gradual character of the transition from a low viscosity latex through the intermediate state with partial dissolution, to the final polymer solution. Detailed rheological characterization of this transition process is described in chapter 5.1.3.1

Regardless of the content and type of the ultrahydrophobe (described in chapter 5.1.3), all samples showed strongly increased dynamic modulus with a characteristic peak upon increasing pH, followed by steep fall and more or less well defined plateau (Figure 33).

This general behavior has been investigated by observation of hydrodynamic radius R_h by Wang *et al.*, where the presence of the peak was explained by the initial swelling of the latex particles, while further fall and plateau was assigned to the dissociation of polymer coils into smaller clusters upon higher degree of

neutralization.^[78, 79] English *et al.* have reported the microgel-like behavior of concentrated solutions of hydrophobically modified alkali soluble latexes, suggesting that in concentrated solutions and above a certain critical content of hydrophobic moieties, the hydrophobic domains resist the complete dissolution and maintain the transitional close-packed array of hydrophobic aggregates.^[59]

These observations can be used to explain the above described peak of the dynamic modulus at intermediate pH values. At these pH values (≈ 7 to 7.5) the degree of neutralization is relatively low due to the increased pK_a of the acid groups in polyelectrolytes (see chapter 4.2.3.1). Partially swollen and dissolved particles and polymer chains start to form an entangled network, resulting in the increased dynamic modulus. In this pH region, yet undissolved swollen particles act as strong “junction points”, contributing to “reinforcement” of the polyelectrolyte network structure. Upon further increase of pH the degree of neutralization is increasing, leading to increased electrostatic repulsion and formation of systems rather similar to true polyelectrolyte solutions, while the mentioned reinforcement disappears. At this final point the rheological behavior of the systems is defined by the inter- and intra-molecular electrostatic repulsion forces between charged polymer chains/chain segments, and by the relatively weak hydrophobic attractive forces, caused by the presence of hydrophobic moieties in the polymer (Figure 33).

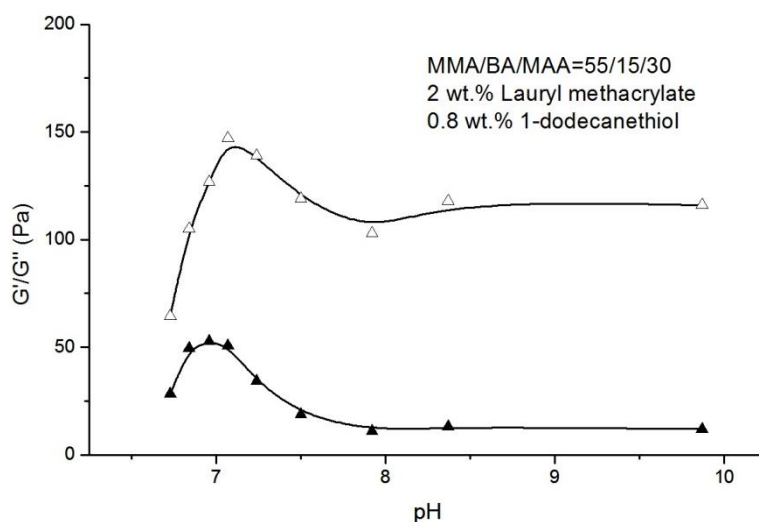


Figure 33: Neutralization curves for the storage (▲) and loss (Δ) moduli of prepared HASE system showing the peak values followed by plateau.

Additional information can be obtained from closer rheological investigation as it will be presented in the upcoming chapters.

5.1.3. Influence of the Type and the Content of the Ultrahydrophobe

As it is mentioned in chapter 4.2, the main advantage of the described miniemulsion-analogous approach is that it enables direct introduction of highly hydrophobic moieties in the polymer chain without complex synthetic procedures, the use of volatile organic compounds, high surfactant contents or specialty macromonomers.

Rheological investigations reveal that small (2 to 5 wt.%) changes in the content of copolymerizable ultrahydrophobe, as well as the variation of its carbon chain length (hydrophobicity), has a drastic influence on the rheological and mechanical properties of the systems and can significantly increase the dynamic modulus of the obtained systems. The corresponding experimental results are provided in chapter 5.1.3.1 and chapter 5.1.3.2. It should be noted that throughout the presented work the term ultrahydrophobe is used equally to the term hydrophobic modifier, due to the fact that the copolymerizable ultrahydrophobe becomes the part of hydrophilic polymer chain, leading to its partial hydrophobic modification.

5.1.3.1. Influence of the Amount of Ultrahydrophobe

Neutralization curves (plots of the rheological parameters vs. pH, similar to the one shown in Figure 33) were built for samples containing different amounts of lauryl methacrylate as ultrahydrophobe (LMA) (Figure 34). For comparison a sample without hydrophobic modification was also prepared and the corresponding neutralization curve is plotted on the same figure (all samples were prepared from 20% solid content latexes as described in the experimental section). As it can be seen from the Figure 34, the values of storage and loss moduli are highly sensitive to the degree of hydrophobic modification (the content of the copolymerizable ultrahydrophobe).

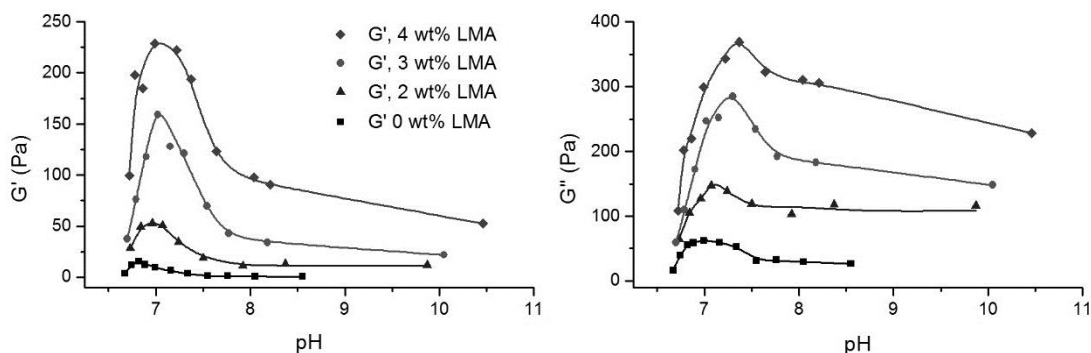


Figure 34: Neutralization curves for the synthesized HASE systems with the composition MMA/BA/MAA=55/15/30 wt.%, 0.8 wt.% 1-dodecanethiol and different amounts of lauryl methacrylate (LMA) showing a drastic change of the rheological behavior upon small change in LMA content.

Besides the above mentioned trends (e.g. strong sensitivity to hydrophobic modifier content and increased dynamic moduli at intermediate pH values) closer examination of Figure 34 reveals several additional noteworthy characteristics.

It is obvious that the shapes of the neutralization curves for storage and loss moduli follow slightly different patterns. Compared to the curve corresponding to loss modulus, the storage modulus shows a much more pronounced peak at intermediate pH values followed by a sharper reduction after the peak value. The trend is more obvious for the samples with higher content of ultrahydrophobe. This observation can be considered as proof for the above mentioned particle reinforced network at intermediate pH values (chapter 5.1.2). The presence of strong reinforcement contributes to a pronounced energy storage mechanism represented by the pronounced peak of storage modulus at intermediate pH. Upon quick and full dissolution of the latex particles with further increase of pH the disappearance of reinforcement is drastically affecting the storage modulus, leading to sharp drop followed by a plateau of dynamic modulus, as shown on the Figure 34.

Such gradual transition from latex to polyelectrolyte solution can be the result of following facts: As described in the previous chapters (see chapter 4.2.4 and chapter 4.2.4.1), a strong composition drift can be observed during the synthesis, which leads to the formation of polymers with different composition. Polymers with different contents of ionogenic groups can possess highly different pK_a values due to different charge densities on the polymer backbone during neutralization.^[88] Besides, even in case of statistical copolymerization, upon neutralization the electrostatic potential of the polymer chains are increasing, leading to a gradual increase of the pK_a values of the acid groups and resulting in hindered dissolution.^[38] This hindered, gradual dissolution can be considered as the main reason for the presence of above mentioned reinforced network structure at intermediate pH values causing the presence of the peak of mechanical properties.

It should be noted that each sample was equilibrated for at least 24 h. at elevated temperature (50 °C) before the rheological measurement. Therefore, the described dependence of dynamic modulus on pH should not be interpreted as the intermediate state due to the kinetically hindered neutralization process, but as the

stable state of the particular system at the particular pH value, defined solely by its structure and pH.

Another important rheological parameter that is worth to be considered in detail is the damping factor ($\tan \delta = G''/G'$, see chapter 2.7.3.1 and chapter 3.3). Figure 35 represents the damping factors of the above investigated systems with different contents of copolymerizable ultrahydrophobe (LMA) as a function of the pH.

It can be clearly observed, that increasing hydrophobic modification does not only drastically affect the dynamic modulus, but it is also changing the viscoelastic behavior in general. Even though the storage and loss moduli are both affected in similar manner (i.e. strong increase is observed), the magnitude of their change is different. Increased hydrophobicity has a stronger impact on the energy storage mechanisms due to the increased physical cross-linking density. This consequently leads to the lower values of the damping factor in corresponding samples (Figure 35).

These observations show that the incorporation of small contents of highly hydrophobic monomers enables the fine tuning of viscoelastic properties, with selective adjustment of storage and loss moduli. This is an important feature for the adhesive behavior of the obtained systems and can be employed for the adjustment of the adhesive and cohesive properties. Besides, it can be further used to tune the system properties for other application fields. It should also be noted that such control of viscoelastic behavior or drastic increase of mechanical properties cannot be achieved via the variation of MMA/BA ratio alone.

Hydrophobic domains, formed by ultrahydrophobic modifiers, can be considered rather similar to micellar aggregates. This similarity (see chapter 2.6.2.1) will be employed as the basis for the selective adjustment of the viscoelastic properties and for obtaining the stimuli responsive systems and will be presented throughout this work (chapters 6 and 6.4) in more detail.

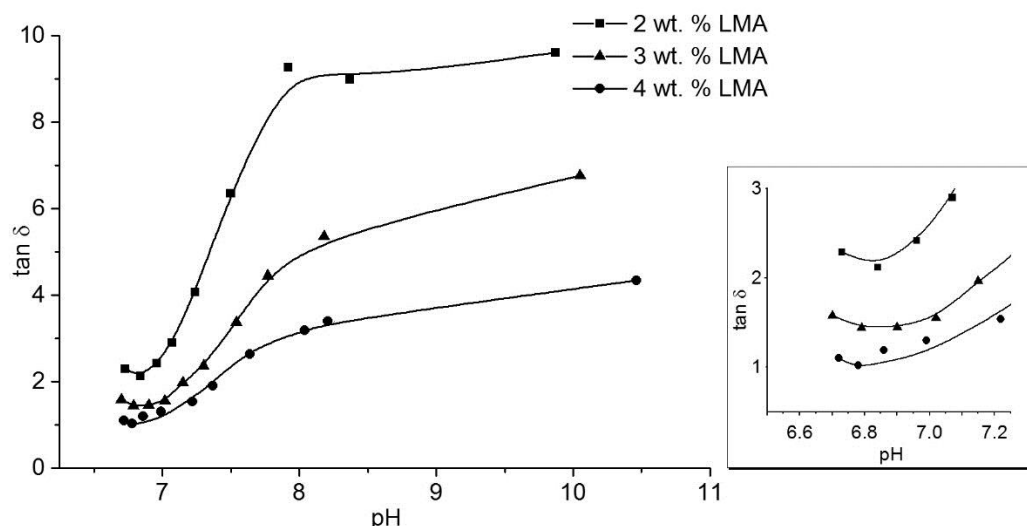


Figure 35: Damping factor ($\tan \delta = G''/G'$) plotted against pH value for the samples with different contents of the ultrahydrophobe (lauryl methacrylate). The decreasing value of the loss factor is caused by relatively fast growth of storage modulus along the increased content of the ultrahydrophobe.

The above suggested model of gradual dissolution can be further supported by monitoring the damping factor as a function of the pH value. Thorough observation on the graphs from the Figure 34 and Figure 35 reveals one more interesting detail.

As shown on the Figure 34 at the initial stage of the neutralization values of G' and G'' are increasing until certain pH value is achieved. However, observing the change of the damping factor in the same pH region (Figure 35 (inset)) it can be noticed that initially the damping factor is slightly reduced (elastic properties take over the viscous behavior) but it starts to increase noticeably earlier before the maximum values of the dynamic modulus is achieved.

This observation suggests that during the neutralization process there is a certain balance at each step between the main mechanisms contributing to the change of the mechanical behavior along the change of pH. These mechanisms can be assigned to the following changes in latex particles: (1) particle swelling (at low degree of neutralization), and (2) dissolution / chain entanglement (due to electrostatic repulsion and corresponding increase of dynamic modulus) combined with described network reinforcement, which define the increased mechanical properties at intermediate pH compared to final polyelectrolyte solution.

At the initial stages of the neutralization (below pH values of ≈ 7), swelling of the particles renders the system highly viscous and optically transparent. This leads to

relatively quick increase of the storage modulus and corresponding decrease of damping factor (Figure 35 inset and Figure 36(B)). At this point partial dissolution of the acid rich polymers at the particle surface cannot be excluded; however, because of the high content of undissolved (swollen) particles the increment of storage modulus compared to loss modulus is higher. Nevertheless, dynamic modulus is still relatively low due to absence of the significant dissolution with corresponding charge repulsion and polymer chain entanglement. This state corresponds to the upward slope on the neutralization curve (Figure 34).

Upon further increasing the pH of the system gradual dissolution takes place. At the same time the role of energy dissipation mechanisms is increasing, which is caused by changing the balance between the electrostatic repulsion and the associative interactions. This results in an increased damping factor. Furthermore, the formation of the above described reinforced network gives rise to corresponding peak of the dynamic modulus on the neutralization curves (Figure 34 and Figure 36(C)). Complete neutralization and dissolution of the latex particles leads to decrease of the dynamic modulus and described plateau values for the storage and loss moduli, as well as damping factor are achieved (Figure 36(D)). The described stepwise neutralization scenario, with initial swelling of the particles followed by gradual dissolution, is in complete agreement with the above mentioned (chapter 5.1.2) neutralization process investigated and described via dynamic light scattering by Wang *et al.*^[78]

Thus, the observed differences between the patterns of the change of dynamic modulus and viscoelasticity against pH can be employed to characterize the gradual process of neutralization.

It should be noted that the calculation of the neutralization degree was found impossible, or rather impossible due to the probable gradient distribution of the acid groups in the particles. According to rough estimation, neutralization degree should be ≈ 0.5 for the systems depicted in Figure 36(B). On the other hand, this estimation seems reasonable only in case when most of the neutralized acid groups are rather closer to particle surface and the integrity of the particles is maintained due to lower content of the neutralized acid groups inside the particles.

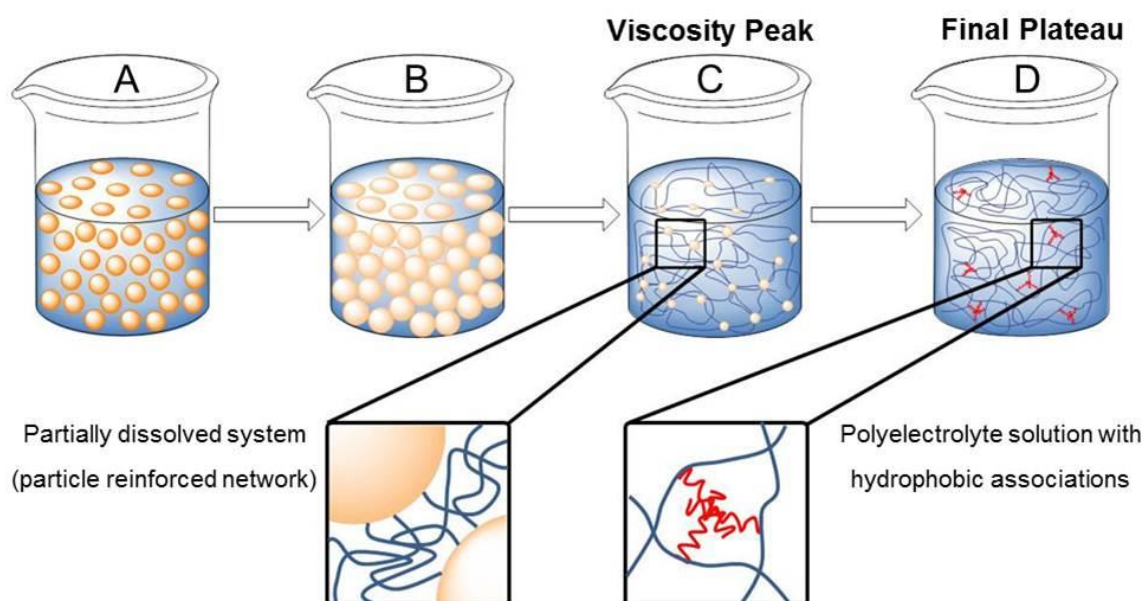


Figure 36: Gradual swelling and dissolution of the latex particles as observed via rheological investigations. Note that particles or hydrophobic associations in Figure 36 (C) and Figure 36(D) do not correspond to their actual sizes. While undissolved particles can be up to a size up to 100 nm, hydrophobic domains cannot exceed usual size of several nanometers. The state shown in Figure 36(B) represent visually transparent system and corresponds to the minimum value of the damping factor as shown in Figure 35 inset.

Besides the structure evaluation, the considered neutralization curves have immense importance for practical application. In the applicable pH region the mechanical and rheological values should preferably be less sensitive towards small changes of pH. On the peak “shoulder” of the dynamic modulus the rheological properties are highly sensitive to smallest changes of the pH. In other words, for the final application the systems are useful mostly within the pH range where the plateau values of the storage and loss moduli and the damping factor are achieved.

5.1.3.2. Influence of the Type of Ultrahydrophobe

The obtained HASE systems exhibit also strong sensitivity of the rheological parameters towards the type of ultrahydrophobe. In these works the investigations has been conducted with reactive ultrahydrophobes of varying carbon chain length (various hydrophobicities). Increasing the carbon chain length of the ultrahydrophobe leads to corresponding dramatic changes of the rheology of the systems. In Figure 37 the dependence of the rheological parameters at different pH values on the carbon chain length of the employed ultrahydrophobe is provided. Molar equivalents of the different ultrahydrophobes (LMA and HDMA) were employed for proper comparison.

Based on these observations an analogy between micellation and hydrophobic association can be made. Similar to surfactant self-assembly in micelles, where the increased hydrophobicity of the hydrophobic tail leads to lower CMC, increased hydrophobicity of hydrophobic side chains in the investigated systems leads to stronger driving force for their association and correspondingly to denser physically cross-linked structures. Besides, the strength of the corresponding hydrophobic domains is also increasing. Similarly to above considered examples, storage and loss moduli also show the peak values at the intermediate pH with following reduction of both moduli and reaching the plateau.

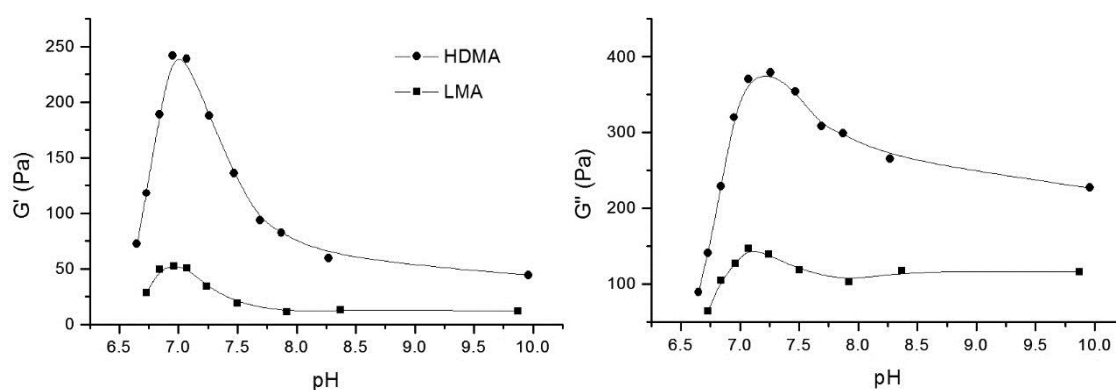


Figure 37: Neutralization curves for the synthesized HASE systems with the composition MMA/BA/MAA=55/15/30 wt.%, 0.8 wt.% 1-dodecanethiol and different ultrahydrophobes. 2 wt.% LMA and analogous molar amount of HDMA were used.

Figure 38 shows the damping factor as a function of pH value. Similar to the previous examples the damping factor shows a minor decrease at the initial stages of the neutralization.

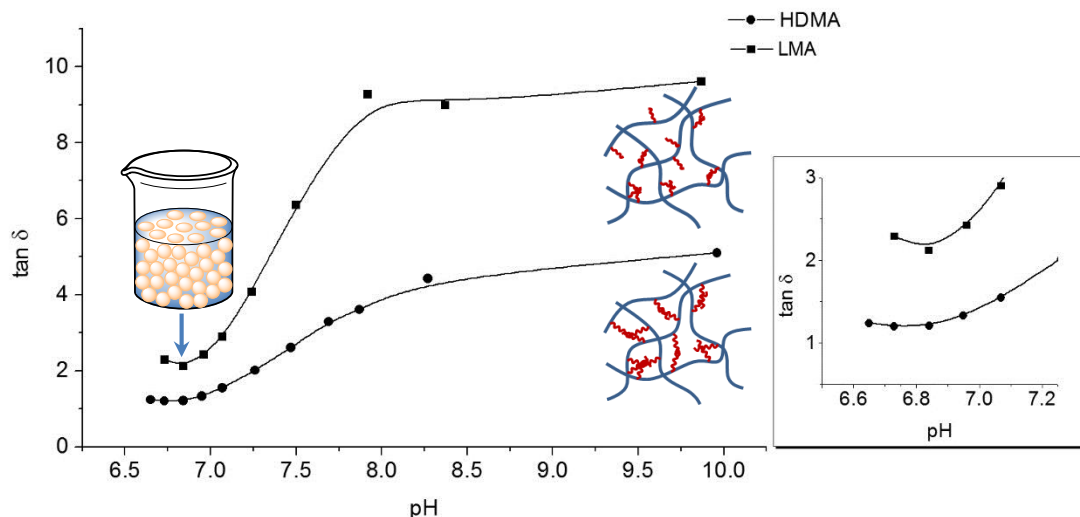


Figure 38: Damping factor ($\tan \delta = G''/G'$) plotted against pH value for the samples with different types of the ultrahydrophobe. Much lower damping factor values are observed for the sample with HDMA due to improved energy storage caused by stronger hydrophobic associations. (For the better understanding of the schematic representations at different pH values see Figure 36 and Figure 9)

Thus, it can be concluded that the rheological behavior can be tuned in various ways, via alteration the content or the type of different ultrahydrophobes and consequently selectively alter the magnitude of the dynamic modulus, as well as the ratio of storage and loss moduli. Taking into account the simplicity of the novel synthetic route (chapter 4.2.1), it can be said that described method represents a versatile tool for preparation of HASE systems for a wide variety of applications.

5.1.4. Response to stress and setting behavior

As described in chapter 2.7, for the rheological measurements defined frequency and strain profiles are applied to the samples and the corresponding stress is measured. As it is expected, after a characteristic time the stress relaxation occurs, which is referred as the relaxation time (τ) of the material. Oscillatory rheology can be employed for the measurement of this parameter and these investigations have immense importance for the practical applications, such as adhesives, paints coatings *etc.*, since they represent the characteristic period, necessary for recovery from forced deformation.

As described above (chapter 4.2.2), the investigated polymers have a wide molecular mass distribution and a strong composition drift can be observed. Therefore it is expected that these materials cannot be characterized by a certain

single relaxation times but rather by a broad relaxation spectra. However, within a certain approximation the relaxation behavior of the materials can be still assessed from the frequency dependency of the storage and loss moduli (chapter 3.3). According to the Maxwell model the crossover frequency of these two moduli is inversely proportional to the relaxation time of the material.^[89]

Figure 39 provides crossover frequencies for samples with different contents of the hydrophobic modifier (LMA) as a function of the pH of the system. Taking into account the mentioned inverse dependence, it is obvious that an increased physical cross-linking density leads to increased relaxation times. Higher relaxation times, as a direct result of restricted chain movement, is in good agreement to the hindered reptation model of polymer chains suggested by Leibler *et al.*^[90] It should be noted that crossover frequencies, similarly to the values of the damping factor (see Figure 35 and Figure 38) do not reach actual plateau upon relatively higher content (3 or 4 wt.%) of ultrahydrophobe or the longer alkyl of the latter. The reason for this behavior is the stronger attractive hydrophobic interaction, which is being gradually outweighed by repulsion forces throughout the whole neutralization process.

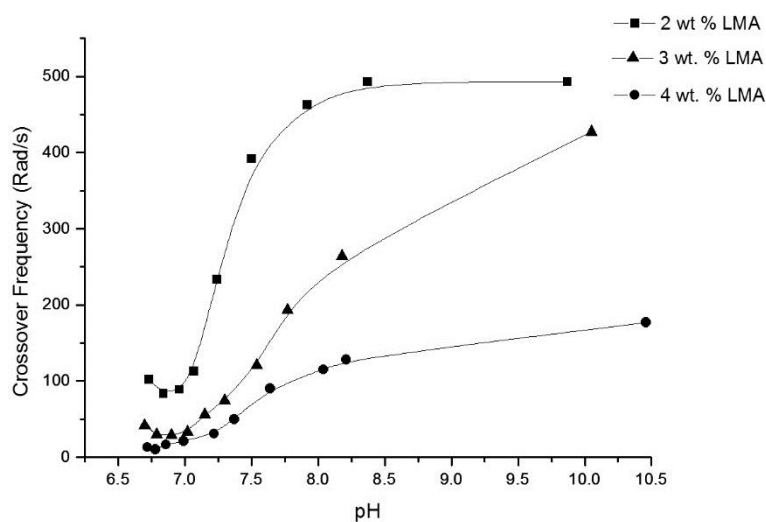


Figure 39: Crossover frequencies of G' and G'' for samples with different contents of lauryl methacrylate at different pH. Lower crossover frequencies correspond to longer relaxation times due to hindered chain mobility.

This model also explains the dependence of the relaxation behavior on the molecular weight variation of the polymers based on the crossover frequencies of the corresponding systems shown in the Figure 40. Besides the overall decrease of storage and loss moduli upon decreased molecular weights (mentioned in the

chapter 4.2.2), the shift of crossover point towards the higher frequencies is also observed, *i.e.* the corresponding relaxation times are decreased. Chain reptation for higher molecular weight samples are hindered to a greater extent due to higher amounts of physical cross-links per polymer chain and stronger chain entanglement. Thus, molecular weight, along with composition, can also be employed for the regulation of the viscoelastic behavior of the systems and for their adjustment for different applications.

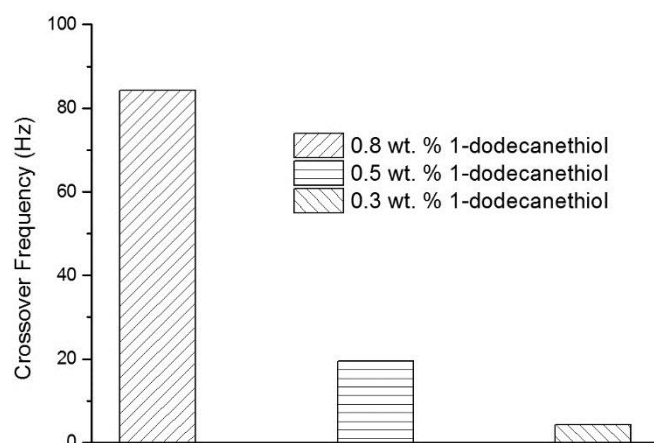


Figure 40: Crossover frequencies for the samples with different molecular weight (See chapters 5.1.1). Decreasing the molecular weight leads to more fluid like behavior and short relaxation times and corresponding shifts in crossover frequencies (see also Figure 32).

The results of chapter 5.1 can be summarized in the following conclusions:

- The rheological behavior of the systems can be tuned in a controlled manner in various ways (molecular weight, ultrahydrophobe content, ultrahydrophobe type)
- The above listed factors can be easily combined to achieve the desired results for a particular application
- Storage and loss moduli and system relaxation characteristics can be tuned independently, thus allowing tailoring of the systems

The considered factors have a major influence on the adhesive behavior of the systems and define their tack, setting behavior and other important properties. More details regarding the corresponding investigations will be provided in the chapter 7.

6. Dependence of Rheological Parameters on Amphiphilic Additives

The rheological behavior of the HASE systems, similarly to regular polyelectrolyte solutions, is highly sensitive to the content and type of different additives. Vast literature data are available describing the influence of low molecular weight electrolytes on the rheological behavior of polyelectrolyte solutions, where various electrostatic interactions lead to sharp changes in the solution viscosity and other properties.^[42, 91-93]

In this work the influence of organic amphiphilic solvents on the rheological behavior of HASE systems is described. The target of the investigations is to achieve specific rheological properties and obtain stimuli responsive systems via selective regulation of different inter- and intramolecular attractive hydrophobic interactions. Short chain alcohols were considered as most optimal amphiphilic additives in such systems due to their environmentally benign character. Intended selective influence on the hydrophobic interactions is graphically represented in Figure 41.

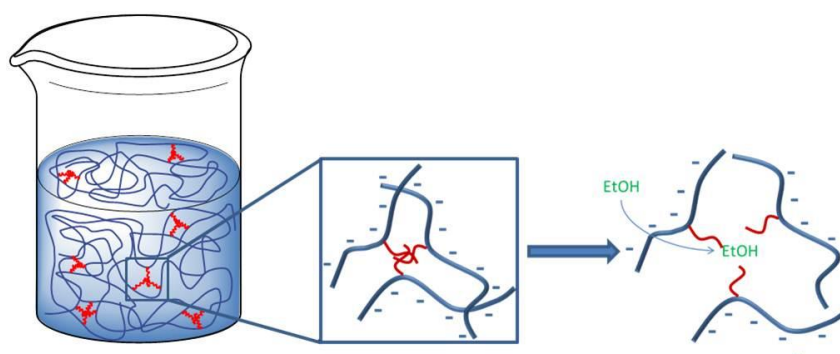


Figure 41: Possible interaction mechanism of an amphiphilic additive (ethanol) with hydrophobic domains.

6.1. Basic Outline

As described in previous chapters, here investigated systems are extremely complex to characterize not only in terms of the composition, but also in terms of their rheological behavior due to strong sensitivity towards a variety of interrelated factors.

In the upcoming chapters the micellation-analogous behavior of hydrophobic moieties of HASE systems is investigated in terms of their rheological response of to

amphiphilic additives. In other words, the target of these experiments is to employ existing basic knowledge regarding the influence of amphiphilic additives (such as alcohols) on the micellation of surfactants and to extend this knowledge to polymeric systems. As it will be shown, the corresponding changes in the rheological behavior of the investigated HASE systems represent a convenient tool for adjusting the interaction between the macromolecules in solution.^[94] As a consequence, stimuli responsive systems with improved characteristics for water based adhesives can be obtained.

A comprehensive understanding of the interaction mechanisms between micelles and amphiphilic additives can be acquired from the existing literature.^[95-100] The conclusions based on these works are summarized and listed below:^[101]

1. The alcohol molecules intercalate between the surfactants ionic head groups to decrease the micelle surface area per head group and increase the ionization. This effect is correlated with modification of the growth and shape of the micelle.
2. The dielectric constant at the micellar interface decreases probably due to the replacement of water molecules in the interface region by alcohol molecules.
3. The molecular order of the interface region of the micelle changes.

These conclusions can further be extended and employed for the in here investigated HASE systems to control of the strength of hydrophobic associations and to tune the rheology response.

In addition to listed effects, for the micellation-analogous HASE systems additional changes in inter- and intramolecular interactions for polyelectrolyte solutions are also expected.

1. Reducing the dielectric constant of the medium also affects the electrostatic repulsion forces, which is the main mechanism leading to increased viscosity. The reduction of electrostatic repulsive interactions due to reduced dielectric constant of the medium can drastically decrease the dynamic moduli values (correspondingly – viscosity) of the systems.
2. Amphiphilic additives can reduce the conformational free energy and increase the flexibility of polymer chains because of improved polymer/solvent

interaction due to their higher compatibility of uncharged hydrophobic polymer segments with amphiphilic solvents.

The described factors lead to overall reduced dynamic moduli. Therefore, in most experiments, the content (or the alkyl chain length) of the ultrahydrophobe was increased to increase the mechanical properties of the initial HASE solutions and account for their reduction upon addition of amphiphilic solvents. Besides, secondary effects of such changes (other than reduced mechanical properties) should also be taken into account and will be described in the upcoming chapters.

It should also be noted that considered effects of the amphiphilic solvent on the micellation-analogous behavior on the one hand, and their effect on the inter- and intramolecular interactions of polymeric chains (e.g. electrostatic interaction and polymer/solvent compatibility) on the other one cannot be assessed independently based on their influence on the overall rheological behavior. Therefore, the rheological response to such additives should be considered as the sum of the different types of interactions.

In the following chapters additional possibilities of fine tuning of the viscoelastic behavior are presented, which are based on the effects of amphiphilic additives on hydrophobic and electrostatic interactions.

6.2. Influence of the Content of Additive on the Rheological Behavior

As mentioned in the chapter 6.1, in the following experiments systems with increased dynamic modulus were prepared via composition variations. These changes can counterbalance the reduction of the viscosity upon addition of the amphiphilic additives. Changes include not only increased amounts of the hydrophobic modifiers, but also the variation of basic monomer composition. However, in these studies the content of the ionogenic monomer (methacrylic acid) was maintained constant in order to obtain polymers with same average charge density along the chain.

In the first set of experiments the content of the relatively hydrophobic monomer (BA) was increased drastically. The target of this change was to increase the role of hydrophobic interactions in overall rheological behavior and thus observe the effect

of disturbed hydrophobic interactions on the rheological properties. As the content of ionogenic monomer was kept constant, the content of the relatively hydrophobic BA was increased while decreasing the content of non-ionogenic, but less hydrophobic MMA. The type of the ultrahydrophobe was changed to longer chain C18 acrylate (octadecyl acrylate, ODA). The overall composition was: MMA/BA/MAA=20/50/30 wt.% with 5 wt.% of ODA and 0.8 wt.% of 1-dodecanethiol. As in all other cases the sample pH was adjusted to 8.4 using 12% solution of NaOH and the influence of the ethanol on the rheological parameters was investigated.

In order to evaluate the effect of the amount of the amphiphilic additive on the rheological behavior, samples with different contents of ethanol were prepared. Table 7 provides a list of samples with corresponding values of dynamic modulus.

Table 7: Dependence of the dynamic modulus on the content of ethanol. pH≈8.4. MMA/BA/MAA=20/50/30 wt.%, 5 wt.% ODA, 0.8 wt.% 1-dodecanethiol, solid content = 20 wt.%.

Sample ID	Ethanol Content (wt.%)	Dynamic Modulus G^* (Pa)	Storage Modulus G' (Pa)	Loss Modulus G'' (Pa)
AD-1	0	529	160	504
AD-2	2	305	50	279
AD-3	4	176	18.6	175
AD-4	6	112	7.5	112

The data shows strongly decreasing dynamic moduli values upon addition of small amounts of the amphiphilic additive. This observation proves the validity of the model suggested above (see Figure 41). However, the above mentioned possible effects on the solvent dielectric constant and the charge repulsion (chapter 6.1) cannot be excluded at this point.

Nevertheless, taking into account that all types of considered interaction mechanisms, either the weakening the hydrophobic domains or changing the dielectric constant of the solvent medium, leads to same overall result in terms of the rheological response, at this stage it is possible to treat the obtained data without further elaboration.

As it will be described throughout the next chapters, the observed effect of the amphiphilic additives on the rheology of the considered systems can be employed for advanced rheology tuning of the investigated systems. This is achieved based on the observed inverse proportionality of the dynamic modulus to the amount of the added amphiphile and the reversibility of the physical interactions that contribute to the modified rheological behavior. Detailed information regarding the advanced tuning possibilities will be provided in chapter 6.4

At this point it is extremely important to mention that storage and loss moduli are affected to a different extent. Figure 42 (A) shows the change of the storage and loss moduli of the samples listed in the Table 7, while the Figure 42 (B) represents the magnitude of the change of both moduli (in percent) in relation to their initial values.

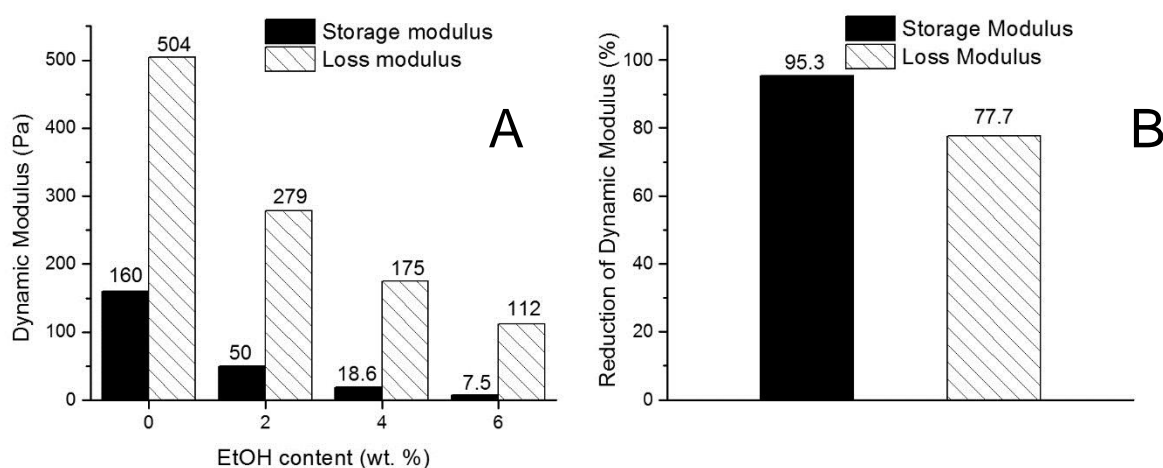


Figure 42: (A) Dependence of storage and loss moduli of the obtained systems on the amount of the added ethanol (B) Change of the absolute values of the storage and loss moduli in percent With 6 wt.% of added ethanol.

From these results it can be concluded that the alcohols more effectively influence and weaken those interactions, which contribute to the storage modulus, i.e. are responsible for the energy storage upon applied strain. The formation of hydrophobic domains, along with the stiffness of the polyelectrolyte chains, contributes to the increased storage modulus in HASE solutions. Selective weakening of these hydrophobic interactions (so-called “disturbed micellation”) and flexibilization of polymer chains (decrease of conformational free energy, see chapter 4.2.3.1) can be the possible reason for the observed different sensitivity of storage and loss moduli to the amphiphilic additives. Besides, this finding is particularly important for the application of the investigated systems as adhesive materials, since the energy

dissipation mechanisms favors adhesion properties, while the cohesion is related to energy storage. Controlled balance between these two, which can be achieved using amphiphilic additives in combination with above described other routes, defines the overall properties and performance of adhesive materials.

6.3. Influence of the Additive Hydrophobicity on the Rheological Behavior

The influence of the alcohol hydrophobicity on the rheological properties of the systems was also investigated. An increased length of the carbon chain changes the hydrophobic/hydrophilic balance of the alcohol and corresponding changes in the overall rheological behavior are expected. Table 8 provides a list and the mechanical modulus of samples with alcohols of various carbon chain length, ranging from C2 to C4.

Table 8: Dependence of the mechanical moduli on the carbon chain length of the amphiphilic additive. pH was adjusted to ≈ 8.4 . MMA/BA/MAA=20/50/30 wt.%, 5 wt.% ODA, 0.8 wt. % 1-dodecanethiol. 2 wt.% of each alcohol was used.

Sample ID	Alcohol type	Dynamic Modulus G^* (Pa)	Storage Modulus G' (Pa)	Loss Modulus G'' (Pa)
AD-1	Ethanol	305	50	279
AD-5	Propan-1-ol	156	14.2	156
AD-6	Butan-1-ol	77	2.95	77

As it can be seen from the values of the dynamic modulus, the carbon chain length of the employed alcohol strongly affects the mechanical properties of the investigated HASE systems. In other words, increased hydrophobicity of the amphiphilic additive has similar overall effect on the rheological response, as the increased content of the amphiphilic additive (chapter 6.2).

It should be noted that due to relatively small differences in dielectric constants ($\epsilon_{EtOH}=25.1$, $\epsilon_{PrOH}=20.3$ and $\epsilon_{BuOH}=17.5$ at 298 K)^[102-104] and small (2 wt.%) amounts of employed additives, change of the solvents dielectric constant is

expected to have relatively small or even negligible effect on the described change of the rheological behavior.

This observation can be considered as a proof that the increasing carbon chain length (consequently also the increasing hydrophobicity) of the amphiphilic additive leads to a more selective and targeted weakening of hydrophobic associations in the considered physically cross-linked networks, leading to reduced values of dynamic moduli and viscosity (Figure 41).

In this experiment, similarly to the observations described in chapter 6.2 different effects of the additives on the storage and loss moduli was observed. Figure 43 provides the storage and loss moduli with the same (2 wt.%) content of different alcohols (Figure 43 (A)) and the relative reduction of the storage and loss moduli while increasing the carbon chain length of the alcohol from C2 to C4 (Figure 43 (B)).

Similarly to the influence of the content of the alcohol, a stronger reduction of the storage modulus was observed compared to the loss modulus while increasing the carbon chain length and correspondingly the hydrophobicity of the alcohol. This observation can be considered as an additional fact, supporting the hypothesized selective influence of amphiphilic additives on the hydrophobic associations. Described observations can be attributed to higher affinity of relatively more hydrophobic additives to hydrophobic cross-links, consequently leading to their more selective disturbance.

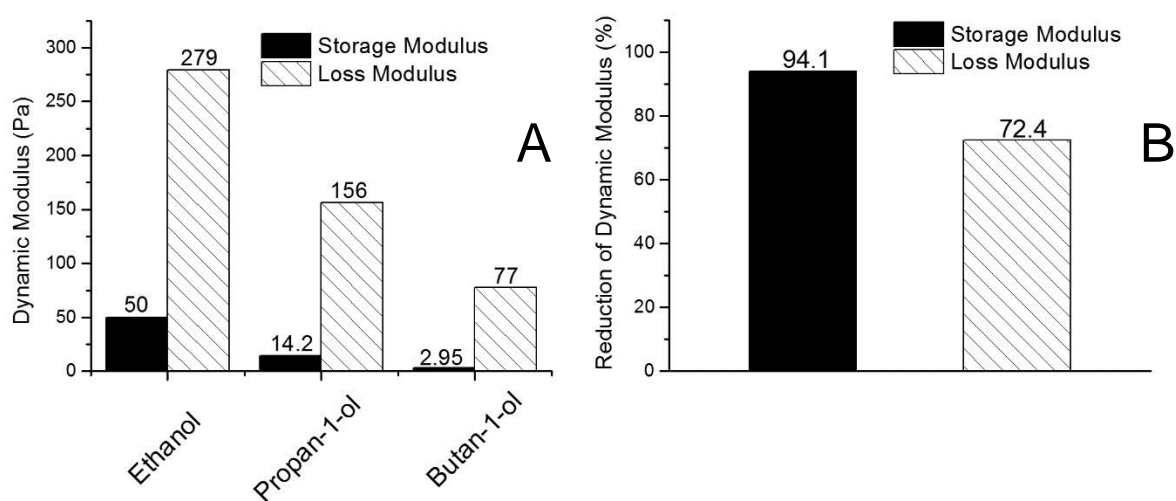


Figure 43: (A) Dependence of storage and loss moduli of the obtained systems on the type of the added ethanol (2 wt.% alcohol used in each case), (B) Change of the absolute values of the storage and loss moduli in percent.

Thus, above presented results show the possibilities of tuning the magnitude of the dynamic modulus and the viscoelastic properties (ratio of G' and G'') in different ways, such as molecular weight, degree of the hydrophobic modification (ultrahydrophobe content) or different additives. This is achieved via selective targeting of certain types of interactions or increased entanglements and hindered chain reptation.

6.4. Fast-Setting Properties and “Dilution-Proof” Adhesives

6.4.1. Basic Outline

The above described experiments (chapters 5.1 and 6) relate to the delicate interactions between macromolecular chains of the synthesized HASE systems and show the influence of specific factors on the rheological properties.

The process of adhesion can roughly be divided into two steps. The first is the wetting of the surfaces and binding them together and the second is the hardening of the adhesive bond. For the first step the adhesive needs to flow relatively easily, which is directly related to the above considered ratios of storage and loss moduli ($\tan \delta$), as well as to their absolute values. On the other hand the adhesive material needs to withstand strong loads during service. For this it is necessary that adhesive undergoes hardening process (chemical or physical).

Two basic categories of adhesives can be distinguished based on their setting mechanism: chemical or physical induced setting systems, sometimes also referred as reactive and non-reactive adhesives. The chemical setting, also described as “curing”, usually corresponds to a (cross-linking) polymerization reaction to develop the cohesive strength, and will not be discussed in details within this contribution.

For the considered HASE based labeling adhesives the transition between wet and dry states (setting process) is a key element of characterizing the overall performance of the adhesive material. The main setting mechanism for HASE based adhesive systems is the quick increase of the dynamic modulus after removal of applied shear force via increased inter- and intramolecular interactions and reconstruction of physically cross-linked network. This includes the polymer chain

relaxation, described above in the chapter 5.1.4, and reassembly of the hydrophobic domains, destroyed upon applied shear force.

6.4.2. Dilution Induced Viscosity Reduction

In this chapter we investigate the sensitivity of obtained HASE systems towards the dilution with water and elucidate its importance for adhesive behavior. As it will be presented, amphiphilic additives can be employed to reduce the sensitivity of the HASE solutions towards dilution. These observations are particularly important for labeling adhesive applications, where the “condensed-water resistance” and corresponding setting time on wet substrate can be drastically improved via this approach.

The proposed mechanism of the reduced sensitivity towards dilutions is presented On the Figure 44. As it was described before, the addition of amphiphile leads to the reduction of the dynamic modulus. Same effect is observed upon dilution of the system with water. However, dilution of the amphiphile containing system with water leads to reduction of the amphiphile concentration, consequently leading to possible improvement of the mechanical properties in case of proper ratios of the system components.

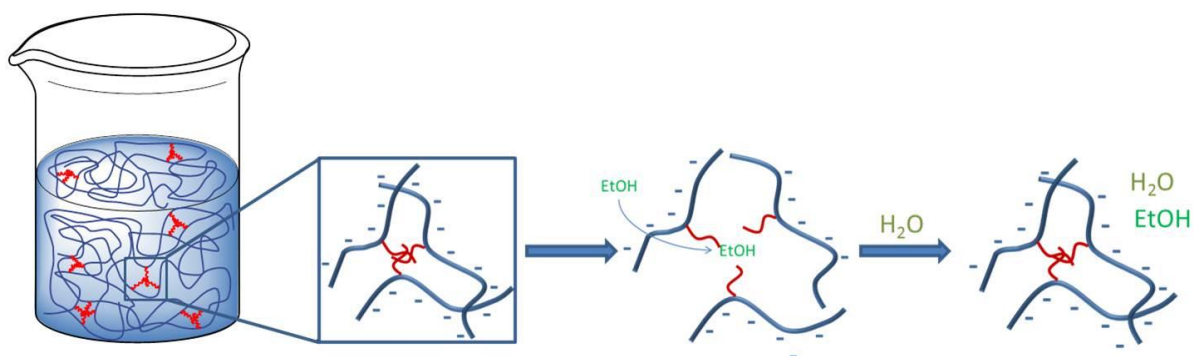


Figure 44: Hypothetical mechanism of the effect of alcohol (amphiphile) on the hydrophobic domains and the reduced sensitivity towards dilution

This mechanism can lead to the described improved setting behavior due to strengthening the physically cross-linked network upon mixing with condensed water on the wet substrate. Even though the reduced sensitivity towards water dilution can be considered as the simplest case of improved setting behavior based on the suggested mechanism, ultimate target could be the complete elimination of the sensitivity of rheological parameters towards dilution.

The following experiments were designed to investigate the sensitivity of the obtained HASE systems towards dilution with water. Unless stated otherwise, the term “dilution” describes the dilution of the system with water. The systems with different contents and different types of amphiphilic additives were investigated. They were diluted with water and the changes of the rheological properties were monitored. In the upcoming chapters corresponding results are provided and the conclusions are drawn.

6.4.2.1. Effect of the Content of Alcohol

Similarly to the above considered cases where the influence of the additives on the rheological behavior has been reported (chapter 6.2 and 6.3), the investigation of the effect of additives on the dilution induced viscosity reduction is divided into two parts. In the first part the influence of the content of the additive is presented, while the influence of the type (hydrophobicity) of the additive is described separately. In this chapter the investigations of the content of additive (ethanol) on the rheological properties of the HASE samples upon dilution is performed and the dilution induced viscosity reduction is assessed. It should be noted that unless otherwise stated, the solid content of the corresponding latexes was 20%.

Analogous to the systems considered in Chapter 6.2, polymers with high content of hydrophobic monomer (BA) and C18 copolymerizable ultrahydrophobe were employed for these observations, with overall composition MMA/BA/MAA=20/50/30 wt.%, 5wt.% ODA and 0.8 wt.% 1-dodecanethiol. Table 9 provides the list of samples with different content of ethanol and corresponding amounts of added water (e.g. dilutions) for these experiments and the values of the dynamic modulus.

Table 9: Contents of the added ethanol and the water (wt.%) to the sample with the composition: MMA/BA/MAA=50/20/30 wt.%, 5 wt.% ODA and 0.8 wt.% 1-dodecanethiol. pH=8.4

Sample ID	Ethanol Content*	Added Water**	Complex Modulus (Pa)
	wt.%	wt.%	
AD-1	0	0	529
AD-1-a	0	0.5	495
AD-1-b	0	1	477
AD-1-c	0	2	447

AD-1-d	0	3	420
AD-1-e	0	5	376
AD-2	2	0	283
AD-2-a	2	0.5	274
AD-2-b	2	1	267
AD-2-c	2	2	259
AD-2-d	2	3	241
AD-2-e	2	5	210
AD-3	4	0	176
AD-3-a	4	0.5	169
AD-3-b	4	1	163
AD-3-c	4	2	157
AD-3-d	4	3	146
AD-3-e	4	5	133
AD-4	6	0	112
AD-4-a	6	0.5	108
AD-4-b	6	1	102
AD-4-c	6	2	96
AD-4-d	6	3	95
AD-4-e	6	5	86

* Ethanol content represents weight percent to neutralized HASE solution

** Amount of added water represents the weight percent to neutralized HASE-solution/ethanol mixture

Rheological measurements were performed for the samples listed in Table 9. The values of the dynamic modulus against the amount of added water (for the systems with different alcohol content) are plotted on Figure 45 A – D. In order to properly evaluate the sensitivity of dynamic modulus towards dilution, obtained values were normalized. The slope values of the linear fit of the obtained data points is used for the evaluation of the sensitivity towards dilution. The more negative the slope value becomes (e.g. the steeper is the slope), the more sensitive is the system towards dilution, e.g. the higher is the reduction of the viscosity or dynamic modulus.

It is observed that the slope values are in correlation with the content of the additive (ethanol) in the investigated systems.

It was found that increasing the content of ethanol leads to increased slope values. Thus, the systems with higher content of ethanol show obviously reduced sensitivity towards dilution. The slope values as a function of ethanol content are provided in Figure 46. It is important to note that the systems show a linear dependency of the slope values on the ethanol content with good correlation, suggesting the validity of the predicted and observed trend.

As described above, the observed reduced sensitivity towards the dilution with condensed water can improve the tack and setting behavior of an adhesive material. In other words, lower or no reduction of the wet tack will occur upon dilution of the adhesive, since the depression of the mechanical characteristics is less pronounced.

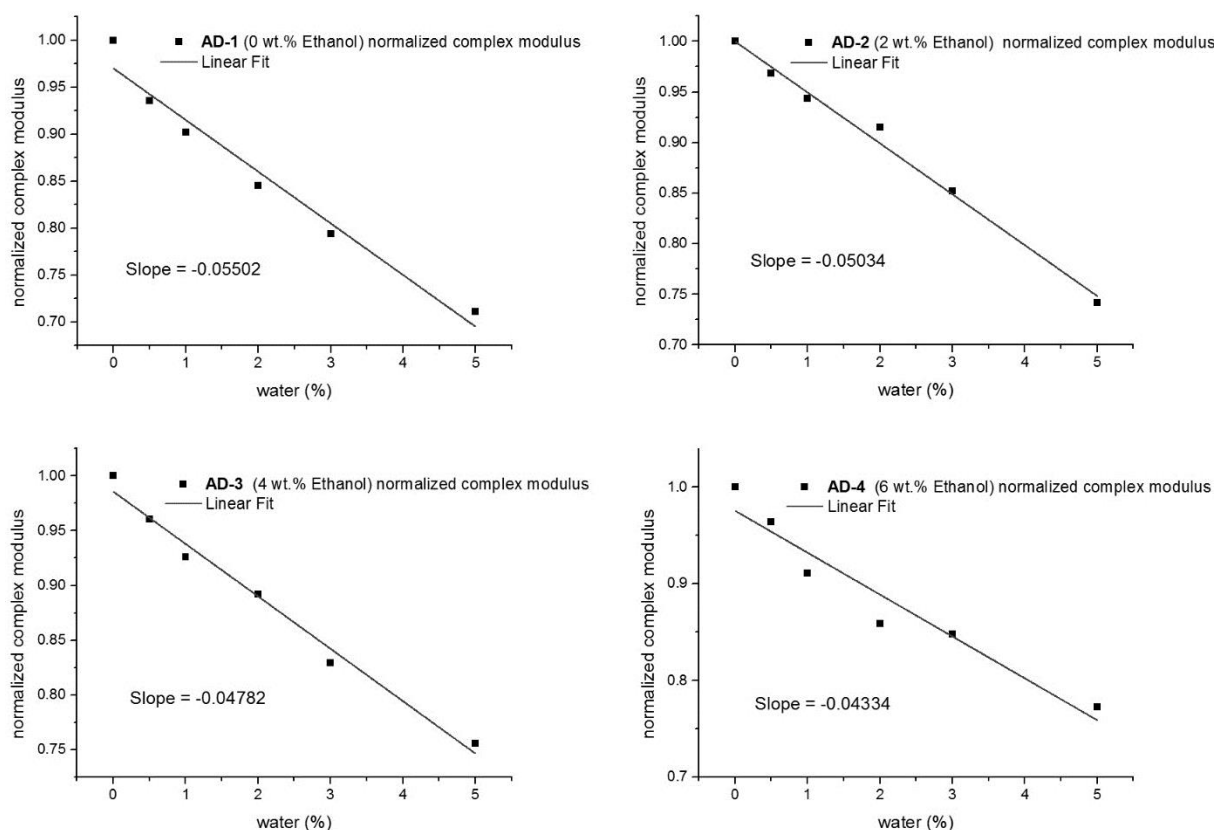


Figure 45: Change of the dynamic modulus upon dilution of the ethanol containing samples with water. Slope values can be used for comparison of the samples with different contents of the ethanol. Values of the dynamic moduli in the Table 9 were normalized for proper comparison.

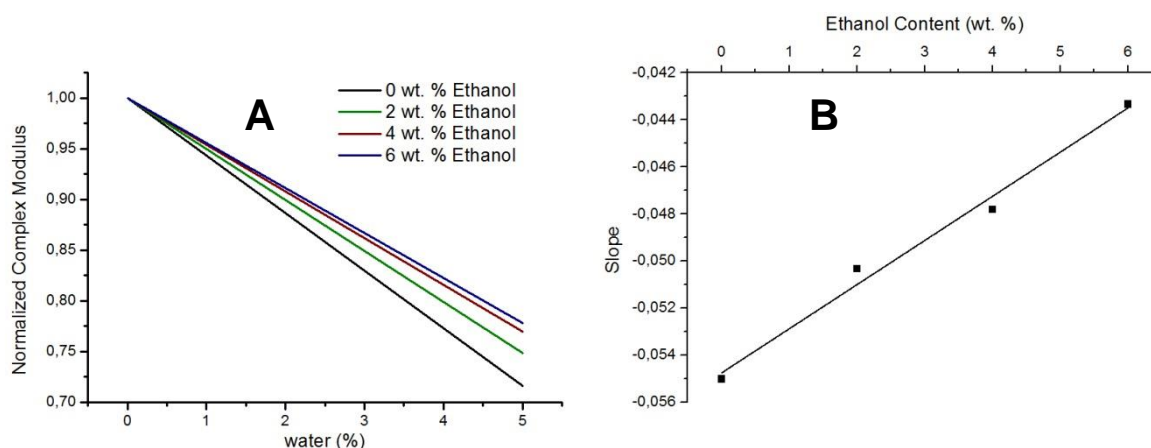


Figure 46: (A) overlay of the linear regressions represented in Figure 45 (note that all plots are normalized to 1 for proper visual representation) (B) The slope values of the linear regressions represented on the Figure 45 as a function of the ethanol content. Both graphs show the reduced sensitivity of investigated systems towards the dilution with water.

The sensitivity of the mechanical properties of HASE systems towards dilution with different contents of other, relatively more hydrophobic alcohol, such as the propan-1-ol was also investigated.

The list of samples with different amounts of the propan-1-ol as an additive and the corresponding complex modulus values upon dilution with different amounts of water is provided in Table 10. It is worth noting that the propan-1-ol has a stronger effect on the dynamic modulus of the obtained HASE systems. This can be explained by the mechanism, suggested in Figure 41 and Figure 44. Consequently, unlike the ethanol containing systems, where the maximum ethanol content is 6 wt.%, the maximum content of the propan-1-ol in listed experiments is only 3 wt.%. General effects of different types of alcohols on the rheological parameters was investigated above (see chapter 6.3)

Table 10: Contents of the added propan-1-ol and the water (wt.%) to the sample with the composition: MMA/BA/MAA=50/20/30 wt.%, 5 wt.% ODA and 0.8 wt.% 1-dodecanethiol. pH=8.4

Sample ID	Propan-1-ol Content wt.%	Added Water wt.%	Complex Modulus (Pa)
AD-5	0	0	470
AD-5-a	0	0.5	452
AD-5-b	0	1	434
AD-5-c	0	2	398

AD-5-d	0	3	375
AD-5-e	0	5	329
AD-5(1)	1	0	248
AD-5(1)-a	1	0.5	265
AD-5(1)-b	1	1	250
AD-5(1)-c	1	2	246
AD-5(1)-d	1	3	218
AD-5(1)-e	1	5	184
AD-5(2)	2	0	156
AD-5(2)-a	2	0.5	151
AD-5(2)-b	2	1	149
AD-5(2)-c	2	2	139
AD-5(2)-d	2	3	131
AD-5(2)-e	2	5	118
AD-5(3)	3	0	97
AD-5(3)-a	3	0.5	94.6
AD-5(3)-b	3	1	92.4
AD-5(3)-c	3	2	92.8
AD-5(3)-d	3	3	82.6
AD-5(3)-e	3	5	76.4

Similarly to the above described case, where ethanol was employed as an amphiphilic additive to observe the dilution induced viscosity reduction (Table 9, Figure 45), the normalized values of complex modulus are again plotted against the amount of added water. The slope values of the corresponding linear regressions are again used for the comparison of the dilution sensitivity. Analogous to the above considered ethanol containing systems, a reduced sensitivity of the propan-1-ol containing systems towards dilution is observed (Figure 47).

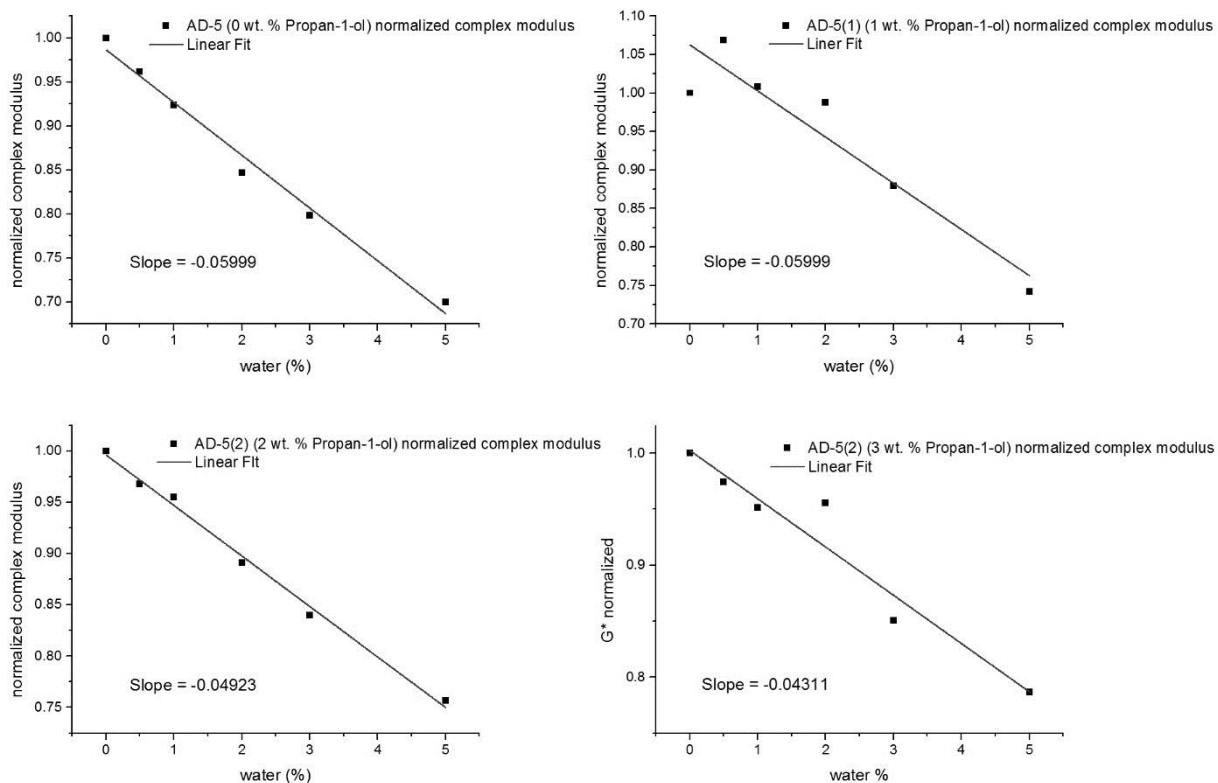


Figure 47: Change of the dynamic modulus upon dilution of the propan-1-ol containing samples with water. Slope values can be used for comparison of the samples with different contents of the ethanol. Values of the dynamic moduli in the **Table 10** were normalized for proper comparison.

As in case of the ethanol, the different contents of the added propan-1-ol also lead to a different sensitivity of the HASE solutions towards dilution. Because of the significant data scattering (caused probably by experimental error in the sample with 1 wt.% propanol, see Figure 47), the slope values for the HASE solution with 0 wt.% and 1 wt.% are identical. However, the overall trend, analogous to the one observed on the Figure 46, is still maintained, showing the lower sensitivity towards dilution for the systems with higher propan-1-ol content.

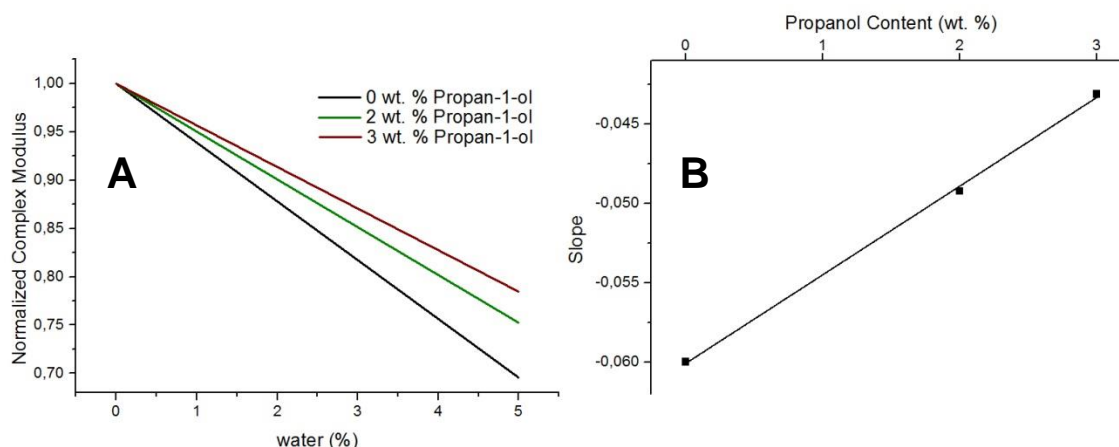


Figure 48: (A) Overlay of the linear regressions represented in Figure 47 (note that all plots are normalized to 1 for proper visual representation) (B) The slope values of the linear regressions represented on the Figure 47, showing the reduced dilution sensitivity of high propan-1-ol containing HASE solutions.

It should be noted that the reference experiments were conducted, where instead of amphiphilic additives, different amounts of water were employed, to exclude above listed effects on hydrophobic associations or altered dielectric constant of the medium (chapter 6.1). In these experiments no increase of the slope values was observed, as opposed to the systems, which contain amphiphilic additives.

From the above described experimental results it can be concluded that amphiphilic additives can be used not only for tuning the storage and loss moduli of the obtained HASE systems, but can increase their resistance towards dilution with water. Easy preparation procedures, together with the simple tuning of rheological behavior makes the investigated systems unique for adhesive applications.

6.4.2.2. Effect of Hydrophobicity of the Amphiphilic Additive

Based on the experimental results, described in the chapter 6.4.2.1, the sensitivity of the systems' rheological behavior towards dilution can be assessed as a function of the type of employed amphiphilic additive.

Based on the data shown in the Figure 45 and Figure 47, in the presence of the 6 wt.% ethanol, the slope values (used to assess the sensitivity towards dilution) increase by $\approx 20\%$. Change of the same parameter in the presence of only 3 wt.% propan-1-ol is $\approx 28\%$. This observation shows much higher efficiency of the longer chain (relatively more hydrophobic) alcohol for the reduction of the sensitivity towards dilution.

This observation is in a good correlation with the hypothesized mechanism, schematically depicted in Figure 41 and Figure 44. Relatively more hydrophobic additive destabilizes the hydrophobic domains to greater extent. Consequently, the reduction of the concentration of such additive upon dilution with water leads to much more pronounced countereffect.

6.4.3. Variation of Composition of Latexes for Improved Effect of Additives on the Dilution Induced Rheology Change

In the above described experiments the highest content of the alcohol is limited by the decrease of the dynamic modulus. Maximal reliable measurements were conducted with the systems containing 6 wt.% ethanol or 3 wt.% propan-1-ol. Higher contents of these additives lead to extremely low values of mechanical modulus for the assessment of the viscoelastic responses. Consequently, even though the interesting trend of reduced sensitivity towards dilution was observed, it was found impossible to obtain the systems with higher tolerance towards dilution.

However, it is highly desirable to extend the observed trends and to achieve an even less pronounced dilution induced viscosity reduction. Based on the previous experiments (see chapter 6.4.2.1 and chapter 6.4.2.2) it is expected that increasing the content of the considered additives the desired effect can be achieved.

In order to increase the content of additives in investigated HASE systems, it is necessary to increase the initial dynamic modulus of the system before the addition of any amphiphilic solvent. Mechanical properties can be improved in different ways as it was described in previous chapters or reported in various publications (increased amount of the hydrophobe, altered composition, altered solid content *etc.*).^[46, 50, 51, 105]

In this chapter the systems with altered composition and increased solid content are investigated. These changes improve the mechanical properties of the systems, thus enabling higher the additive contents. The results of these experiments are described below in detail.

It should be noted that HASE systems, specifically synthesized for these experiments are characterized with much higher values of dynamic modulus after neutralization compared to the systems investigated earlier in chapter 6. Therefore,

besides the tuning of the dilution sensitivity, amphiphilic additives play dual role and reduce the dynamic modulus to the range of interest.

6.4.3.1. Dilution Sensitivity for Systems with Altered Monomer Composition

In the first set of experiments systems with altered monomer composition were investigated. Polymers with the composition MMA/BA/MAA=55/15/30 wt.%, 0.8 wt.% of 1-dodecanethiol and \approx 4.8 wt.% of HDMA (molar equivalent of 4 wt.% of LMA, analogous to above described experiments with 5.1 wt.% ODA) were prepared. As mentioned above, corresponding solutions upon neutralization show much higher mechanical modulus compared to the systems investigated in chapter 6.4.2.1. To investigate the sensitivity towards dilution, rheological measurements were conducted for systems containing 10 wt.% of ethanol and further diluted with different amounts of water. Table 11 provides the values of dynamic modulus for the investigated samples. As it can be observed, the values are in approximately the same region as for the samples investigated above (Table 9 and Table 10).

Table 11: Dynamic modulus of the systems with the monomer ratio MMA/BA/MAA=55/15/30, 0.8 wt. CTA and 4.8 wt.% HDMA with 10 wt.% ethanol and different amounts of added water, pH \approx 8.

Amount of Added Water (wt.%)	Dynamic modulus G* (Pa)
0	268
0.5	264
1	265
1.5	259
2	259
3.5	247

Analogous to above described experiments (chapter 6.4.2) a linear regression plot was built for the normalized values of the dynamic modulus (Figure 49) for the samples listed in Table 11. As in above described cases the linear regression was used to observe the slope value, which is the measure of the system's tolerance towards dilution. A significantly higher slope value is observed in this experiment as compared to the systems with lower ethanol content (-0.0217 as compared to -

0.04311 observed in AD-5(2) (chapter 6.4.2.1)). This observed strong slope increase is caused by a drastically reduced sensitivity (higher tolerance) towards the dilution.

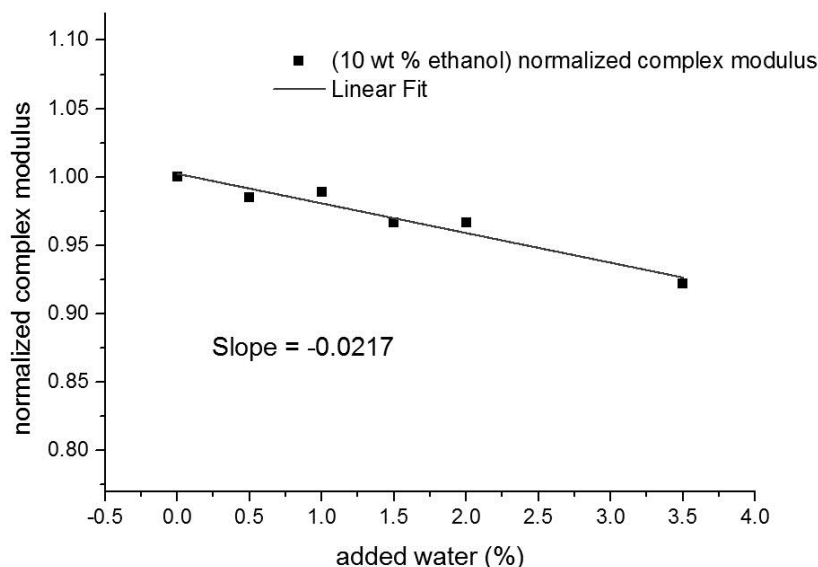


Figure 49: Normalized complex modulus of the systems with the composition MMA/BA/MAA=55/15/30 wt. %, 4.8 wt.% HDMA and 0.8 wt. % 1-dodecanethiol against the amount of the added water. pH \approx 8. Higher value of the slope shows the lower sensitivity towards dilution in comparison to above investigated samples.

It should be noted that due to extremely high viscosity of the corresponding polyelectrolyte solution, the reference measurements without ethanol were found impossible to perform. However, based on this results it is obvious that the systems with tailored rheological properties and higher tolerance towards dilution can be obtained.

It is also important to take into account that the reduced sensitivity towards dilution can be not solely a result of the described effect of amphiphilic additive (Figure 44), but also caused by higher T_g values (due to altered composition) and corresponding lower flexibility of the polymers, involved in this experiments. However, it is important that cooperative effect of these factors can lead to the systems with intended rheological properties and lower sensitivity towards dilution.

6.4.3.2. Dilution Sensitivity of Systems with Increased Solid Content

Systems with higher solid content were also employed for the investigation of the sensitivity towards dilution. Latexes with 30 % solid content were prepared using the surfactant Dowfax 2A1 (see chapter 4.2.1.3 and chapter 8.1.1). As expected, these systems are also highly viscous and the dynamic modulus is reduced to intended

values only in the presence of the added amphiphile (ethanol). Besides, in such systems the presence of the ethanol is necessary already at the stage of the neutralization due to extremely high viscosity, which hinders the neutralization process. The additional hindrance also arises due to the described presence of the peak in the viscosity at intermediate pH values.

In these systems as high as 20 wt. % ethanol was employed as an amphiphilic additive. Observations on the sensitivity towards dilution were performed as described previously. In addition, one extra measurement point with as much as 7 wt. % of added water was also performed in order to avoid uncertainty, caused by improper fit upon data scattering at relatively high (close to 0 or > 0) slope values. The results are provided on the Figure 50.

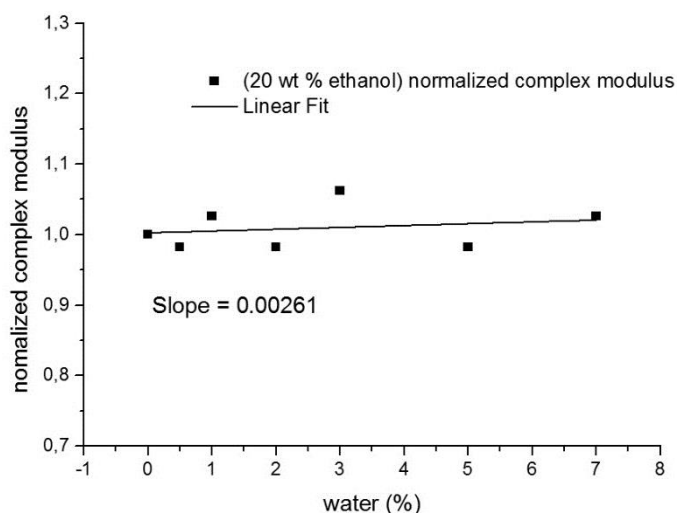


Figure 50: Normalized complex modulus of the systems with same composition as shown on the Figure 49, but with 30 % solid content and 20 wt. % ethanol content vs. the amount of added water.

The obtained positive slope value described the extremely important system characteristic, where the dilution with water leads to actual increase of dynamic modulus and the phenomenon can be referred as “dilution induced thickening”. However, it should be taken into account that the degree of freedom, where the composition of the polymer and the additive content can be varied for such results is relatively small. Besides, the term “thickening” should be handled with care due to possible experimental error and significant data scattering while handling highly viscous systems in described experiments.

As a conclusion of the rheological investigations and observations described in chapter 6, it can be said that manipulation of the composition and amphiphilic additive content can lead to the systems with extremely suppressed sensitivity towards dilution, which is highly important for various adhesive applications. Reduced sensitivity towards dilution can potentially simplify the development of labeling adhesives, via directly correlating their rheological properties to their adhesive behavior, neglecting the potential decrease of the adhesive performance due to dilution with condensed water. Besides, above mentioned “dilution induced thickening” can improve the wet tack and setting behavior of the material owing to the improved mechanical properties of HASE based adhesives upon dilution with condensed water.

The data, presented in Figure 48, Figure 49, and Figure 50 clearly show that even though the systems, corresponding to these data, are different in composition and solid content, the mechanism, suggested in Figure 44 represents a valid concept for manipulating with reversible interaction mechanisms and for the obtaining the dilution resistant HASE based adhesive systems. Figure 51 provides the overlay of these data-lines for better visual representation, showing the drastic change of the response of complex modulus towards dilution.

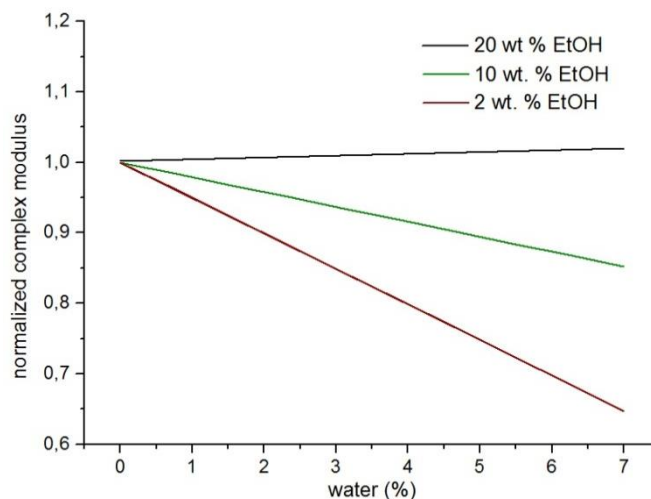


Figure 51: Overlay of the graphs showing the dilution response of different systems described above and provided in Figure 48, Figure 49 and Figure 50. Data have been extrapolated to same range for better visual perception.

7. Adhesion Behavior and its Correlation with Rheological Properties

Adhesion characteristics of the obtained HASE solutions for their implementation in labeling adhesive systems are one of the major topics addressed in this research. Various characteristics for the adhesion of the label paper on the substrates have been investigated via different methods. Measurements from relatively simple film formation and setting behavior studies to more complex wet tack and peel strength behavior were performed to find the correlation between rheological behavior and adhesive properties of HASE based adhesives. The obtained results are provided and discussed in upcoming chapters.

7.1. Film Formation Characteristics of the Obtained HASE Solutions

As it was described multiple times throughout the work, that here considered HASE based adhesives form the viscous liquids upon neutralization, able to flow under applied shear stress or under the influence of gravity. They form continuous films upon drying at room temperature. This feature is important for the application of the systems as adhesives. A continuous layer between the substrate and the label (or between two substrates) is highly desired to achieve the maximum mechanical properties and the highest durability of the adhesive system during service.

As it was described above, systems with different compositions were investigated throughout the work. It should be noted that upon increasing the hydrophobicity the turbidity of the obtained HASE solutions is increasing due to bigger size of the hydrophobic aggregates. At pH values above 7.5 the systems with the composition MMA/BA/MAA=55/15/30 wt.% forms completely transparent solutions, while the systems with higher content of more hydrophobic BA (MMA/BA/MAA=20/50/30 wt.%) are obviously opaque as shown on the Figure 52. However, upon drying microscale phase separation between hydrophilic polymer solution and hydrophobic domains disappear. Correspondingly no difference between the refractive indexes of the considered two phases are observed and completely transparent films are obtained (Figure 52).

Visual transparency of the obtained films is highly important for the final applications of the described systems as labelling adhesives for transparent labels and on the glass or plastic substrates.

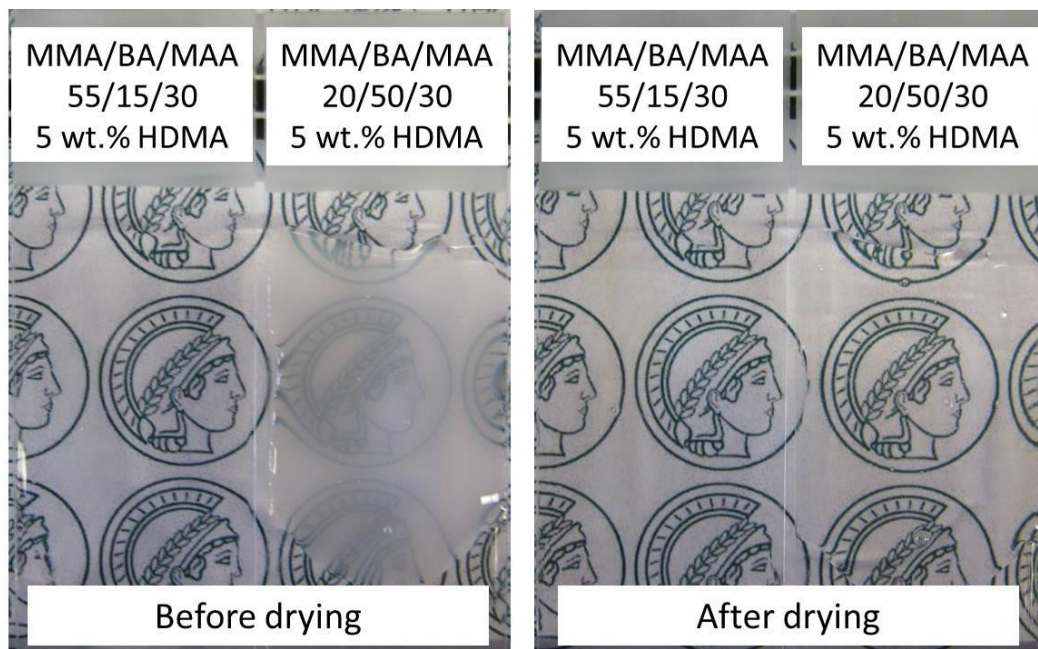


Figure 52: Formation of transparent films upon drying on the glass substrate. Both samples with high and low relative hydrophobicity are transparent after drying despite obvious differences of the initial solutions

7.2. Investigations of the wet tack of the obtained adhesive systems on the solid substrates

The wet tack behavior of adhesives is very sensitive to the applied measurement methods and can be employed mostly in comparative investigations. Here provided results are obtained according to the standardized experimental procedure described in chapter 8.11.

Tack is the property of an adhesive material, which allows it to adhere to another surface on immediate contact. It is the "stickiness" of the adhesive while being a fluid (e.g. fluid adhesive) or semi-fluid (e.g. pressure sensitive adhesive) state. There are two stages that must be considered with this concept. The first is the wetting stage where the tacky material must wet the substrate. This initial stage is controlled by physical-chemical properties, such as critical surface tension, viscosity, adhesive thickness, etc. The second stage is that of debonding the probe from the surface, and here viscoelastic properties of the adhesive come into play.

In other words, tack is the resistance to separation. Tack is not a true physical property of an adhesive, such as viscosity, modulus, or specific gravity. It is a complex property that has broad and somewhat qualitative meaning, but one that is very useful in practice. The quantitative meaning can only be defined through specific application conditions, as it will be presented below for the wet tack test of labelling paper on the polypropylene (PP) and glass substrates.

As described, tack properties are highly sensitive not only to the characteristics of substrates, but also to the rheological properties of the material. Therefore in these investigations we observe the wet tack behavior of the materials with different hydrophobicity and solid content on the different substrates and make corresponding comparison.

In order to investigate the influence of the rheological properties of obtained HASE adhesives on the wet tack behavior, systems with different compositions and equal (20%) solid content of the latex were studied. Samples with the same basic monomer composition (MMA/BA/MAA=55/15/30 wt.%) and different contents and types of the ultrahydrophobes (2 wt.% LMA, 4 wt.% LMA and 2 wt.% HDMA) were used in the observations.

Table 12 provides the list of samples, their corresponding dynamic modulus, as well as content and type of the ultrahydrophobe and the peel strength measurement results on polypropylene and glass as two different bonding surfaces as described in the experimental section (see chapter 8.11).

Table 12: List of the wet tack experiments on the different substrates with the latexes of different hydrophobicities and corresponding peel strength values (MMA/BA/MAA=55/15/30, rheological measurements: Frequency = 10 rad/s, strain = 0.1%).

Substrate	Type of the Ultrahydrophobe	Content of the Ultrahydrophobe (wt.%, to monomer)	Dynamic Modulus ($G^*/G'/G''$) (Pa)	Force (mN)
PP	LMA	4	485/199/442	200
PP	LMA	2	87/10/86	340
PP	HDMA	2	348/123/326	170

Glass	LMA	4	485/199/442	160
Glass	LMA	2	87/10/86	130
Glass	HDMA	2	348/123/326	160

For visual representation and comparison the peel strength results are provided on the Figure 53.

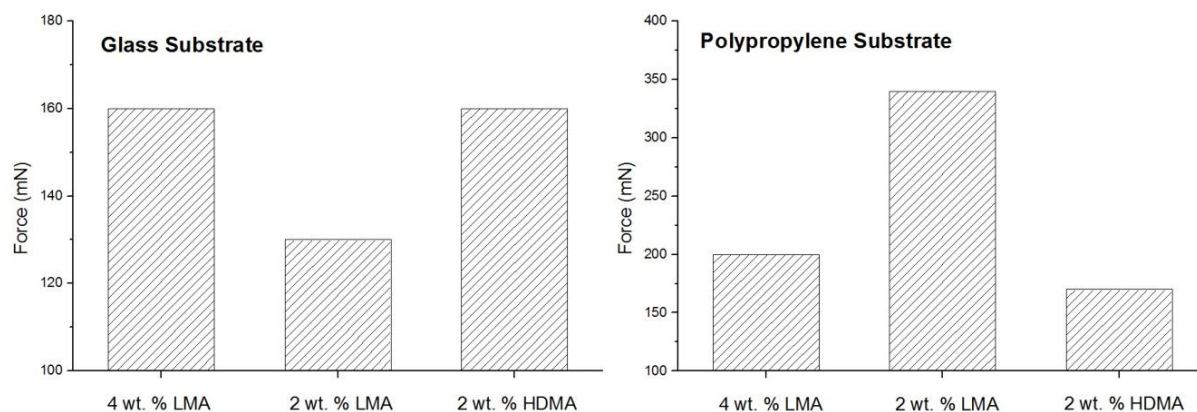


Figure 53: Peel strength measurements for the wet tack investigation of labelling paper on the polypropylene and glass substrates using different HASE based adhesive systems with various types and contents of ultrahydrophobe (note the different scales for different substrates).

The observed trends show that the wet tack behavior is directly related to the type of the substrate, as well as to the rheological properties of the HASE based adhesives. Lower values of G' and G'' as well as a complex modulus leads to lower tack values on glass substrates, while the opposite trend is observed in case of the polypropylene substrates.

Taking into account the low surface energy of polypropylene substrates, the high tack of the mentioned adhesive can be explained by its better flow characteristic due to lower cohesion and low viscosity. It can be speculated that at such low solid contents and low surface energy the polymer/substrate interaction has a relatively low effect on the tack properties and that the rheology of the fluid adhesive is the determining factor for the obtained values. This suggestion is further supported in experiments with samples containing 30% polymer.

On the other hand, the high surface energy of the glass substrate can contribute to a better interaction between adhesive and the substrate, while the higher dynamic

modulus of the corresponding samples leads to higher cohesion and therefore higher tack values.

Similar experiments were also conducted for the HASE adhesive systems with higher solid content (30%) on both substrates ($G^*=2590$ Pa, $G'=1540$ Pa and $G''=2090$ Pa at 10 rad/s frequency and 0.1% deformation). For these investigation the sample with the basic composition (MMA/BA/MAA=55/15/30) and 2 wt.% LMA was used, since it showed a best tack behavior on the polypropylene substrate.

As expected, it was found that the increasing solid content strongly influences the wet tack behavior. However, an additional important change was observed and is discussed below. The results of the measurements are provided on the Figure 54.

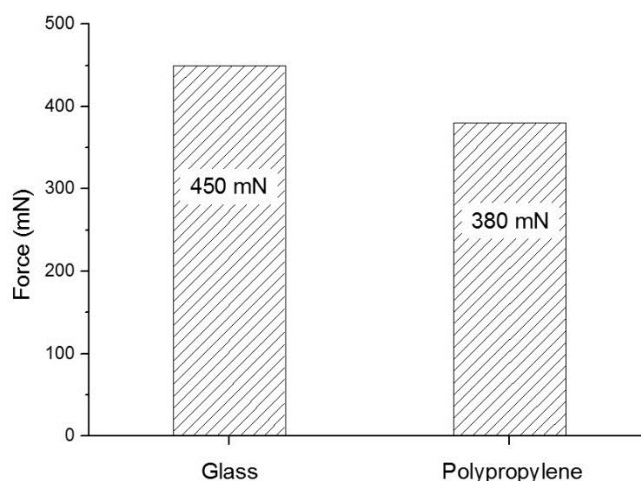


Figure 54: Experimental results of the wet tack behavior of the labelling paper on glass and polypropylene substrates with HASE based adhesive (MMA/BA/MAA/55/15/30 wt. %, 2 wt.% LMA).

As it can be seen, compared to the systems with 20% solid content, the peel strength values are much higher. However, interestingly the higher tack on glass substrates was observed in repeatable experiments, as compared to the polypropylene substrates.

This result does not coincide with the results obtained for the 20% solid content samples with analogous composition. As suggested above, the possible reason for such behavior is that at low solid content the better flow characteristics lead to different wetting of the substrate, governing the wet tack characteristic. On the other hand, in case of the high solid content systems much higher dynamic modulus there is no or minor effect of the adhesive flow during peeling process.

Neglecting the easier wetting of the substrate due to easy flow, the interaction between polymer and the substrate (or the adhesive and the substrate) has a more pronounced effect on the wet tack behavior. Consequently, an expected strong interaction with a high energy surface of the glass leads to the higher tack force on glass substrate.

Thus, it can be concluded that a minor variation of the composition (ultrahydrophobe content) can greatly affect the wet tack behavior, which is caused by the corresponding variation of the rheological behavior. Solid content, as another tool for the rheology tuning, has been presented to be also of high significance for the improvement of adhesive properties.

The observed correlations are of high importance for development of adhesive materials based on the known mechanisms of rheology adjustment.

7.3. Setting Behavior of the HASE Based Adhesives

The setting behavior of the adhesives represents an important characteristic behavior. It defines the ability of the adhesive to transform from its original state at the time of application to the final “hardened” state, which will be able to withstand the separation forces of different mechanical loads during the service.

It is extremely important that the setting time is optimized based on the particular application, e.g. it should not be too short, to enable the application on the substrate, and not too long, so that final hardening is achieved within a reasonable time scale. Similar to wet tack, this characteristic is also a rather qualitative one. A meaningful quantitative assessment can be given for particular application conditions only. Consequently, as in case of the wet tack tests, the assessment is made only for the particular compositions of the polymer solutions on selected substrates and the comparison is made. Besides, due to higher experimental error the data are usually rather more scattered.

The setting behavior studies were conducted according to the standardized experimental procedure described in chapter 8.11. The results are provided in the Figure 55.

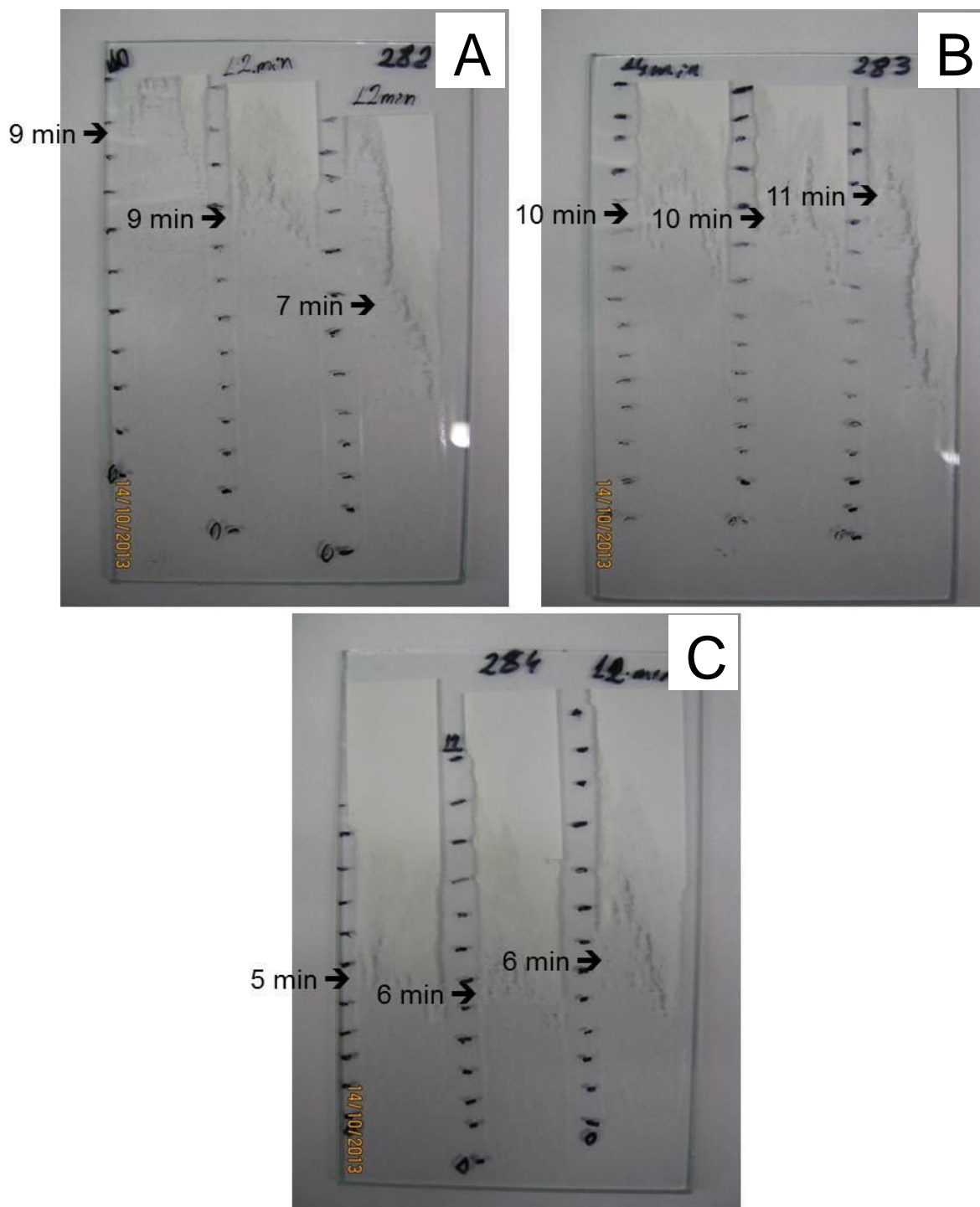


Figure 55: Setting behavior of the adhesive on glass substrate with a solid content of 20%, basic composition MMA/BA/MAA=55/15/30 wt.% and (A) 4 wt.% LMA, (B) 2 wt.% LMA and (C) 2 wt.% HDMA as hydrophobic modifier.

As it can be concluded from these experiments, the setting behavior is closely related to the composition and the corresponding mechanical properties of the obtained adhesives. Therefore the adhesive behavior can be tuned easily as described for the tuning of the rheological properties. A comparison of the times at

which fabric tear occurs for different systems, shows that systems with higher wet tack properties (see Figure 53) show shorter setting time, while the influence of the hydrophobicity (content of the ultrahydrophobe, Figure 55(A) and Figure 55(C)) can also be noticed, but can obviously not correlate to other properties due to intrinsic inaccuracy of the method.

It should be noted that the investigation of the same systems on the polypropylene substrate showed no fabric tear and even after complete drying the adhered label is easy to remove without damage. This result is not unexpected considering the fact that polypropylene is a low surface energy material, while employed adhesives represent solutions of hydrophilic polymer. Agirre *et al.* have reported the improved adhesion of the ODA containing pressure sensitive adhesives on the low energy substrates.^[84] However, no such trend was observed in above described cases. The possible reason is that in the HASE based adhesives the compatibility of the hydrophobic ODA with polypropylene substrate is probably largely outweighed by cohesive force, which is caused by the formation of hydrophobic domains in the considered water-based system.

Setting behavior on different substrates was also studied as a function of the solid content of HASE based adhesive. Sample with 30% solid content, described in the wet tack behavior studies (see chapter 7.2), was used for these observations. The results are provided in Figure 56.

It was found that unlike the wet tack, solid content does not have any significant influence on the setting behavior of the investigated HASE based adhesives within the experimental error. Surprisingly, even slightly longer setting times were observed for high solid content systems, which can probably be explained by slower drying, caused by the higher content of ionic groups, which are able to retain water. Taking into account the longer setting time, it should also be considered, that high solid content systems are characterized by higher wet tack, compensating for slower setting. Besides, slightly improved adhesion to the low surface energy polypropylene substrate was observed.

Nevertheless, it can be concluded that the observed trends concerning solid content and composition, investigated systems allow significant improvements of the adhesion properties via further optimization of these parameters.

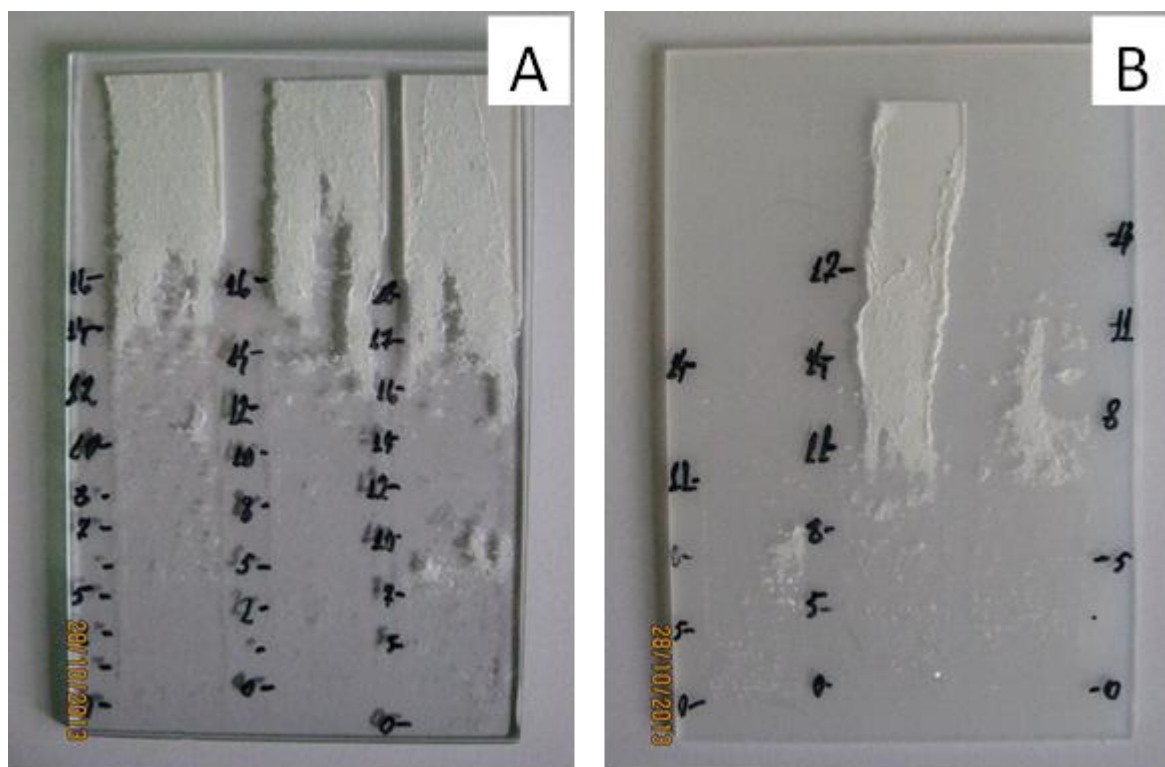


Figure 56: Setting behavior of the adhesive systems with the 30% solid content on (A) glass and (B) polypropylene substrates, with the composition MMA/BA/MAA/55/15/30 wt.%, 2 wt.% LMA.

From the experimental results given in this chapter it can be concluded that the obtained HASE based adhesive systems can relatively easily be adjusted to almost any particular applications on different substances. Increasing the solid content and the content of the hydrophobic BA, also leading to decrease of the glass transition temperature, can potentially improve the adhesion behavior to the low energy substrates.

8. Experimental Section

8.1. Synthesis of Alkali Soluble Latexes

Highly acid functionalized polymers were prepared by the miniemulsion polymerization techniques similarly to that reported elsewhere.^[106] In the standard procedure 72 mg of surfactant (SDS) was dissolved in 22 ml of water (except where the influence of surfactant concentration was investigated), while 100 mg of Initiator (KPS) was dissolved in 2 ml of water. (For oil soluble initiators, only the surfactant was dissolved in 24 ml water, while the initiator was premixed with monomers). 6g of monomer mixture (composed of three main monomers, polymerizable ultrahydrophobe (2-4 wt.%) and optional 0.048 g (0.8 wt.%) chain transfer agent (CTA, 1-dodecanethiol)) was added to the surfactant solution and pre-emulsified by stirring at 1000 rpm for 10 min. The miniemulsion was prepared by ultrasonication of the pre-emulsion at 90 % amplitude for 120 s (Branson sonifier W450 Digital, 1/2" tip) in an ice bath to prevent overheating. Then the miniemulsion was placed in a round bottom flask and bubbled with nitrogen to get rid of dissolved oxygen under magnetic stirring. The temperature was increased to 70 °C and the initiator solution was added. Samples were stirred at this temperature for 2 h. Full conversion was monitored with solid content analyzer. pH values of the system were ≈3 throughout the whole polymerization process.

8.1.1. Synthesis of the latexes with high solid content

Above given standard procedures apply to the latexes with 20% solid content. However, it cannot be employed for the systems with a solid content of 30% or above. In this case a different surfactant, Dowfax-2A1 was employed. The rest of the procedures are similar as described in the section 8.1.

8.1.2. Synthesis of semicrystalline pH responsive latexes

Semicrystalline pH responsive latexes, described in chapter 4.3, were synthesized according to above described procedure. Stable systems were obtained with Dowfax 2A1 as surfactant and a maximum content of 60 wt.% ODA relative to the total monomer amount. Systems with different ratios of MMA, BA, MAA and ODA were found unstable in the presence of the SDS as surfactant.

8.2. Observation of the Copolymerization Behavior

The course of reaction was observed by withdrawing samples from the reacting mixture at regular time intervals. The withdrawn samples were immediately added to a solution of the inhibitor 4-*tert*-butylcatechol in ethanol in order to quench any further polymerization before analysis. The inhibitor concentration was 500 mg/l. The samples were analyzed using gas chromatography (GC). 1 wt.% of hexan-1-ol relative to monomer content was added to the reaction system prior to miniemulsification as nonreactive substance and internal standard for GC, in order to follow conversion over time. The degree of conversion is defined as: $1-M/M_0$. M_0 and M represent the amount of the monomers at the beginning and upon specific time of the reaction.

8.3. Partitioning of the Monomers

Monomer partitioning studies were conducted in the following way: In a 20 ml vial 3 g of monomer mixture (including 2 wt.% tetradecylacrylate relative to total monomer content) was mixed with 12 g water and 35 mg surfactant (SDS) so that a final mixture is analogous to the ones employed in latex synthesis. The vials were capped with PTFE/silicon caps and the mixture was vigorously shaken for 10 min and then left 24 h in the oven at 70 °C to allow phase separation. The water phase was carefully withdrawn from the samples, placed in volumetric flasks, weighed and diluted with ethanol to avoid phase separation before measurement upon cooling down and analyzed using GC. Concentrations of monomers in organic phase were calculated by a mass balance. The densities used for water and monomers at experiment temperature were calculated according to literature.^[107] The partition coefficient of monomer i , k_{M_i} , is defined as the ratio of the molar concentration of monomer i in the organic phase ($[M_i]_o$) to the concentration of the same species in the aqueous phase ($[M_i]_w$):^[108]

$$k_{M_i} = [M_i]_o/[M_i]_w \quad (42)$$

8.4. Potentiometric Titration

The neutralization behavior of the synthesized latexes was investigated by the following typical procedure. 1 ml of latex (solid content 20 %) was diluted to 50 ml with distilled water. 0.1 M NaOH solution was added to the latex at constant rate of 0.1 ml/min with constant stirring using a magnetic bar. The pH change was monitored and the data was automatically logged at regular time intervals of 30 s. In this work potentiometric titration curves are given as they were recorded, pH against the amount of added alkali solution. The recalculation to ionization degree was not performed due to ambiguity of defining zero and complete ionization points.

8.5. Sample Preparation for Rheological Investigations

For the rheological investigations so-called neutralization curves were plotted adjusting the pH of the samples to different values and measuring rheological parameters at each pH value. 12% NaOH solution was used for pH adjustment. Defined amounts of NaOH solutions were added to the samples slowly and then stirred with a mechanical stirrer at 35 °C for 15 min. Highly viscous samples were left overnight in the oven at 50 °C to get rid of bubbles and assure equilibrium state throughout the sample

All rheological investigations were conducted at 20 (± 0.1) °C. Amplitude-sweep oscillatory experiments were conducted at fixed 10 rad/s angular frequency to determine the linear viscoelasticity region (LVR). Almost all samples exhibited linear viscoelasticity behavior within deformation range from 0.01% to 100% (small deviations were observed in highly viscous samples at deformations higher than 80%). Therefore, all frequency sweep experiments were conducted at 0.1% deformation. All frequency sweep experiments were conducted within frequency range 0.628 rad/s – 628 rad/s (0.1-100 Hz). Data points for comparison of loss factor values in different samples were picked up from measurements at 10 rad/s angular frequency and 0.1% of deformation. For the experiments described in chapter 6 (dependence of rheological behavior on the amphiphilic additives), the measurements were conducted at 30 rad/s frequency and data points from LVR at 0.1 % deformation were used for evaluation

8.6. Particle Size Measurements

The size of the latex particles were evaluated by dynamic light scattering using a Nano-Zetasizer (Malvern Instruments) at 25 °C. Before measurement the latexes were diluted by deionized water.

8.7. Gas Chromatography

Agilent 7820A GC system, equipped with column length of 50 m and the stationary phase HP-FFAP, suitable for the determination of organic acids in the mixture, was used. Oven temperature was gradually increased from 40 °C to 250 °C at heating rate of 10 °C/min.

8.8. Rheological Investigations

Rheological investigations were conducted on the Anton-Paar MCR 302 modular rheometer with the cone plate measuring system, Peltier element for precise temperature control and the evaporation blocking hood. Measurements were conducted at 20 °C. Diameter of the measuring cone and plate was 50 mm with cone angle 0,999°.

Amplitude sweep experiments were conducted in the range of 0.01 % to 100 % of deformation at the frequency of 10 rad/s. Different frequency (30 rad/s) was used in particular cases (investigation of the effect of amphiphilic additives, chapter 6), to enable the measurement of low viscosity systems.

Frequency sweep experiments were conducted in the frequency range of 0 – 100 Hz. The fixed deformation value (0.1 %) was chosen for frequency sweep experiments since all the samples at these deformations are in the linear viscoelasticity region.

8.9. Thermal Analyses

Differential scanning calorimetry (DSC) was measured on a TA instrument Q1000 analyzer. Freeze dried latex samples were examined in the temperature range 0 °C to 100 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

8.10. X-ray Diffraction Analyses

Crystallization of the polymers was investigated by X-ray diffraction (XRD) with a Philips Goniometer PW 1820 at a wavelength of 1.5418 Å (Cu-K α) on freeze-dried latex samples.

8.11. Wet-Tack and Setting Behavior

Wet tack of the obtained adhesives was measured according to following the standard procedure:

- Layer of viscous adhesive of 30 μm thickness was coated on the 25 mm wide labeling paper using a wire-bar
- The label was placed on the glass or polypropylene substrate and small pressure was applied with the brush
- The sample was clamped in the tensile-test machine (see chapter 3.4) and peeled at 180° at a rate of 300 mm/min
- Obtained force values (mN) are used for comparison of different adhesives on different substrates.

Setting time (fabric tear) was investigated as described below:

- 30 μm layer of viscous adhesive was coated on the 25 mm wide labeling paper using the wire-bar
- The label was gently pressed on the substrate with a brush
- Then the label was slowly peeled off from the substrate at regular time intervals and the time, at which the fabric tear occurs, was measured. Three parallel experiments were conducted to limit the error due to the inaccurate character of the method.

8.12. Materials

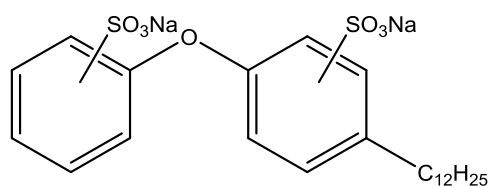
Material	Abbreviation	Supplier	Purity
2,2'-Azobis(2-methylpropionitrile)	AIBN	Wako (Japan)	Reagent grade
Ascorbic acid	AsAc	BDH Prolabo®	Reagent grade
1-Dodecanethiol	DDM	Alfa Aesar	98 %
2,2'-azobis(2-methylbutyronitrile)	V-59	Wako (Japan)	Reagent Grade
4- <i>tert</i> -butylcatechol		Sigma-Aldrich	>98 %
Butan-1-ol			
Butyl acrylate	BA	Acros Organics	>99 %
Dowfax-2A1		Dow Chemicals	≈50 % Sol.
Ethanol	EtOH		reagent Grade
Hexadecane	HD	Merck	>99 %
Hexadecanoic acid		Merck	>98 %
Hexadecyl alcohol		Sigma	99 %
Hexadecyl methacrylate	HDMA	ABCR	98 %
Lauryl methacrylate (dodecyl methacrylate)	LMA	Aldrich	96 %
Methacrylic acid	MAA	Merck	>99 %
Methyl methacrylate	MMA	Merck	99 %
Octadecyl acrylate	ODA	Sigma	97 %
Potassium persulfate	KPS	Merck	>99 %
Propan-1-ol			Reagent grade

Experimental Section

Sodium dodecyl sulfate	SDS	BASF	Reagent grade
Sodium Formaldehyde Sulfoxylate	SFS	Merck	Reagent grade
Sodium hydroxide	NaOH	Karl Roth GmbH	>99 %
Tetradecyl acrylate	TDA	ABCR	95 %
<i>tert</i> -butyl hydroperoxide		Acros Organics	70 % sol. In water

Chemical Structure:

Dowfax 2A1



9. Conclusions and Outlook

In this work we have presented a novel single step synthetic procedure for hydrophobically modified alkali soluble latexes (HASE) via a miniemulsion-analogous method. This facile method simplifies the copolymerization of the monomers with basically “opposite” character in terms of their hydrophilic/hydrophobic nature, which represent one of the main challenges in water based systems. Considered systems do not represent classical miniemulsions due to a high content of water soluble monomers. However, the polymerization mechanism was found to be rather similar to miniemulsion polymerization process.

The influence of the different factors on the system stability has been investigated. It has been concluded that unlike classical miniemulsions highly hydrophobic hexadecane cannot be employed as a costabilizer due to a probable incompatibility with the relatively hydrophilic polymers. The utilization of oil-soluble initiator was found also not suitable and did result in partial or complete coagulation. This observation can be explained by a strong composition drift, where the hydrophobic monomers initially polymerize within droplet while the hydrophilic monomers polymerize at the later stage, thus creating a so-called “hairy layer”, leading to particle bridging and coagulation.

The copolymerization behavior studies typically showed strong composition drifts during copolymerization. It was found that the copolymer composition drift can be suppressed via changing the initial monomer ratio. Thus, not only the ratio and hydrophobicity of nonionogenic monomers, but also the suppressed copolymer composition drift contributes to alkali solubility of the obtained systems.

The neutralization behavior of the obtained HASE systems was investigated via potentiometric titration. It was found that at higher acid contents the pK_a of the acid groups was independent of the ratio of ionogenic monomers, while significant sensitivity was observed in the systems with low acid content. This behavior was explained via the balance between charge repulsion and conformational free energy, which is caused by chain flexibility and weak attractive interactions.

The rheological behavior of the obtained systems as a function of the different parameters, such as pH, composition (ultrahydrophobe content) and additive type and content has been investigated.

pH dependent rheology studies revealed that at intermediate pH values the investigated systems exhibit a sharp increase in viscosity, with characteristic peak, followed by the relatively small reduction of mechanical properties and more or less well defined plateau.

Detailed investigation of the storage and loss moduli, damping factor and the crossover frequencies of the samples showed that at the initial stages of the neutralization the systems show microgel-like behavior. It was concluded that the change of the refractive index of the latex particles at this stage make the systems visually transparent while no dissolution has occurred yet and the systems represent swollen particles, where the refractive index of the solvent and the particle match.

Besides, the pH depend rheology studies was later employed to determine the region where the rheological properties are reproducible and less sensitive to subtle pH regulation.

The dependence of the rheological properties on the content and the type of the ultrahydrophobe showed that the tuning of the mechanical properties can be easily achieved via minor (few percent) but significant changes in the content of the latter. Besides, changing the hydrophobicity of the ultrahydrophobe via increasing the carbon chain length represents another simple method for achieving the same results. Generally speaking, the overall hydrophobicity of the hydrophobic modifier and the corresponding hydrophobic attractive interactions, combined with the electrostatic repulsion forces, can be used for fine-tuning the rheological properties.

The influence of amphiphilic additives (especially alcohols) on the rheological behavior of the obtained systems has been studied. An analogy was made between micellation of surfactants and the formation of hydrophobic domains between hydrophobic groups of the polymer side chain.

It was revealed that the content of the alcohol reduces the dynamic moduli via weakening the hydrophobic interactions, while the altered charge repulsion due to change of the dielectric constant of the medium can also contribute to similar overall

effect, though supposedly this latter effect is relatively weaker. It was also found that storage modulus is more sensitive to the additive content compared to loss modulus.

Closer investigations of the influence of the hydrophobicity of amphiphile (carbon chain length of the alcohol) showed also similar trends regarding the rheological behavior of the system. Increasing the carbon chain length leads to decreased dynamic modulus, while the storage modulus is affected to greater extent compared to loss modulus.

Dilution induced viscosity reduction was investigated in different systems, without or with different amounts or types of the amphiphilic additive. Possibility of the controlled response to dilution was explored. It was concluded that the sensitivity towards dilution can be reduced, and in extreme cases even the increase of the dynamic modulus can be observed, which is of high importance for the setting behavior of the adhesive material.

In the last part of this work, the adhesive behavior of the obtained HASE systems was investigated on different substrates (polypropylene and glass) for the standard labeling paper. Wet tack and setting behavior was studied and the trends for possible applications have been evaluated.

The novel synthetic procedure, investigation of rheological properties and the possibility of the tuning via additives, investigated in this work create a firm background for the development of the HASE based adhesives as well as rheology modifiers with vast variety of possible applications due to ease of tuning the mechanical and rheological properties of the systems.

10. Abbreviations and Symbols

10.1. Abbreviations

AIBN	Azobisisobutyronitrile (2,2'-Azobis(2-methylpropionitrile))
ASE	Alkali Soluble Emulsion
BA	Butyl Acrylate
CTA	Chain Transfer Agent
DLS	Dynamic Light Scattering
EA	Ethyl Acrylate
EtOH	Ethanol
FID	Flame Ionization Detector
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HASE	Hydrophobically Modified Alkali Soluble Emulsion
HDMA	Hexadecyl Methacrylate
HLB	Hydrophilic-Lipophilic Balance
KPS	Potassium Peroxydisulfate
LMA	Lauryl Methacrylate
LVR	Linear Viscoelasticity Region
MAA	Methacrylic Acid
MMA	Methyl Methacrylate
NMR	Nuclear Magnetic Resonance
ODA	Octadecyl Acrylate
O/W	Oil in water
PP	Polypropylene
SDS	Sodium Dodecyl Sulfate
TDA	Tetradecyl Methacrylate
VOC	Volatile Organic Compounds

V-59	2,2'-Azobis(2-methylbutyronitrile)
wt. %	Weight Percent
W/O	Water in oil

10.2. Symbols

ε	Dielectric Constant
ε_0	Permittivity of Vacuum
γ_{12}	Surface Tension between phases 1 and 2
γ	Strain
$\dot{\gamma}$	Derivative of the Strain
δ	Phase Angle
η_s	Solution Viscosity
$[\eta]$	Intrinsic Viscosity
η	Viscosity
κ^{-1}	Debye Length
$\Pi_{osmotic}$	Osmotic Pressure
σ	Shear Stress
τ	Relaxation Time
ω	(Radial) Frequency
A	Hamaker Constant / Surface Area (defined in text)
D_e	Deborah Number
D	Diffusion Coefficient
d	diameter
F	Force
G^*	Complex Modulus
G'	Storage Modulus
G''	Loss Modulus

H	Interparticle Distance / Constant Assigned to Hydrophilic Group (defined in text)
I	Ionic Strength
k, k_B	Boltzmann Constant
k_{xy}	x and y monomer copolymerization reaction rate constant. x being the active end-group of copolymer chain
k_{M_i}	Monomer Partitioning Coefficient
l_b	Bjerrum length
L_0	Thickness of Polymer Layer for Steric Stabilization
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
n_H	Number of Hydrophilic Groups
n_H	Number of Hydrophobic (lipophilic) Groups
Pdl	Polydispersity Index
pK_a	Acid Dissociation Constant
R	Universal Gas Constant
R_h	Hydrodynamic Radius
R_T	Retention Time
S	Entropy
r_1 / r_2	Monomer Reactivity Ratios
T	Temperature (in Kelvin)
V_T	Total Potential Energy
V_A	Potential Energy of Attractive Interactions
V_R	Potential Energy of Repulsions

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Appendix

Publication during PhD study

1. Facile Synthesis of Tunable Alkali Soluble Latexes. **A. Dundua**, K. Landfester, A. Taden. In press, *Polymer*, DOI: [10.1016/j.polymer.2013.08.028](https://doi.org/10.1016/j.polymer.2013.08.028)

Oral and poster presentation during PhD Study

- 05/2013 Third International Symposium – Frontier in Polymer Science, Sitges, Spain
Poster Presentation: “Joint emulsions/miniemulsion polymerization for tailored rheology response”

Publication before PhD Study

1. Synthesis of polysiloxanes with pendant methoxy-substituted aromatic fragments. O. Mukbaniani*, G. Titvinidze, **A. Dundua**, M. Doroshenko, T. Tatrishvili. *Journal of Applied Polymer Science*. Volume 107, Issue 4, pages 2567–2571, 15 February 2008

Erklärung

Hiermit Versichern ich gemäß & 10 abs. 3d der Promotionsordnung vom 24,07,2007, das ich die als Dissertation vorgelegte Arbeit selbst angefertigt und alle benutzte Hilfsmittel (Literatur, Apparaturen, Material) in der Arbeit angegeben habe

Mainz, den 27.02.2014

Alexander Dundua

Summary

Novel single step synthetic procedure for hydrophobically modified alkali soluble latexes (HASE) via a miniemulsion-analogous method is presented. This facile method simplifies the copolymerization of the monomers with basically “opposite” character in terms of their hydrophilic/hydrophobic nature, which represent one of the main challenges in water based systems. Considered systems do not represent classical miniemulsions due to a high content of water soluble monomers. However, the polymerization mechanism was found to be rather similar to miniemulsion polymerization process.

The influence of the different factors on the system stability has been investigated. The copolymerization behavior studies typically showed strong composition drifts during copolymerization. It was found that the copolymer composition drift can be suppressed via changing the initial monomer ratio.

The neutralization behavior of the obtained HASE systems was investigated via potentiometric titration. The rheological behavior of the obtained systems as a function of the different parameters, such as pH, composition (ultrahydrophobe content) and additive type and content has also been investigated.

Detailed investigation of the storage and loss moduli, damping factor and the crossover frequencies of the samples showed that at the initial stages of the neutralization the systems show microgel-like behavior.

The dependence of the rheological properties on the content and the type of the ultrahydrophobe showed that the tuning of the mechanical properties can be easily achieved via minor (few percent) but significant changes in the content of the latter. Besides, changing the hydrophobicity of the ultrahydrophobe via increasing the carbon chain length represents another simple method for achieving the same results.

The influence of amphiphilic additives (especially alcohols) on the rheological behavior of the obtained systems has been studied. An analogy was made between micellation of surfactants and the formation of hydrophobic domains between hydrophobic groups of the polymer side chain.

Dilution induced viscosity reduction was investigated in different systems, without or with different amounts or types of the amphiphilic additive. Possibility of the controlled response to dilution was explored. It was concluded that the sensitivity towards dilution can be reduced, and in extreme cases even the increase of the dynamic modulus can be observed, which is of high importance for the setting behavior of the adhesive material.

In the last part of this work, the adhesive behavior of the obtained HASE systems was investigated on different substrates (polypropylene and glass) for the standard labeling paper. Wet tack and setting behavior was studied and the trends for possible applications have been evaluated.

The novel synthetic procedure, investigation of rheological properties and the possibility of the tuning via additives, investigated in this work create a firm background for the development of the HASE based adhesives as well as rheology modifiers with vast variety of possible applications due to ease of tuning the mechanical and rheological properties of the systems.

Zusammenfassung

Die vorliegende Arbeit beschreibt die Entwicklung einer neuartigen einstufigen Synthese zur Darstellung hydrophob-modifizierter alkali-löslichen Dispersionen (HASE) mithilfe einer „miniemulsionsanalogen“ Methode. Mit Hilfe dieses Ansatzes ist es gelungen, die Copolymerisation von Monomeren grundsätzlich gegensätzlicher Natur in Bezug auf ihren hydrophilen, beziehungsweise hydrophoben Charakter entscheidend zu vereinfachen. Dieses repräsentiert eine der größten Herausforderungen im Bereich wasserbasierter Dispersionen. Die entwickelten Systeme repräsentieren dabei keine Miniemulsion im klassischen Sinne, da ein hoher Anteil an wasserlöslichem Monomer vorliegt. Dennoch wurde ein der Miniemulsionspolymerisation sehr ähnlicher Mechanismus beobachtet.

Der Einfluss verschiedener Parameter auf die Stabilität des Systems getestet. Die Untersuchung des Copolymerisationsverhaltens ergab eine starke Verschiebung der Zusammensetzung während der Copolymerisation. Es wurde herausgefunden, dass dieser Drift durch Variation der Monomierzusammensetzung unterdrückt werden kann.

Das Neutralisationsverhalten der erhaltenen HASE Systeme wurde mittels potentiometrischer Titration untersucht. Ihr rheologisches Verhalten wurde in Abhängigkeit verschiedener Parameter, wie pH, Zusammensetzung (Ultrahydrophob Menge), sowie Art und Menge des Additives wurden ermittelt.

Eine Detailuntersuchung des Speicher- und Verlustmoduls, sowie des Dämpfungsfaktors und der Crossover-Frequenz zeigte ein mikrogelartiges Verhalten der Proben zu Beginn der Neutralisation.

Aufgrund der Abhängigkeit der rheologischen Eigenschaften von der Zusammensetzung und Art des Ultrahydrophobes konnte gezeigt werden, dass die mechanischen Eigenschaften bereits durch kleinere Anpassungen (wenige Prozent) signifikant beeinflusst werden können. Vergleichbare Ergebnisse konnten durch gezielte Änderung der Hydrophobizität des Ultrahydrophobs durch Verlängerung der Kohlenstoffkettenlänge erreicht werden.

Weiterhin wurde der Einfluss amphiphiler Additive (insbesondere Alkohole) auf die rheologischen Eigenschaften der erhaltenen Systeme studiert. Dabei wurde eine Analogie zwischen der Mizellbildung von Tensiden zu den hydrophoben Domänen zwischen den hydrophoben Gruppen in den Polymerseitenketten hergestellt.

Verdünnungsinduzierte Viskositätserniedrigung wurde in An- und Abwesenheit der amphiphilen Additive untersucht. Dabei wurde die Möglichkeit einer kontrollierten Reaktion der Systeme auf Verdünnung erforscht. Es wurde herausgefunden, dass die Sensitivität der Systeme auf Verdünnung stark verringert werden kann, in Extremfällen konnte sogar eine Erhöhung des dynamischen Moduls erreicht werden, welches eine große Bedeutung für das Abbindeverhalten des Klebstoffes hat.

Im letzten Teil der Arbeit wurde das Adsorptionsverhalten der erhaltenen HASE Systeme auf verschiedenen Substraten (Polypropylen und Glas) für Standard-Etiketten untersucht. Die Nassklebrigkeit sowie das Abbinden wurden verfolgt und Trends für potentielle Anwendungen wurden ausgewertet.

Der neuartige Syntheseweg, die Untersuchung des rheologischen Verhaltens und die Möglichkeit des Tunings durch Additive, die im Rahmen dieser Arbeit umgesetzt wurden generieren einen starken Hintergrund für die Entwicklung HASE-basierter

Klebstoffe, sowie Rheologie-Modifikationen mit großem Anwendungsspektrum aufgrund der einfachen Möglichkeit, die mechanischen und rheologischen Eigenschaften der Systeme anzupassen.