



# Shear Thinning: Determination of Zero-Shear Viscosities from Measurements in the Non-Newtonian Region

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Experimental information on the viscosities,  $\eta$ , of polymer solutions and of polymer melts as a function of shear rate is modeled by means of an approach that describes the diminution of  $\ln \eta$  as a function of shear stress,  $\tau$ , in terms of an exponential decay. The approach uses the following three adjustable parameters: the zero-shear viscosity of the system, a characteristic shear stress, quantifying its susceptibility toward shear thinning, and a dimensionless parameter stating the magnitude of the effect. This procedure gives access to the Newtonian behavior also in cases where direct measurements are impractical or impossible; it discloses two phenomena not reported so far: a qualitative change in the efficacy of  $\tau$  at a characteristic concentration and indicates the occurrence of two different disentanglement mechanisms in thermodynamically unfavorable solvents.

## 1. Introduction

The present study was initiated by problems with the experimental determination of zero shear viscosities: Some polymer solutions—like that of high molecular weight polysaccharides in water—are so susceptible against shear that standard rheometers fail to reach the Newtonian flow regime. For that reason we wanted to find out whether there exist ways to obtain the desired information by reliable extrapolation methods. To the best of our knowledge no such procedures were reported in the literature, despite the fact that the influence of shear rate on the viscosity of polymer solutions was very topical from the beginning of polymer science and still is, as demonstrated by a recent review article on that subject.<sup>1</sup> This contribution describes an option to solve the problem using a “kinetic” model that quantifies the effects of the disentanglement processes on the viscosity as a function of shear stress. The present study uses exclusively published data; detailed experimental information can be found in the cited literature.

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## 2. Modeling

The present treatment is based on some assumption/premises.

- In contrast to the usual procedure, the changes in the viscosity  $\eta$  of polymer containing systems caused by shear should not be modeled as a function of the shear rate,  $\dot{\gamma}$ , but rather as a function of shear stress,  $\tau = \eta \dot{\gamma}$ . The reason is that it is the force per area that should be decisive for the fraction of entanglements that is opened. This approach does not claim the existence of a threshold stress.

- Treating the disentanglement process by way of trial as a first order reaction, it appears expedient to study the relative changes in  $\eta$  as a function of  $\tau$ . This assumption implies that  $\ln \eta$  should decrease exponentially with rising  $\tau$ .
- Finally, for the modeling of the shear thinning of polymer solutions it appears recommendable to replace  $\ln \eta$  by  $\ln(\eta/\eta_{\text{rel}})$  (i.e., by the relative viscosity  $\ln \eta_{\text{rel}}$ ) because the solvent is normally not directly involved in disentanglement processes.

The above considerations yield the following Ansatz

$$\ln \eta_{\text{rel}}^{\tau} = \ln \eta_{\text{rel}}^0 - A1 \left(1 - e^{-\tau/\tau_1^*}\right) \quad (1)$$

where the superscripts  $\tau$  and  $0$  indicate data referring to arbitrary shear stresses  $\tau$  and to their limiting values for  $\tau = 0$ . The characteristic shear stress  $\tau_1^*$  measures the susceptibility of the system toward shear thinning (resistance against disentanglement) and the dimensionless parameter  $A1 = \ln \eta_{\text{rel}}^0 - \ln \eta_{\text{rel}}^{\infty}$  states the maximum shear effect that would be *hypothetically* reached for infinite shear stress. Equation (1) describes the majority of experimental data reported in the literature, as will be demonstrated hereinafter.

For some of the systems under investigation a modification of Equation (1) turned out to be necessary. Equation (2) accounts for two dissimilar disentanglement processes by introducing the additional parameters  $A2$  and  $\tau_2^*$ .

$$\ln \eta_{\text{rel}}^{\tau} = \ln \eta_{\text{rel}}^0 - A1 \left(1 - e^{-\tau/\tau_1^*}\right) - A2 \left(1 - e^{-\tau/\tau_2^*}\right) \quad (2)$$

The subsequent examination of the suitability of the above relations for the modeling of experimental data is not confined to polymer solutions but also includes some examples of polymer melts. In the latter cases  $\ln \eta_{\text{rel}}$  is simply replaced by  $\ln \eta$ .

The following relation<sup>2</sup> was used for the modeling of the composition dependence of the zero shear viscosities

$$\ln \eta_{\text{rel}}^0 = \frac{\tilde{c} + \alpha \tilde{c}^2}{1 + \beta \tilde{c} + \gamma \tilde{c}^2} \quad (3)$$

$\tilde{c} = c [\eta]$  is the reduced polymer concentration, where  $c$  is given in mass/volume, and  $\alpha$ ,  $\beta$ , and  $\gamma$  are system specific parameters;  $\alpha$  can be set zero in the majority of cases.

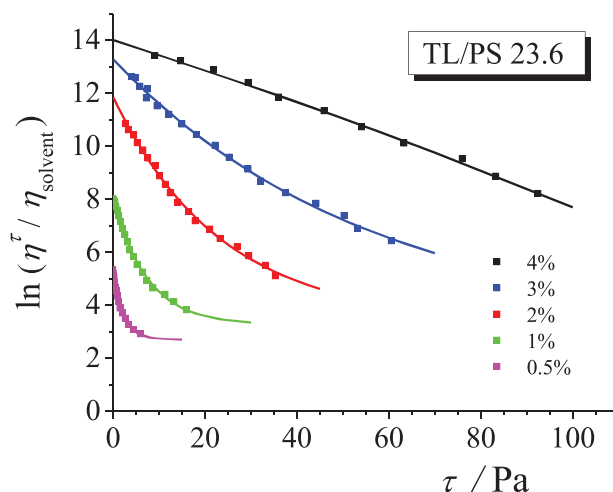
### 3. Results and Discussion

#### 3.1. Polymer Solutions

All experiments evaluated in this section were performed at 25 °C. Solvents, polymers, and their molar masses as well as concentrations are detailed in **Table 1**, which also collects the parameters obtained from the reported data by means of Equations (1) and (2).

##### 3.1.1. Toluene (TL)/Polystyrene (PS)<sup>3</sup>

The shear thinning behavior of PS in the thermodynamically good solvent TL has been studied extensively by Kulicke and



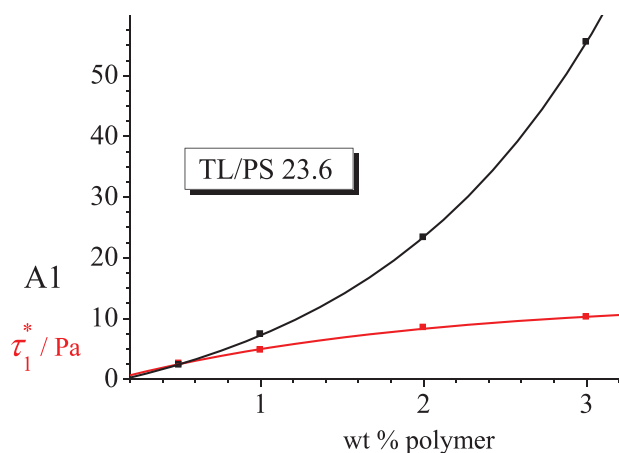
**Figure 1.** Relative viscosities as a function of shear stress  $\tau$  for the indicated concentrations. The curves are modeled by means of Equation (1).

Knieske<sup>3</sup> with respect to the influences of polymer concentrations. The dependencies of the relative viscosities on the shear stress  $\tau$  are shown in **Figure 1**. The graph reveals that the curvature changes with rising concentration from positive to negative. Directed experiments would be required to find out how

**Table 1.** Collection of the polymer solutions for which flow curves were modeled according to Equations (1) and (2) plus parameters obtained.

Solvent <sup>a)</sup>	Polymer	10 <sup>-6</sup> M	wt%	ln $\eta_{\text{rel}}^0$	A1	$\tau_1^*$ [Pa]	A2	$\tau_2^*$ [Pa]
Toluene	PS	23.60	0.50	5.30	2.56	2.32		
		23.60	1.00	8.10	4.80	7.39		
		23.60	2.00	11.70	8.29	23.30		
		23.60	3.00	13.30	10.22	55.50		
		23.60	4.00	14.10	-22.30	-402.60		
Decalin	PS	2.00	11.60	11.00	4.15	421.00	6.15	3068.00
Water	PAAm	0.51	5.00	5.26	-0.14	-81.20		
		1.70	2.00	6.24	3.61	60.40		
		3.90	1.00	2.56	-0.09	-1.36		
		3.90	2.00	8.85	6.73	62.20		
		3.90	5.00	13.80	-17.00	-777.00		
		5.30	1.00	6.70	3.69	13.70		
		5.30	2.00	10.70	7.20	52.50		
Glycerol	PAAm	1.70	1.00	6.02	1.73	62.80		
		5.30	1.00	8.42	2.35	56.40	1.56	7.06
		1.70	1.00	4.48		102.00		
Formamid	PAAm	1.70	1.00	4.48		8.77		
		5.30	1.00	5.61	2.89	37.16		
		0.17	5.00	2.20	1.28			
Pentamer of PDMS	PDMS	0.17	10.00	3.57	-2.15	-115.50		
		0.17	20.00	5.65	-0.28	-41.80		
		0.17	40.00	8.35	-0.39	-185.00		

<sup>a)</sup>PS: polystyrene 25 °C, PAAm: polyacrylamide 25 °C, PDMS: polydimethylsiloxane 60 °C.



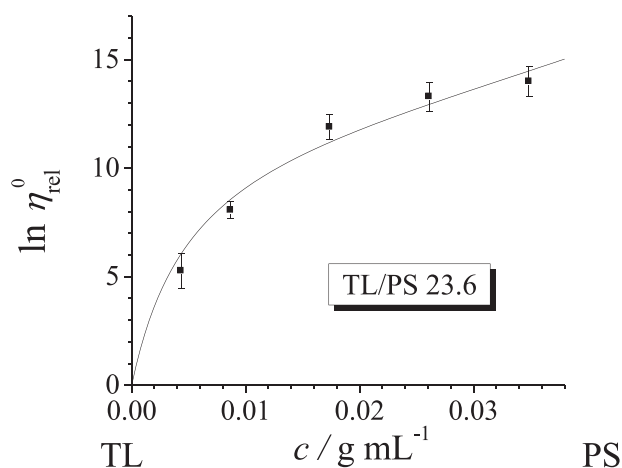
**Figure 2.** Concentration dependence of the parameters  $\tau_1^*$  and  $A1$  for the dilute solutions. Both curves are modelled by an exponential decay.

the thus defined characteristic composition correlates with coil-overlap and crossover concentrations.

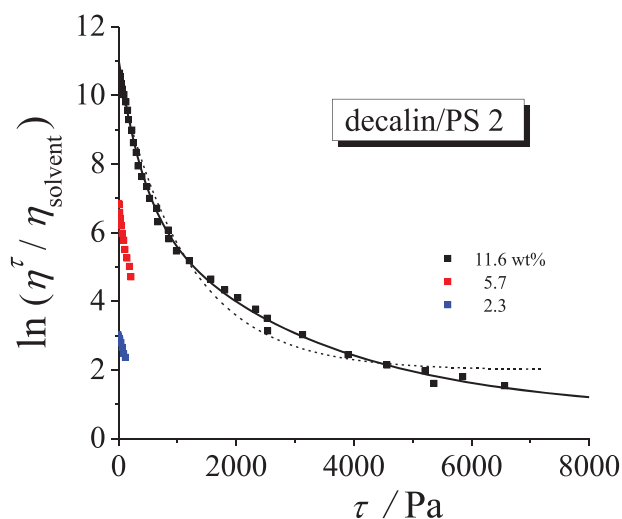
Figure 2 shows how the parameters of Equation (1) vary with composition for the four lowest concentrations; sign and magnitude of the data for 4 wt% reveal (cf. Table 1) a fundamentally different dependence beyond a critical composition of the system located between 3 and 4 wt%. Both parameters become zero in the limit of infinite dilution, consistent with theoretical considerations.

In order to check whether the zero shear viscosities obtained from the above evaluation can be modeled by means of the generally applicable three parameter approach<sup>2</sup> formulated in Equation (3), the relative viscosities are in Figure 3 plotted accordingly.

The experimental errors in  $\eta^0$  were estimated to be 5% for all concentrations, except for lowest for which it is 15%. Calculating the intrinsic viscosity  $[\eta]$  from the known molar mass of the polymer by means of a published Kuhn–Mark–Houwink relation<sup>4</sup> and setting the parameter  $\alpha = 0$  yields the following values for the two remaining parameters:  $\beta = 0.075$ ,



**Figure 3.** Evaluation of the zero shear viscosities shown in Figure 1 according to Equation (3).



**Figure 4.** As Figure 1 but for the system decalin/polystyrene. Only the data for the two lower concentrations can be modeled by Equation (1). For 11.6 wt% this relation fails (dotted line) and Equation (2) must be used.

$\gamma = -0.0002$ . This outcome is typical for the present type of polymer solutions.

### 3.1.2. Decalin/Polystyrene<sup>5</sup>

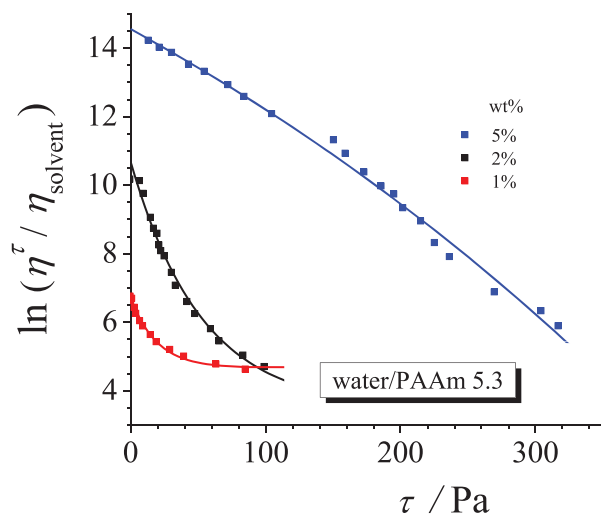
The shear thinning behavior of PS in the thermodynamically unfavorable solvent decalin has been studied by Kulicke and Porter.<sup>5</sup> The evaluation of these results is shown in Figure 4.

The shear stress up to which the measurements were performed for the highest concentration is uncommonly large. In this case the results can no longer be modeled quantitatively by means of Equation (1). The reason why two different disentanglement processes are required for the description is presently unclear. It could simply lie in the large range of  $\tau$  values under investigation; on the other hand one could speculate that this behavior is caused by the marginal solvent quality of decalin for polystyrene. Under such conditions it would not be unreasonable to distinguish between two types of entanglements, the normal ones typical for good solvents and “dry” entanglement for which the polymer segments are in direct contact and no longer separated by solvent molecules. Such a situation should necessitate two sets of parameters. Analogous observation for the system glycerol/polyacrylamide (cf. Figure 7) favors the latter interpretation.

### 3.1.3. Water/Polyacrylamide<sup>6</sup>

The shear thinning behavior of polyacrylamide (PAAm) in water, glycerol, and in formamide has been studied by Klein und Kulicke<sup>6</sup> for different molar masses; Figures 5 and 6 show two examples for water.

The results shown in Figures 5 and 6 document once more that the dependencies of  $\ln \eta_{rel}^{\tau}$  on  $\tau$  change their curvature as the polymer concentration rises. In both cases the critical composition lies between 2 and 5 wt%.



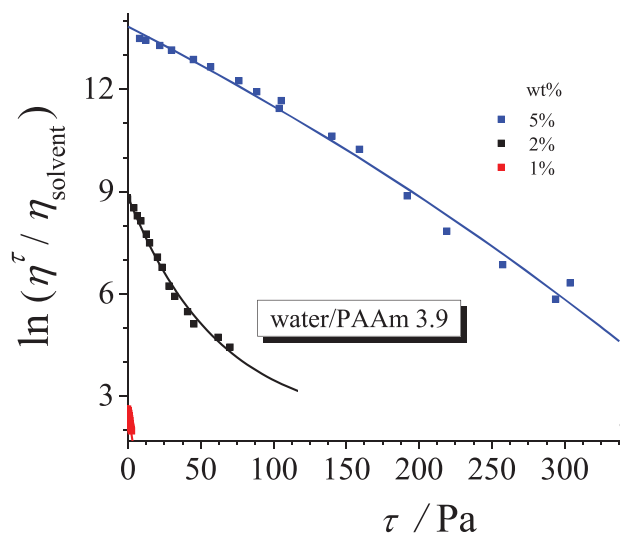
**Figure 5.** As Figure 1 but for the system water/polyacrylamide  $M = 5.3 \times 10^6$ .

### 3.1.4. Glycerol/Polyacrylamide<sup>6</sup>

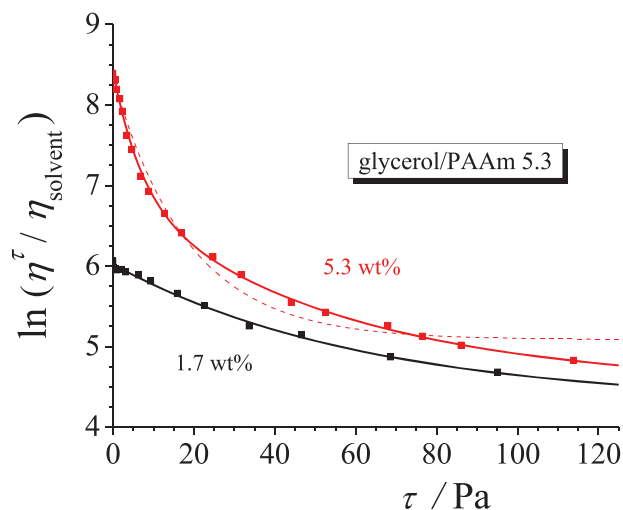
Like decalin for polystyrene, glycerol and formamide should be unfavorable solvents for polyacrylamide, as compared with water, according to the zero shear viscosities of **Figure 7**. The fact that Equation (2) is required for the modeling of the results for 5.3 wt% might be taken as a further indication that the reason for this behavior lies in the solvent quality. However, it remains open why this is not the case for 1.7 wt%. One might argue that the “wet” entanglements are already opened at low  $\tau$  values and that the higher values required for the opening of “dry” entanglements are not reached.

### 3.1.5. Comparison of Solvents for Polyacrylamide<sup>6</sup>

**Figure 8** compares the shear thinning of 1 wt% solutions of PAAm in different solvents. The  $\tau$  region under investigation is



**Figure 6.** As Figure 1 but for the system water/polyacrylamide  $M = 3.9 \times 10^6$ .

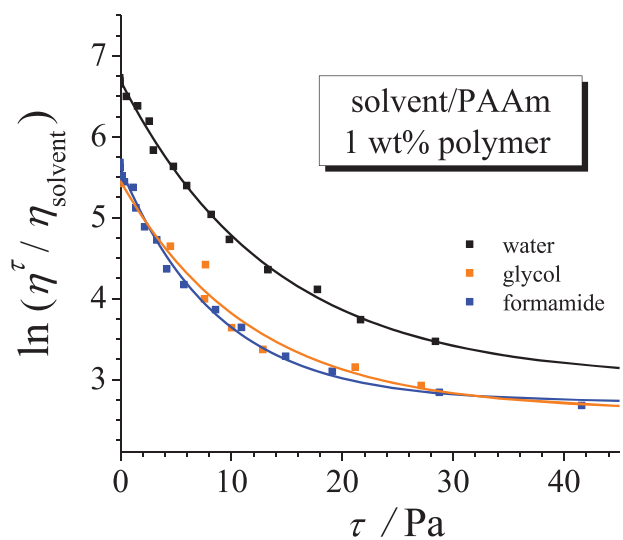


**Figure 7.** As Figure 1 but for the system glycerol/polyacrylamide with the molar mass 5.3 kDa.

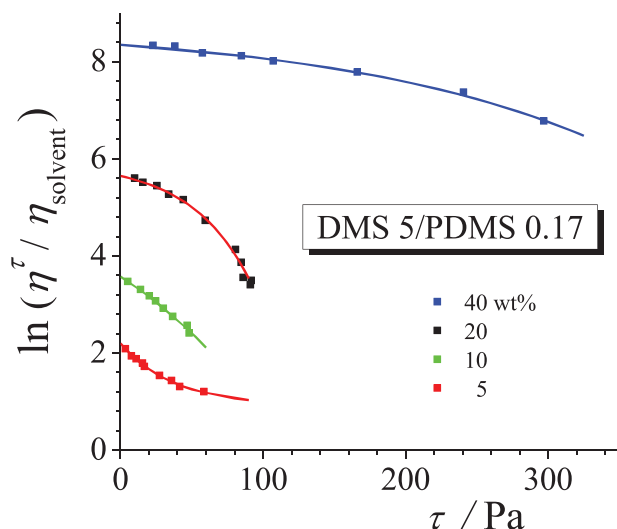
considerably lower than with all other PAAm solutions. For this reason it is not surprising that Equation (1) suffices for the modeling in all cases. The fact that the extrapolated zero shear viscosities for glycol and for formamide are much lower than for water documents once more the inferior solvent quality of these liquids.

### 3.1.6. Solutions of Polydimethylsiloxane (PDMS) in Its Pentamer<sup>7</sup>

The shear thinning behavior of PDMS solutions in its homologous pentamer (DMS 5) has been studied by Ito and Shishido<sup>7</sup> covering uncommonly large ranges of shear stresses for different concentrations. Only the results for low  $\tau$  values are evaluated here. The complete dependence of  $\ln \eta_{rel}$  on shear stress exhibits a sigmoidal form. It is presently unclear whether this phenomenon is a particularity of PDMS or typical for many systems. In either case it demonstrates that the present modeling refers to the initial behavior only.



**Figure 8.** As Figure 1 but for 1 wt% solutions of polyacrylamide with the molar mass of 1.7 kDa in different solvents.



**Figure 9.** As Figure 1 but for solutions of polydimethylsiloxane (1.7 kDa) in its pentamer.

The behavior shown in **Figure 9** proofs once more that the curvature changes with increasing polymer concentration. In the present case the critical composition lies between 5 and 10 wt%, i.e., in the same range as with the other systems.

### 3.2. Polymer Melts

Unlike the situation with polymer solutions the measuring temperatures vary widely. Information on the molar masses of the samples, where available, and the parameters of Equations (1) and (2) obtained from the reported data is collected in **Table 2**.

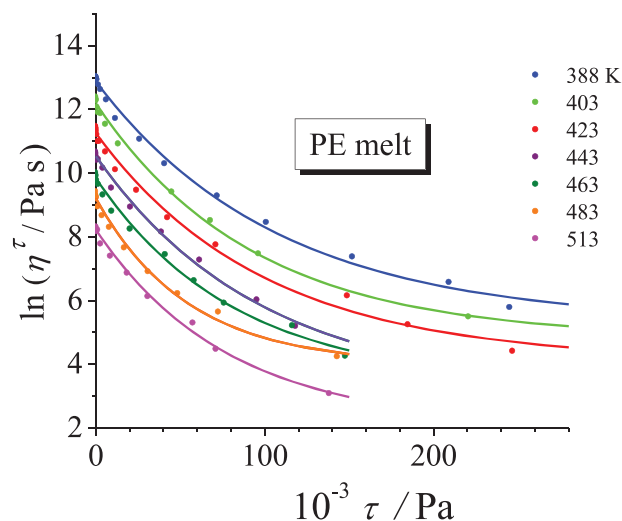
#### 3.2.1. Polyethylene (PE)<sup>8</sup>

Meissner<sup>8</sup> has studied the flow behavior of the PE melts over wide ranges of temperatures and shear stresses. The reported data were evaluated according to the Equations (1) and (2) despite

**Table 2.** Collection of polymer melts for which flow curves were modeled according to Equation (1) and parameters obtained.

Polymer <sup>a)</sup>	10 <sup>-6</sup> M	T [K]	ln η <sub>rel</sub> <sup>0</sup>	A1	τ <sub>1</sub> <sup>*</sup> [Pa]
PE	Not specified	388.00	12.90	7.55	107.50
		403.00	12.20	7.36	93.00
		423.00	11.25	7.14	99.00
		443.00	10.50	7.39	97.40
		463.00	9.80	6.43	81.50
		513.00	8.20	6.15	78.00
PDMS	0.80	T [°C]			
		23.00	12.90	4.38	22.30
		23.00	10.70	6.63	49.80

<sup>a)</sup>PE: polyethylene, PDMS: polydimethylsiloxane; LG2 and BG are the abbreviations used by the authors for the PDMS samples.



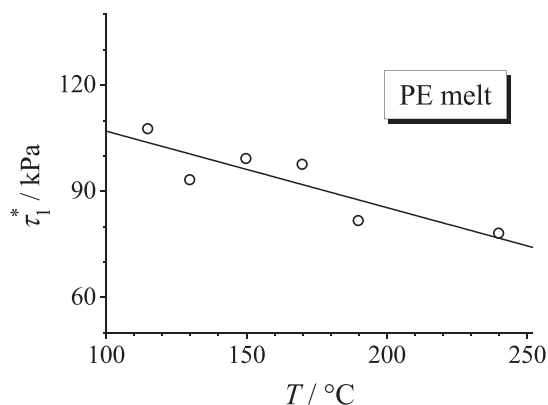
**Figure 10.** Viscosities of polyethylene melts as a function of shear stress  $\tau$  at the indicated temperatures.

the poor characterization of the sample; the author only states that the sample is branched, but does not give a molar mass. This course of action appears justified because it is the sole purpose of the present evaluation to check, whether Equation (1) can also model flow curves of polymer melts.

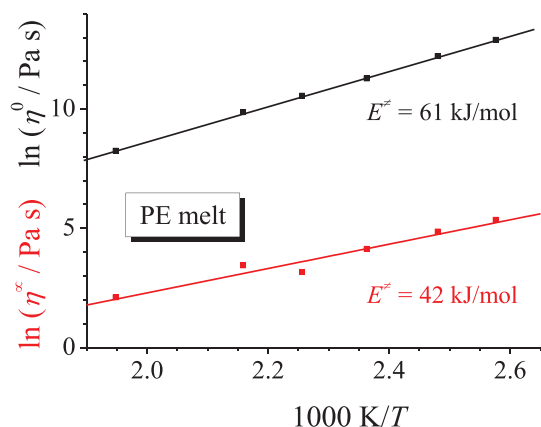
According to the data presented in **Figure 12**, the shear rate dependence of the viscosities for the PE melts looks very similar to those observed for the polymer solutions, however, with the fundamental difference that the  $\tau$  values required to yield a comparable reduction in viscosity are by approximately three orders of magnitude larger. This behavior has to be expected due to the much higher viscosities of polymer melts as compared with that of polymer solutions.

How the characteristic  $\tau_1^*$  values obtained from the evaluation of the data shown in **Figure 10** depend on temperature is illustrated in **Figure 11**. Owing to the fact that  $\tau_1^*$  represents a derived quantity, the scattering of the data is considerable; the observed diminution with rising  $T$  reflects the reduction in the viscosity of the melt.

Zero shear viscosities and (hypothetical) limiting viscosities for infinitely high shear stress obtained from the above



**Figure 11.** Temperature dependence of the characteristic shear stress for polyethylene.



**Figure 12.** Arrhenius plots for zero shear viscosities and for  $\ln \eta_{rel}^{\infty}$  (hypothetical values for  $\tau \rightarrow \infty$ ).

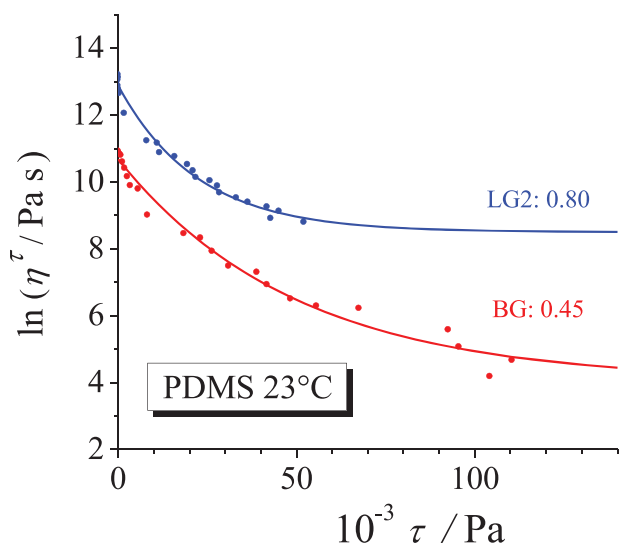
evaluation are in **Figure 12** evaluated in terms of Arrhenius plots. The activation energy  $E^{\infty}$  for the fully entangled melt results expectedly much larger than for the disentangled case.

### 3.2.2. Polydimethylsiloxane<sup>9</sup>

El Kissi<sup>9</sup> and co-workers have studied a series of nine silicone fluids (PDMS). Their results—as far as relevant for the present considerations—are evaluated in **Figure 13** using the nomenclature of the authors. The non-Newtonian behavior of PDMS resembles that of PE.

## 4. Conclusions

The most important outcome of the present study lies in the aptness of the communicated approach to acquire reliable zero



**Figure 13.** Like Figure 10 but for polydimethylsiloxane.

shear viscosities from measurements outside the Newtonian flow regime. This statement applies to polymer solutions as well as to polymer melts.

Moreover the approach yields two helpful system specific parameters: A characteristic shear stress  $\tau_1^*$ , which quantifies the sensitivity of the viscosity of polymer containing liquids toward shear stress, and the dimensionless parameter  $A_1$ , which measures the magnitude of the effect. The latter information must, however, be treated with caution because it normally characterizes the behavior only in a limited range of shear stress and—in the case of solutions—up to moderate polymer concentrations only.

The present method of data evaluation offers additional insight in two ways:

- It reveals the existence of a critical polymer concentration for solutions. Below this value the disentanglement processes slow down with rising shear stress  $\tau$ ; above it they accelerate with rising  $\tau$ . It is presently unclear how this critical value correlates with independently determined coil-overlap and crossover concentrations. Directed experiments are required to clarify this item.
- The current results yield indications for the existence of two separate disentanglement processes in thermodynamically unfavorable solvents. This observation is tentatively attributed to two dissimilar types of entanglements: Such that are surrounded by a high number of solvent molecules (good solvents) and others that are surrounded by polymer clusters (marginal solvents). This hypothesis requires directed experiments again.

## Conflict of Interest

The author declares no conflict of interest.

## Keywords

modeling shear thinning, polymer melts, polymer solutions, shear thinning, zero shear viscosity

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