Rheooptical investigations of shear-induced aggregation of polymers in dilute solutions

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Abstract

The phenomenon of shear-induced aggregation has been investigated in dilute solutions of high molar mass polystyrene standards in phthalic acid esters by light scattering and simultaneous rheometrical measurements. An optical-rheological correlation is found which can easily be understood by simple molecular kinetic models. Systematic examination of the polymer solutions, varying temperature, concentration, and molar mass, shows a dependence of the aggregation on these parameters which fits thermodynamic models.

Introduction

It has been known for several years that the solution behavior of polymers depends not only on concentration, temperature and the quality of the solvent but also on the flow conditions in the solution. As early as in 1955 Eliassaf et al. described a sol/gel-transition of aqueous polymethacrylic acid solution under shear flow [1]. Other examples followed, and today a great amount of structure formation under shear is known, interpreted partly as shear induced anisotropy, partly as shear induced crystallization and thermodynamic phase separation. In [2] a good summary of literature data is published in form of a table.

Recently the polymer/solvent system polystyrene (PS) in dioctyl phthalate (DOP) has been precisely examined by several groups. Ver Strate and Philippoff [3] were the first who reported a dramatic increase of turbidity in a semidilute solution under shear and interpreted it as indication of a shear-induced phase transition. But this explanation in terms of thermodynamics only has been called into question because of the non-equilibrium conditions that a shear flow causes in the solution. Pine et al.[4] determined the structure factor S(q, $\dot{\gamma}$) by light scattering and explained the obtained butterfly pattern according to a mechanism proposed by Helfand and Fredricksen [5] in which concentration fluctuations are enhanced by a coupling between the polymer concentration and the shear flow through the concentration-dependent viscosity and normal stress coefficients. The first direct observation and visualisation of this effect was done by Hashimoto et al. [6] with a cone/plate geometry by replacing the screen for light scattering detection by a microscope. The appearing 'ripple structures' were interpreted in the same way. Fuller et al. [7], who examined the birefingence and dichroism of the system in extensional flow, also explained 'their experimental findings by the Helfand-Fredricksen mechanism.

All these investigations were done in semidilute solutions, which means that the molecules overlap and entangle even at rest. It would also be interesting to describe these proceedings on the scale of a single molecule as it is observed in dilute solution by wide angle light scattering. Link et al. [8] showed the orientation and deformation of PS molecules in DOP under shear by this method. Towards higher shear rates of several hundreds s^{-1} he also found the strong increase in the intensity of scattered light as reported from the semidilute regime. The more cautious term 'aggregation' was used for this effect by which the scope of his examinations was limited at that time.

In this paper measurements are presented which continue this observation method towards shear rates at which aggregation occurs and combine it with simultaneous rheological measurements in a new apparatus. We hope to be able to observe what really happens during aggregation in a molecular dimension. In order to better understand the driving forces of this aggregation, systematic variations of concentration, temperature and molar mass have been performed. This allows us to check thermodynamic models and predictions.

Polymers and Solvents

The investigated polymers, attained from Polymer Laboratories, UK, are narrowly distributed PS standards of the following weight averaged molar masses M_w and uniformity M_w/M_n, where M_n is the number average of the molar mass:

name	M_w [g/mol]	M_w/M_n
PS1.8	$1.8 \cdot 10^6$	1.06
PS3.0	$3.0 \cdot 10^6$	1.06
PS5.5	$5.5 \cdot 10^6$	1.10
PS8.5	$8.5 \cdot 10^6$	1.20
PS17	$17 \cdot 10^6$	1.20

The solvent for all polymers were dioctyl phthalate (DOP), Merck, Synth. Grade, which is a poor solvent for PS and near to a Θ-solvent at 25°C. The intrinsic viscosity for PS in DOP at this temperature expressed by the Mark-Houwink equation is $[\eta] = 45.2 \cdot 10^{-3} \cdot M^{0.54}$[ml/g]. The solvent viscosity at 25°C is $\eta_0 = 61.0$ [mPa s]. (cf.[8])
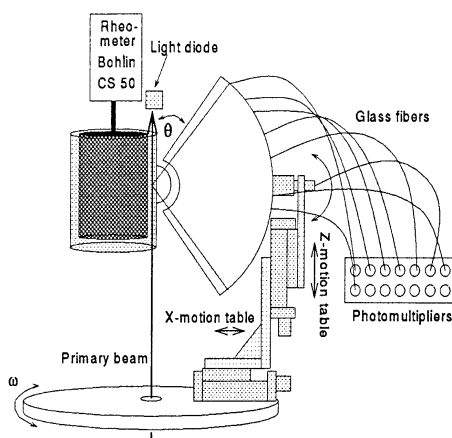
PS17 was also solved in diethyl phthalate (DEP), Merck, Synth. Grade, which is a better solvent for PS (Mark-Houwink equation: $[\eta] = 7.59 \cdot 10^{-3} \cdot M^{0.71}$ [ml/g] at 20°C and $\eta_0 = 13.7$ [mPa s].)[9].

All solutions were prepared at temperatures between 25 and 40°C without stirring. Solvents were filtered through regenerated cellulose filters (Sartorius) with a pore size of 0.8 μm. Solvation takes several weeks for PS in DEP and up to several months for PS in DOP. All prepared solutions were of a concentration below the overlap concentrations c* which, according to *Simha* [10], is $c* = 1/[\eta]$.

Experimental Setup

The experimental setup of our older apparatus is described in [8]. Here we want to introduce a new self-constructed rheo-Wide-Angle-Light-Scattering (rheo-WALS) apparatus:

The detector consists of a segment of a circle in which glass fibers are fixed at 14 angles from $\Theta = 40°$ to 140°. The light detection is realized by photo-multipliers. The detector can rotate around the $\Theta = 90°$ position, so it is possible to measure the scattered light in the shear plane, given by the directions of the flow velocity and shear gradient, and in the Zimm planes, given by primary beam and direction of observation. Latter is seen in the figure on the left. The Zimm planes can be moved by a rotate-able plate between $\omega = 65°$ and 115° in the shear plane.

For measurements in shear plane the detector assumes a position perpendicular to the one shown in picture. Here the angle ω in the shear plane is equal to the angle Θ on the detector segment. The shear cell consists of an outer cylinder made of optical glass with a correcting lens focusing at the scattering center and a rotating inner cylinder which is blackened by eloxation in order to prevent light reflection. These concentric cylinders form a so-called Searle arrangement which generates a simple shear flow with a shear gradient of $-\frac{dv_y}{dx}$, whose absolute value is referred to as shear rate $\dot{\gamma}$. Because of the high solvent viscosity, the flow is laminar up to a shear rate of about $10000 s^{-1}$. The rotor is part of a rheometer BOHLIN CS 50; thus, it is possible to detect scattered light and viscosity of the solution simultaneously. An argon ion laser beam is focused between the gap of the shear cell which is 1 mm wide. The light passing through the solution is detected by a diode.
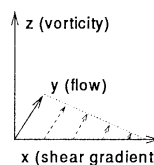
The new measuring device has two explicit advantages over the old setup: First, it is now possible to measure scattered light and viscosity simultaneously, second, the detector records all 14 angles at once. Through this we can guarantee that conditions are the same for a whole set of detection angles, which is important for substances that show a pre-shear effect. Additionally we can measure kinetic effects throughout the whole range of detection angles in one run.

Experimental procedure

In the shear experiments the polymer solutions were exposed to a quasi continuously increasing shear rate, i.e. the shear rate was increased every 10 minutes at a rate of 10 s^{-1}, starting from zero and reaching a maximum shear rate of 750 s^{-1} in 12 and a half hours. This allows us to reach an almost steady state at any shear rate. The scattered light in the shear plane, the light passing through the solution, and the viscosity of the solution were detected at an interval of a few seconds. After the maximum shear rate was reached, we continued the measurement for another 10 minutes at quiescent solution to verify that the initial state was reached again. This was always the case after several minutes.

Orientation angle

Polymers in solution have ellipsoidal shape with three different axes [11]. In static light scattering at rest, though, the time average is spherical.
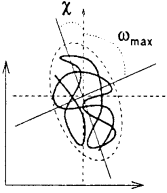
But as the shear gradient increases, the longest axes will take a preferred orientation more and more in the direction of the flow. This is indicated by a maximum of scattered light in the direction of the smallest axes due to the least destructive intra-molecular interference [12]. Thus, the orientation angle χ of the molecules at any shear rate can be determined from a plot of scattered light vs. shear plane angle, taking into account that $\chi = 90 - \omega_{max}$.
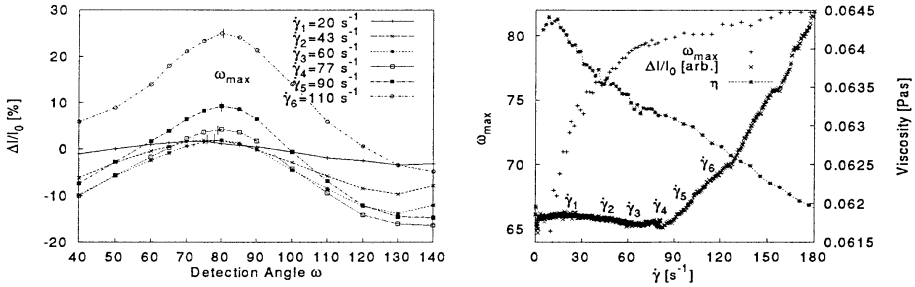
Fig. 1: Orientation and aggregation of PS17 in DOP, c=0.77 g/l, T=25°C

In fig.1 (left) this is shown in a manner proposed by Peterlin [13],[14] scaling the scattered intensity I to the intensity I_0 at quiescent solution: $\frac{\Delta I}{I_0} = \frac{I(\dot{\gamma}) - I(\dot{\gamma}=0)}{I(\dot{\gamma}=0)}$. The curves for the increasing shear rates $\dot{\gamma}_1, ..., \dot{\gamma}_6$ form a maximum at ω_{max} which becomes sharper for higher shear rates and tends to increase towards 90°. The average scattering intensity remains unchanged until aggregation begins.

During aggregation the intensity of scattered light is increased at all angles in the shear plane. Fig.1 (right) shows the viscosity and scattering intensity under a detection angle of $\omega = 70°$ as a function of shear rate. Also in the plot the maximum angle ω_{max} determined by the procedure described before is shown. It can been seen that this angle does not reach the maximum orientation of $\omega_{max} = 90°$ (i.e. $\chi = 0$) but stops rising, though not abruptly, when aggregation occurs and then fluctuates around an end-value of about $\omega = 70°-85°$ (averaging all runs). But it is obvious that at this shear rate no *single* molecules scatter the light any more.

Aggregation

The strong increase of the intensity of scattered light above a certain shear rate, in the following text called the 'critical shear rate' $\dot{\gamma}_{crit}$, is interpreted as the beginning of the aggregation. With a thermodynamic approach suggested by B.A. Wolf [15],[16], a prediction about $\dot{\gamma}_{crit}$, interpreted here as the beginning of a real phase separation, can be made: In addition to the free enthalpy for polymer solutions according to Flory and Huggins, another term is taken into account, the so-called stored enthalpy G_s, which includes the changed condition under shear: $\Delta G = \Delta G^{Flory} + G_s(\dot{\gamma})$.

Following an idea of Marucci [17], who could show that the energy needed to deform a polymer coil, particularly to enlarge its end-to-end-distance, can be expressed by the trace of the stress tensor $\underline{\underline{\sigma}}$, the following expression is used for the stored enthalpy: $G_s = \frac{1}{2}$ Tr ($\underline{\underline{\sigma}}$). According to Lodge [18], in a laminar shear flow this trace is equal to the first normal stress difference: Tr ($\underline{\underline{\sigma}}$) = σ_{11} - σ_{22}. The latter can be expressed by a relaxation time spectrum of the system [19]: $\sigma_{11} - \sigma_{22} = 2\dot{\gamma}^2 \nu k T \sum_{i=1}^{N} \tau_i^2$, where ν is the number of chain molecules per volume and N the number of segments per chain. T and k resp. R have the usual meanings. Using the most common relaxation time spectrum for polymers, the Rouse spectrum $\tau_{R,i} = \frac{6}{(i\pi)^2} \frac{[\eta]\eta_0 M}{RT}$, yields a closed expression for the stored enthalpy

$$G_s = \frac{6}{15} \cdot \frac{cM}{RT} \cdot ([\eta]\,\eta_0\dot{\gamma})^2 \qquad (1)$$

which explicitly includes the dependence on shear rate $\dot{\gamma}$, temperature T, molar mass M, and concentration c, whose unit is g/l.

For a system with a small negative ΔG^{Flory}, i.e. a polymer in a poor solvent, $G_s(\dot{\gamma})$ can become sufficiently large to result in a positive overall ΔG. This leads to phase separation in terms of thermodynamics or aggregation in a more kinetic sense. This G_s^{crit} corresponds to a $\dot{\gamma}_{crit}$ for which eqn.1 becomes

$$\dot{\gamma}_{crit} = \frac{1}{[\eta]\eta_0}\sqrt{\frac{15}{6} \cdot G_s^{crit} \cdot \frac{RT}{cM}} \quad \sim \quad \sqrt{\frac{T}{cM}} \qquad (2)$$

In our shear experiments we determined $\dot{\gamma}_{crit}$ by the tangent method. $\dot{\gamma}_{crit}$ can be reproduced when the experiment is repeated with the same solution or with fresh ones provided that temperature, concentration, and molecular mass are held constant. (Fresh solutions may show a lower $\dot{\gamma}_{crit}$. However, we believe this to be the result of incomplete solvation rather than shear-induced degradation, because subsequent GPC measurements did not show a decrease in the molar mass.)
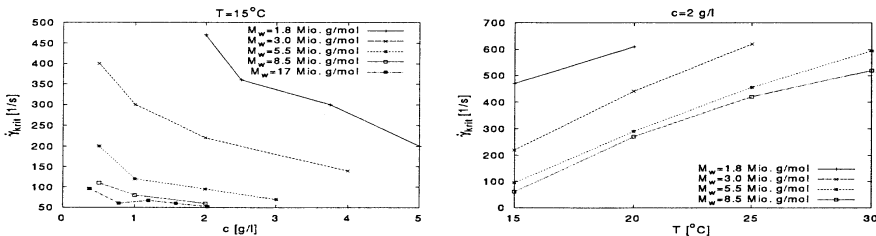

Fig. 2: T, c, M dependence of the critical shear rate for PS in DOP

Variation of these three parameters leads to a shift of $\dot{\gamma}_{crit}$ which is shown as a function of concentration c at constant temperature T in fig.2 (left) and as a function of temperature T at constant concentration in fig.2 (right) for the four resp. five polymer standards. The rise of $\dot{\gamma}_{crit}$ with temperature is found to be less than linear, though it

is difficult to verify the square root dependence of eqn.2 exactly, because the measured temperature interval is small on the Kelvin scale. The dependence on concentration is found to be reciprocal in good agreement with eqn.2. A distinct dependence on molar mass is found as well, which means that not only the amount of polymer segments in the solution is crucial for aggregation, but also the shape of the single molecule.

Rheological-optical correlation

With the new apparatus, it is possible to record the viscosity of the solution at any time.

PS1.8 in DOP, T=20°C, c=5 g/l
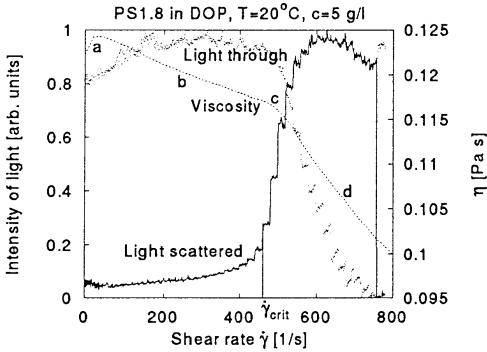
Depicted in the same plot as the intensity of the scattered light, one can see a characteristic drop in the viscosity in the area of aggregation. This is at somewhat higher shear rates than the increase of the scattered light but concurrent with the decrease of the light passing through. (The decrease of the scattered light at even higher shear rates is due to turbidity and the resulting multiple scattering). The decrease of viscosity is significantly higher than the normal shear-thinning at lower shear rates which is due to the orientation of the macromolecules. These observations lead to the following simple scheme of the processes taking place:
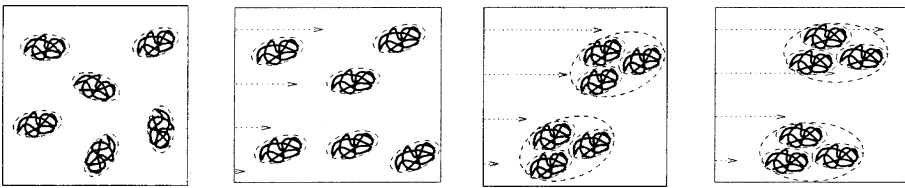
a. Isotrope solution at rest

b. Orientation in the shear gradient

c. Aggregation

d. Orientation of the aggregates

In quiescent solution the polymer coils form ellipsoids which are aligned isotropically (a). A small shear gradient orientates the molecules, thinning the solution slightly (b). When aggregation occurs many molecules are tied together, leaving a significantly thinner solution behind (c). This is according to the rule of thumb that many small particles hinder flow more than a few large one At still higher shear rates the aggregates are oriented as well (d).

Measurements in DEP

So far only measurements of PS in DOP have been shown. We will now discuss some differences in the data for PS in the better solvent DEP.

Fig.3 shows the plot corresponding to fig.1 right, now with the solvent DEP. The behavior of the orientation angle is basically the same. The maximum angle rises towards 90° (i.e. the orientation angle towards 0°) and levels off when aggregation occurs. However, the increase in the intensity of scattered light is generally not as dramatic as in DOP, and only in DEP does the curve show a second significant increase at higher shear rates. The viscosity curve does not deviate much from the normal shear-
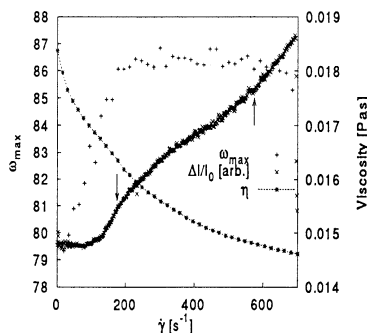

Fig. 3: PS17 in DEP, c=0.6 g/l, T=20°C

thinking behavior in the area of aggregation. The light passing through the solution is not weakened in a detectable way (and is therefore not pictured here), while in DOP the light passing through decreases after the scattered light has begun to increase.

This leads to the assumption that the aggregation has not yet reached the extent of the PS in DOP pictured in part c. of the previous scheme. Instead it remains in an intermediate state between b. and c. where the molecules arrange themselves in some kind of order that results in higher scattering lengths, raising the intensity of the scattered light. However, no particles with larger shape are formed yet, and therefore the viscosity and the light passing through are not effected as much as in DOP. At much higher shear rates (which can not be reached with our experimental setup for the time being) we assume that this effect appears as well.
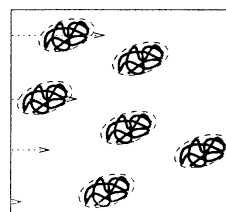
b-c. Intermediate state of order

Final discussion and conclusion

Although PS shows differences in the shear-induced aggregation in DOP and in DEP, the general tendencies are the same in both solvents. After the molecules are oriented in the shear flow, they adopt a shape and/or order in which it is more favorable to aggregate. Despite the non-equilibrium conditions that even a simple shear provides, it seems reasonable to formulate this tendency to aggregate in terms of thermodynamics, as the dependency of the aggregation on the parameters temperature, concentration, and molar mass can be predicted from thermodynamic models. This is in agreement with recent measurements of Pine et al. [20] at comparably high shear rates, which are interpreted as phase separation.

However, the comparison of the aggregation of PS in DOP and in DEP makes it clear that a lot of questions concerning the actual process of aggregation lie beyond the thermodynamic prediction of possible phase transitions but in the kinetics of the process. The simple schemes on the previous page are a figurative proposal but well-founded only up to part b. In the future we expect to get more information, especially on the shape of the aggregates, by examining the length of the axes of the molecules under shear up to the point of aggregation and beyond.

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