Rheooptical detection of shear-induced orientation of high molar mass polystyrene in dilute solution

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The shear-induced orientation of high molar mass polystyrene ($M_w > 9 \times 10^6\,\mathrm{g\,mol^{-1}}$) is investigated by means of rheooptical wide-angle laser light scattering in dilute solution at 20°C in the near-theta solvent *trans*-decalin and in thermodynamically good mixed solvents consisting of oligostyrene in toluene. From these measurements the orientation of the macromolecules with respect to the direction of flow is obtained as a function of shear rate and polymer concentration. The orientational behaviour is discussed with respect to the influence of viscosity, solvent power and shear rate, and finally compared with theoretical predictions and with literature data obtained by light scattering and flow birefringence. The results obtained by the new rheooptical light scattering photometer are within the theoretical limits but differ in the degree of orientation, especially at very low shear rates, from the experimental results given in the literature. This deviation is at least partly explained by means of polydispersity and chain stiffness.

(Keywords: light scattering; shear flow; dilute polymer solution)

INTRODUCTION

The rheological properties of flowing polymer solutions are mainly influenced by the orientational and deformational behaviour of the macromolecules effected by hydrodynamic and frictional forces. Flow birefringence[1,2] was probably one of the first among the optical methods employed for the study of flowing polymer solutions. Despite a very complete set of theoretical work and improved detection arrangements, flow birefringence studies remain localized in a small number of laboratories. An alternative method is the application of light scattering[3,4], which is the only method that can provide the dimensions of the macromolecule deformed by the flow with a minimum of assumptions.

A new method involving rheooptical laser light scattering[5] was presented some years ago which enables the detection of the molecular orientation and deformation of polymers in dilute solutions subjected to a Searle-type shear flow. The optical and rheological conditions for the application of this method to polymer solutions and the first measurements on high molar mass polystyrene in benzene have been discussed in a previous paper[6]. Further measurements on high molar mass polystyrene ($M_w = 9.35 \times 10^6\,\mathrm{g\,mol^{-1}}$ and $M_w = 10.3 \times 10^6\,\mathrm{g\,mol^{-1}}$) have been performed in *trans*-decalin, which is a theta solvent for polystyrene at 18.8°C, and in mixed solvents consisting of 11.4 wt% and 32.1 wt% oligostyrene in toluene. The fraction of oligostyrene in toluene raises the viscosity of the solution and therefore the accessible range of shear rates for the rheooptical investigation before the appearance of flow instabilities caused by the Searle-type shear flow. On the other hand, there is only a weak influence on solvent power, and therefore the oligostyrene–toluene compositions turn out to represent good solvents for polystyrene at 20°C.

THEORY

Subjected to shear flow, any anisotropic particle becomes oriented to the direction of flow when the action of shear flow overcomes the Brownian motion, i.e. when the reduced shear rate β described by the molecular relaxation time τ and the shear rate G becomes

$$\beta = \tau G \geqslant 1 \tag{1}$$

It is well known[7,8] that flexible polymer chains in solution are in the shape of anisotropic ellipsoidal coils, where the anisotropy grows with chain length and excluded volume. In a solution at rest, owing to rotatory diffusion, the time-averaged shape of these coils appears to be spherical and their radius of gyration can be determined by classical static light scattering. Using the viscometrically relevant rotatory relaxation time τ_r, the reduced shear rate for macromolecules in dilute solution is given by

$$\beta = \tau_r G = \frac{[\eta]\eta_s M}{RT} G \tag{2}$$

with $[\eta]$ being the intrinsic viscosity, η_s the solvent viscosity and M the molar mass. R and T have their usual meanings.

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In two-dimensional shear flow the molecular rotation in the flow plane, defined by the direction of flow and the direction of the shear gradient (*Figure 1*), is non-uniform, i.e. depending on the shear rate the anisotropic coil remains parallel to the direction of flow for longer than it is perpendicular to this direction. With increasing shear rate the time-averaged major axis of the polymer coil becomes more and more oriented to the direction of flow, while at the same time deformation of the coil in the flow plane occurs.

Owing to orientation and deformation the gyrational space of the macromolecules in shear flow changes from the spherical shape at rest to a shear dependent, anisotropic ellipsoidal form, and conventional static light scattering can no longer be applied. In their theoretical work Peterlin *et al.*[9,10] demonstrated how the angular distribution of the scattered light intensity in the flow plane is correlated with the orientation of the gyrational space of the molecules. At a constant rate of shear this scattering distribution has a maximum at a certain angle $\omega_{\max}$ which is predicted to coincide with the direction of the minor axis of the oriented coil in the flow plane. With increasing shear rate $\omega_{\max}$ should approach 90° (*Figure 2*), while the major axis of the coil, which is perpendicular to the minor axis in the flow plane, moves to the direction of flow. Hence the angle between the orientation of the major axis and the direction of flow, generally denoted as the orientation angle χ (*Figure 1*), is determined by

$$\chi = 90° - \omega_{\max} \tag{3}$$

Similar predictions for rigid particles were also given and experimentally proved by Heller *et al.*[11,12]. In the limit of zero shear flow $\chi = 45°$, and with increasing shear force χ changes from 45° to 0°, while $\omega_{\max}$ changes from 45° to 90°. However, perfect orientation ($\chi = 0°$) of macromolecules will not be achieved in shear flow because a simple shear flow is generally a weak flow, and even rigid particles are known to be only partly oriented in a weak flow, whereas they will be aligned with the flowlines in a strong flow, for example in extensional flow.

EXPERIMENTAL

Samples

The light scattering measurements were performed on two high molar mass polystyrene standards with $M_w = 9.35 \times 10^6\,\mathrm{g\,mol^{-1}}$ ($M_w/M_n = 1.20$) and $M_w = 10.3 \times 10^6\,\mathrm{g\,mol^{-1}}$ ($M_w/M_n = 1.25$), in the following denoted as PS9 and PS10, purchased from Polymer Laboratories, UK. For the rheological characterization of the solution properties some more polystyrene standards of lower molar mass down to $M_w = 1.86 \times 10^6\,\mathrm{g\,mol^{-1}}$ were used.

The solvents used were *trans*-decalin, purchased from Fluka, Switzerland (purity >99%) and Merck–Schuchardt, Germany (purity >98%), and mixtures of oligostyrene (commercial product kindly donated by BASF, Germany), $M_w = 1300\,\mathrm{g\,mol^{-1}}$, in toluene. The commercial oligostyrene sample contained 50 wt% toluene. The solvent mixtures contained 11.4 wt% (oligo10) and 32.1 wt% (oligo30) of the commercial product in toluene (i.e. the pure fractions of oligostyrene in oligo10 and oligo30 were 5.7 wt% and about 16 wt%, respectively). All commercial samples were used as obtained. To distinguish between the two samples of *trans*-decalin, which differ in their abilities to dissolve polystyrene, they were denoted as decalin(FL) (FLuka) and decalin(MS) (Merck–Schuchardt) according to the names of the manufacturers.

Rheology

In order to compare the orientational behaviour of polystyrene in different solvents and against the theoretical models, the orientation angle χ has to be plotted against the reduced shear rate β. For this reason the solvent viscosity and the intrinsic viscosity of the polymer (equation (2)) had to be determined. For the discussion of the influence of solvent power on orientation, the parameters a and K of the intrinsic viscosity–molar mass relationship (Mark–Houwink equation)

$$[\eta] = KM^a \tag{4}$$

were evaluated in the molar mass range $1.86 \times 10^6\,\mathrm{g\,mol^{-1}} \leqslant M_w \leqslant 10.3 \times 10^6\,\mathrm{g\,mol^{-1}}$.

The viscometric measurements were performed with a Couette-type rotational viscometer (CV100, Haake, Germany) up to a maximum shear rate $G = 1000\,\mathrm{s^{-1}}$. Because of the viscoelasticity of the high molar mass polystyrene, the intrinsic viscosity was determined by extrapolating the shear dependent reduced viscosity to zero concentration and zero shear rate. According to a modification suggested by Zisenis and Springer[13], the

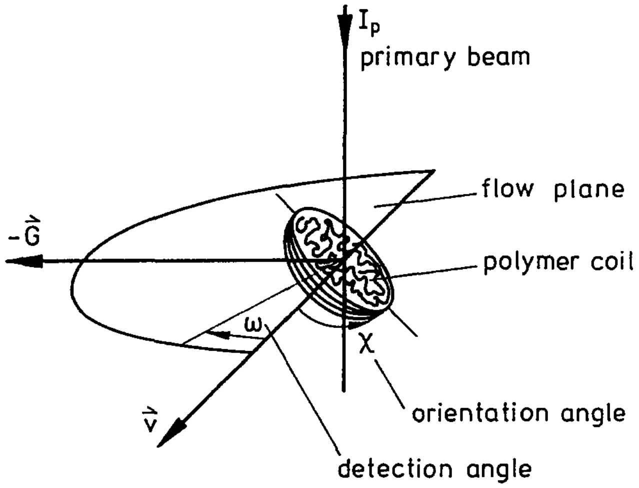

Figure 1 Orientation in a two-dimensional shear flow. The flow plane is defined by the vectors of flow velocity $\vec{v}$ and shear gradient $\vec{G}$

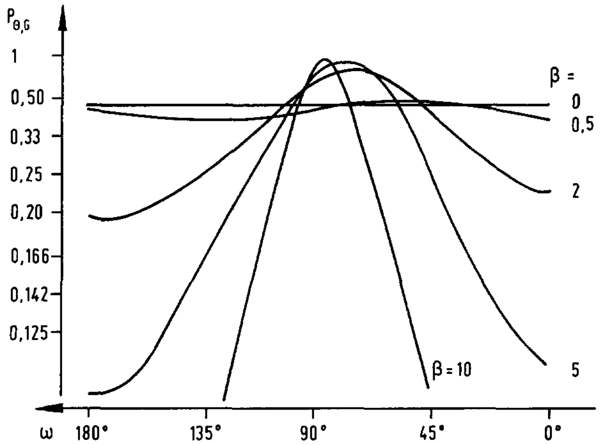

Figure 2 Peterlin[9] scattering function for an elastic dumb-bell under shear in the flow plane for various reduced shear rates β

Mark–Houwink parameters a and K were calculated from the slope of the Tanaka plot[14] by assuming a constant value $K_\theta = 76 \times 10^{-3}\,\mathrm{ml\,g^{-1}}$. The Tanaka plot gives a straight line for $([\eta]/M^{1/2})^{5/3}$ *versus* $M^{1/2}$ over the entire range of molar mass, with the ordinate intercept at $K_\theta^{5/3}$.

The results of the rheological characterization of the different polystyrene–solvent systems are shown in *Table 1*. Newtonian fluid properties for the oligostyrene–toluene compositions were proved for up to 52 wt% of the oligostyrene sample in toluene. All viscometric measurements were performed on dilute solutions with a maximum polymer concentration of about double the overlap concentration, defined by $c^* = 1/[\eta]$.

Light scattering

The rheooptical measurements were performed with the Springer–Wölfle rheophotometer[5] as shown in *Figure 3*. The gap of the double-cylinder shear cell with a rotating inner cylinder was passed vertically by a polarized argon-ion laser beam ($\lambda = 514$ nm under vacuum). Relating to the developments of Peterlin, Heller and coworkers, the scattered light intensity of the solutions was determined in the flow plane from $\omega = 40°$ to $\omega = 140°$ with respect to the direction of flow. Instead of scanning ω at a constant shear rate, the detection of the scattered light was performed by increasing the shear rate linearly from zero to its maximum value whilst the detection position ω was kept constant. The increase in shear rate G was kept as slow as necessary to give a steady state for each step in G. It was also shown that none of the solvents, and especially none of the mixtures, shows shear dependent scattering. Although the investigated solutions exhibited an adequate refractive index increment, the shear-induced variation of scattered light intensity I_β from the intensity I_0 at rest was small. To reach a higher sensitivity in the determination of $\omega_{\max}$, relative light-scattering intensities $I_{\mathrm{rel}} = (I_\beta - I_0)/I_0$ were plotted against ω instead of absolute intensities.

Table 1 Solvent viscosity η_s and Mark–Houwink parameters for polystyrene

Solvent	T(°C)	η_s(mPa s)	a	$10^{-3}K$(ml g^{-1})
Decalin(FL)	20	2.43	0.523	56.8
Decalin(MS)	25	2.17	0.590	23.2
Oligo10	20	0.92	0.760	5.48
Oligo30	20	2.42	0.747	5.61

The plot for PS9 in decalin(MS) (*Figure 4*) demonstrates how the angular distribution of I_{rel} in the flow plane changes with increasing shear rate. At $\beta < 1$, where Brownian motion is dominant, the distribution is relatively wide and shows (in this example) a maximum at about $\omega = 60°$. If with $\beta = 1$ the action of shear flow overcomes the Brownian motion, the scattered light distribution takes its significant form, and from there on with increasing shear rate the maximum increases and tends towards $\omega = 90°$. During this orientational phase at a certain angle ω, which depends on the polymer–solvent pair, the intensity remains constant. This is consistent with the predictions of Peterlin and Heller. If with increasing shear rate, owing to the low viscosity of the solutions and the Searle-type shear flow, laminar flow instabilities (i.e. formation of a Taylor vortex flow[15,16]) are superimposed on the original shear flow, the intensity decreases over all ω. If, on the other hand, shear-induced aggregation or phase separation occurs, the intensity should rise for each ω.

Usually the orientation angle χ is plotted against β. Following the predictions from theory[9–12] and the results of comparable rheooptical investigations, the orientation angle determined by flow light scattering methods is expected to coincide with the extinction angle known from flow birefringence. For this reason, the flow birefringence theory relating to the orientational behaviour of macromolecules in shear flow can be used for the discussion of results obtained by light scattering. Hence, the shear rate dependence of χ can be compared with the calculated relations of Kuhn (elastic dumb-bell), Rouse (spring–bead model; free-draining coil) and Zimm (spring–bead model with hydrodynamic interactions; impermeable coil) given by

$$\cot(2\chi) = \beta/m \tag{5a}$$

with $m = 1$ (Kuhn), 2.5 (Rouse) and 4.88 (Zimm), and by

$$\chi = 0.5\arctan(m/\beta) \tag{5b}$$

Although these models are relatively simple and, for example, do not account for the non-linear viscoelasticity

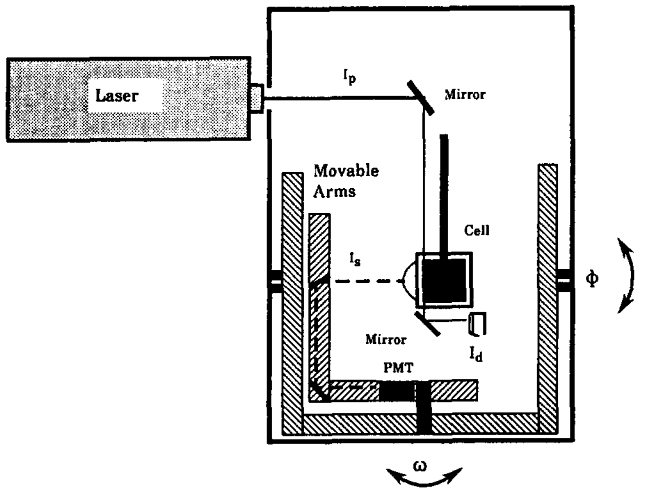

Figure 3 Laser light scattering photometer. PMT, photomultiplier; I_p, primary intensity (incident beam); I_s, scattering intensity; I_d, photo diode; ϕ, angle determining the position of the outer moveable arm

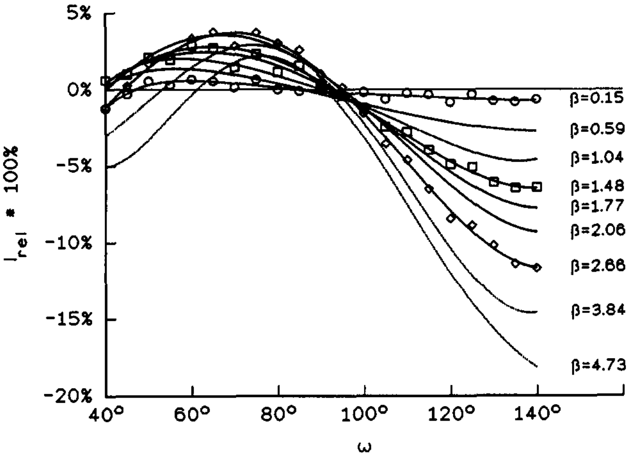

Figure 4 Angular distributions of the relative scattering intensity as a function of reduced shear rate, described by polynomial fits. The sample was PS9 ($M_w = 9.35 \times 10^6\,\mathrm{g\,mol^{-1}}$), $c = 1.570\,\mathrm{g\,l^{-1}}$, in decalin(MS) at 25°C

of high molar mass polymers in dilute solution, they are still widely referred to in the literature[17]. For this reason, we are also going to compare our experimental results with these theoretical predictions. Furthermore, the validity of the above theories is restricted to the ideal, perfectly flexible chain model and to the range of low shear rates, where the shear rate dependence of χ is nearly linear. Nevertheless, at higher shear rates the comparison of the experimental data with the theoretical behaviour can at least be qualitative.

As the experimentally observed orientational behaviour is known to be strongly influenced by the polydispersity of the sample, a polydispersity correction has to be introduced to β. According to Peterlin[18], a rough estimate of this correction is given by

$$\beta_{\text{cor}}^2 = \frac{(z+2+2a)!}{(z+1)^{2+2a}z!}\beta^2 = p\beta^2 \qquad (6)$$

where p is a function of the polydispersity parameter, $P = M_w/M_n = (z+2)/(z+1)$, and the solution properties, which are simply described by the exponent a in equation (4).

For the sake of clarity only the designation β is used for the reduced shear rate in the following; hence, for the experimental data in the present investigation $\beta = \beta_{\text{cor}}$.

RESULTS AND DISCUSSION

Influence of solvent and viscosity on orientation

The rheooptical detection of the shear dependent orientation was performed on several dilute solutions of each polystyrene–solvent pair. In the range of low polymer concentration, i.e. $c < c^*$, all the detected χ data fall in the region between the limiting lines calculated according to the theoretical relations (equation (5b)) of the Kuhn and Zimm models as shown in *Figure 5*, which contains the data for PS10 in decalin(FL) and oligo30 at 20°C. These two systems represent a near-theta solution and a thermodynamically good solution, respectively. While the solvent viscosities of these different solutions are almost equal, the stronger orientation occurs in the thermodynamically better solution. If, however, the data for PS10 in oligo10 and oligo30 (see *Figure 6*) are compared, again a slightly better orientation appears in oligo30, although these two polystyrene–solvent systems are quasi-equivalent in solvent power ($a_{\text{oligo10}} = 0.760$, $a_{\text{oligo30}} = 0.747$). While the different orientational behaviours in decalin(FL) and oligo30 can be traced back to the larger expansion of the coil in oligo30 owing to the excluded volume effect, the more than two-fold higher solvent viscosity could be responsible for the stronger orientation in oligo30 in comparison to oligo10. However, the influences of the excluded volume, the intrinsic viscosity $[\eta]$ and the solvent viscosity η_s should be eliminated by the use of β.

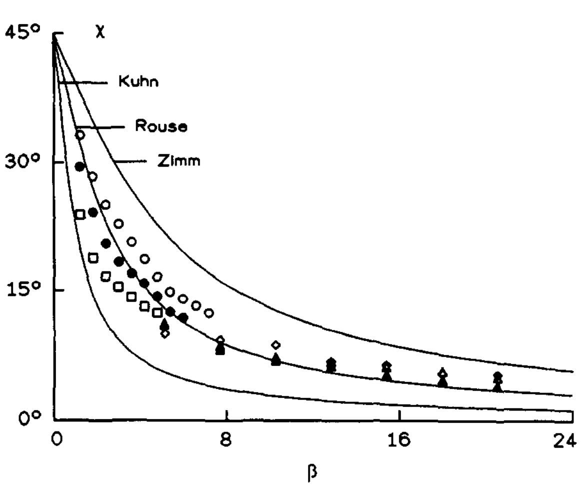

Figure 5 Orientation data for PS10 in decalin(FL) and oligo30 at 20°C as a function of reduced shear rate in comparison to the theoretical curves. For decalin: (○) $c_a = 0.646\,\mathrm{g\,l^{-1}}$; (●) $c_b = 1.322\,\mathrm{g\,l^{-1}}$; (□) $c_c = 2.024\,\mathrm{g\,l^{-1}}$. For oligo30: (△) $c_1 = 0.4144\,\mathrm{g\,l^{-1}}$; (▲) $c_2 = 0.6378\,\mathrm{g\,l^{-}}$; (◇) $c_3 = 0.8654\,\mathrm{g\,l^{-1}}$

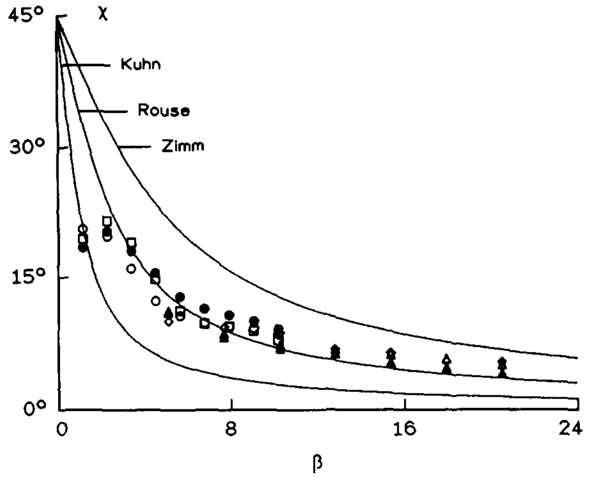

Figure 6 Orientation data for PS10 in oligo10 and oligo30 at 20°C as a function of reduced shear rate in comparison to the theoretical curves. For oligo10: (○) $c_a = 0.3334\,\mathrm{g\,l^{-1}}$; (●) $c_b = 0.4856\,\mathrm{g\,l^{-1}}$; (□) $c_c = 0.6702\,\mathrm{g\,l^{-1}}$. Same data as in *Figure 5* for oligo30

It is generally known[17] that χ depends only on mechanical and dimensional parameters relating to the elasticity, expansion and shape of the oriented particle. In the case of chain macromolecules these parameters are, in a simplified way, described by M, $[\eta]$ and η_s. Further relevant parameters are the coil flexibility, the form anisotropy of the coil, described by the ratio of its major axis to its minor axis, and the degrees of coil draining and hydrodynamic interaction. With increasing solvent power coil flexibility decreases and the axis ratio increases[7], and consequently the orientation becomes stronger[18]. Therefore, the difference between the degrees of orientation of PS10 in oligo10 and oligo30 and the degree of orientation in decalin(FL) may at least partly originate from the decreased coil flexibility.

In general, the orientation data in the present investigation are quantitatively of the expected magnitude and exhibit qualitatively the correct dependence on shear rate in comparison to the theoretical lines. Nevertheless, they do not coincide with any of the models, but cross with increasing shear rate the Rouse-type line from below and approach the Zimm-type line at higher shear rates.

Influence of concentration

For the purpose of a correct comparison of the experimental results with theory, the orientational behaviour of the isolated polymer molecule has to be estimated. For this reason, the experimental data have to be extrapolated to zero concentration. From the measurements in decalin(FL) (*Figure 5*), the influence of polymer concentration on orientation is clearly seen. With increasing concentration lower values of χ are detected at a constant value of reduced shear rate, displaying stronger orientation. The measurements in oligostyrene–toluene compositions (*Figure 6*), however, do not show a distinct influence of polymer concentration on χ, nor is there a significant variation in χ or a regular increase in orientability with concentration, as seen with decalin. This behaviour appears to agree with the experimental results of Champion and Davis[3], who found that below a certain concentration of polystyrene ($M_w = 4.6 \times 10^6\,\mathrm{g\,mol^{-1}}$) in cyclohexanone there was no concentration influence on the orientational behaviour. Surprising, however, is the deviation of the χ data obtained in the low shear regime in oligo10 from the generally observed shear dependence.

For a more precise investigation of the influence of polymer concentration on orientation, experiments were performed on PS9 in decalin(MS) with the polymer concentration ranging from $c = 0.2c^*$ to $c = 1.7c^*$ (*Figure 7*). These measurements were performed at 25°C, because this decalin sample did not have exactly the same properties as that used previously. However, this does not matter, as the solution properties are rheologically characterized (*Table 1*). The orientation data obtained from solutions of very low polymer concentration, i.e. $c < 0.4c^*$ for PS9 in decalin(MS), did not show a significant influence of concentration. For this reason, only the data for the lowest concentration within this range, $c = 0.2c^*$ ($= c_1$ in *Figure 7*), are shown. The data obtained from solutions of higher concentration, however, show a regular decrease in χ with increasing polymer concentration. Generally, the data for solutions in the range $c \leqslant 0.8c^*$ (c_1–c_3) are quantitatively in the right region covered by the theoretical lines and show the expected shear rate dependence. This changes when the polymer content reaches the overlap concentration c^* (c_4). Above this concentration (c_5–c_7), the orientation curve $\chi = f(\beta)$ may be divided into two parts. Below $\beta = 1.5$, the data can be fitted to curves similar to those for the orientational behaviour of solutions of low concentration with an initial value of $\chi = 45°$ at vanishing shear rate, only with a steeper decrease. Above $\beta = 1.5$, however, the shear dependence of the orientation nearly vanishes when $c > c^*$.

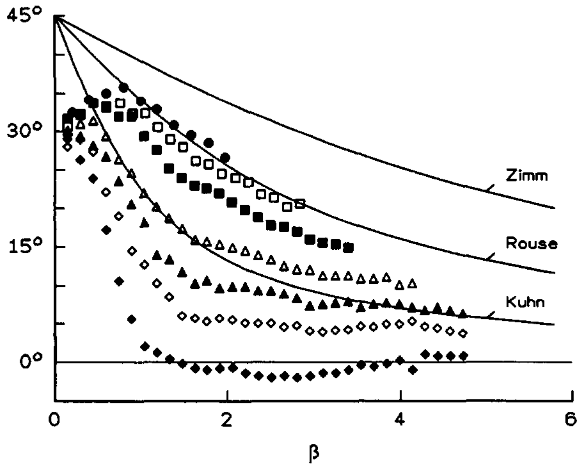

Figure 7 Orientation data for PS9 in decalin(MS) at 25°C as a function of concentration and shear rate: (●) $c_1 = 0.571\,\mathrm{g\,l^{-1}}$; (□) $c_2 = 1.570\,\mathrm{g\,l^{-1}}$; (■) $c_3 = 2.351\,\mathrm{g\,l^{-1}}$; (△) $c_4 = 3.088\,\mathrm{g\,l^{-1}}$; (▲) $c_5 = 3.869\,\mathrm{g\,l^{-1}}$; (◇) $c_6 = 4.135\,\mathrm{g\,l^{-1}}$; (◆) $c_7 = 5.207\,\mathrm{g\,l^{-1}}$

With increasing polymer concentration the orientation becomes stronger and seems to be perfect at $c_7 = 1.7c^*$, where the experimentally obtained orientation angle χ is about 0°. The negative values of χ may be traced back to experimental error. In contrast to theory, the observed orientation at the beginning of shear is not $\chi = 45°$. Moreover, in this polymer–solvent system the experimentally obtained orientation starts at about $\chi = 30°$, shows an initial small increase for $c \leqslant c^*$, and finally changes to the above-mentioned orientation curves, whose courses can be extrapolated back to the theoretical initial value at zero shear rate.

This complex behaviour will be more understandable if the data are transformed such that a parameter m is calculated from the experimental χ data according to a transformation of equation (5b) given by

$$m = \beta \tan(2\chi) \qquad (7)$$

and again plotted *versus* the reduced shear rate β. From flow birefringence and dynamic viscosity theory[1,19], m is known as the reciprocal value of the reduced steady-state shear compliance J_{eR}. This correlation, however, is restricted to the validity of the stress-optical law[1], which was originally derived for rubber-like networks and then generalized to temporary networks, the dumb-bell model and the spring–bead models, based on an ideally flexible random flight chain.

For theta solvents, $J_{eR} = 0.206$ is predicted when there is strong hydrodynamic interaction such that the polymer coil behaves like a non-draining sphere (Zimm case), while $J_{eR} = 0.4$ is predicted when hydrodynamic interaction between segments is assumed to be absent and the coil behaves like a free-draining sphere (Rouse case). For good solvents, J_{eR} is predicted to have an intermediate value because of excluded volume effects. Initially, the shear compliance is the inverse of the shear modulus. In practice, J_{eR} describes the compliance of the dissolved polymer to shear force, and therefore the contrary in sense m represents the resistance of the coil towards orientation through shear force.

The correlation between the orientation angle obtained by flow light scattering and the extinction angle obtained by flow birefringence has been derived by Peterlin, Heller and coworkers[10,11]. Based on this correlation a discussion of the orientational behaviour detected by light scattering in relation to the stress-optical law is possible. Nevertheless, owing to partial chain rigidity caused by excluded volume effects in good solvents, an experimental deviation from the ideally flexible chain is apparent. Therefore, it may be more reasonable to define m as the shear resistance of the coil rather than characterize m as the reciprocal of the reduced shear compliance. In our definition, the shear resistance m is a relative value characterizing the apparent resistance of the particle in shear flow towards orientation as a function of shear rate, particle dimensions and particle flexibility. Through this practical definition the discussion of m is not restricted to the validity of the stress-optical law.

The transformation of χ data to m data is shown in *Figure 8* with the same data set as in *Figure 7*. In the investigated range, m seems to increase linearly with shear rate when $\beta \geqslant 1$; furthermore, the slope b of this increase apparently does not depend on polymer concentration. With this assumption the estimation of zero concentration properties is possible by linearly extrapolating the concentration dependent m data to zero shear rate, and finally estimating the intrinsic value m_0 at zero concentration from these data. A description of zero concentration properties is then given by $m = m_0 + b\beta$.

Of special interest is the initial part of the curves below $\beta = 1$ in *Figure 8*, where Brownian motion is thought to be dominant. Although the determination of $\omega_{\max}$ in this low shear region is rather inexact because of the weak curvature of the scattered light distribution (see *Figure 4*), the correlation of the data cannot be denied. An extrapolation of the m data for all concentrations in the low shear regime to zero shear rate apparently results in $m_0 = 0$; this is in opposition to any theory or experimental results given in the literature. Following the variation in m with increasing shear rate, for all concentrations m at first increases quasi-linearly up to a certain value below $\beta = 1$, and then changes to the linear shear dependent behaviour as mentioned above. With increasing concentration m decreases and finally is about zero for the investigated system at c_7. In terms of shear resistance this means that, owing to increasing intermolecular interaction with increasing polymer concentration, orientation becomes easier, and therefore the apparent resistance of the macromolecule towards orientation becomes weaker.

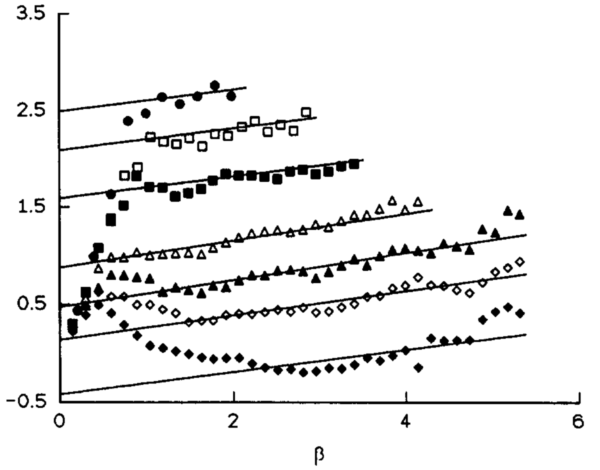

Figure 8 Shear resistance m of PS9 in decalin(MS) at 25°C as a function of concentration and shear rate (symbols as in *Figure 7*). The lines demonstrate the extrapolations to zero shear rate

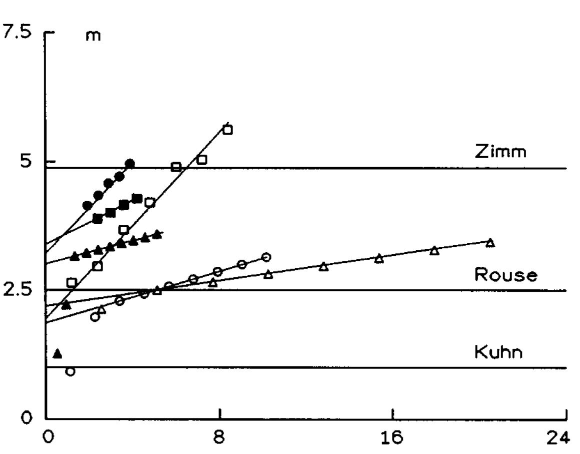

Figure 9 Comparison of zero concentration results: (●) PS9 in decalin(FL)[20]; (■) PS10 in decalin(FL); (▲) PS10 in decalin(MS); (○) PS10 in oligo10; (□) PS9 in oligo20[20]; (△) PS10 in oligo30. The lines demonstrate the extrapolations to zero shear rate

The above evaluation has also been applied to the data for PS10 in decalin(FL), oligo10 and oligo30 to compare the zero concentration behaviour with theory. While extrapolation to zero concentration is easily done for decalin(FL), the data for the oligo solutions generally obey the same shear dependence, but do not show any regular dependence on concentration. For this reason, average values have been taken from these data for the comparison. Although the χ data for oligo10 and oligo30 are slightly but significantly different, the corresponding m data are very close to each other and show nearly the same shear dependence. Nevertheless, the intrinsic shear resistance m_0 is larger for oligo30, while the shear dependence of m, i.e. the slope b, is slightly stronger for oligo10. Similar to the data in *Figure 8*, for oligo10 m data are obtained in the low shear regime which differ in shear dependence from the m data at higher shear rates. An extrapolation of these data at low shear rates to zero shear rate may also result in $m_0 = 0$, as seen with the data for PS9 in decalin(MS) (*Figure 8*). But for oligo30 no experimentally usable data could be gained in the region of very low reduced shear rate. A definite explanation for this strange behaviour cannot be given now, but it might be related to the experimental method or the viscoelasticity of these high molar mass polymers.

Comparison of results

In *Figure 9* the averaged m data for the oligo solutions and the zero concentration data obtained in decalin are compared to the values from the Kuhn, Rouse and Zimm models. With reference to the general experience of flow birefringence[1,17], the intrinsic shear resistance m_0 of flexible macromolecules is predicted to be 4.88 (Zimm) in theta solvents, and finally approach 2.5 (Rouse) in good solvents. The experimentally obtained values in the present investigation for the thermodynamically weak systems are $m_0 = 3.39$ (PS10 in decalin(FL)) and $m_0 = 3.01$ (PS9 in decalin(MS)); $m_0 = \text{ca.}\,2.0$ for PS10 in good solvents ($m_0 = 1.89$ in oligo10 and $m_0 = 2.18$ in oligo30). With increasing shear rate the shear resistance generally becomes stronger. Through equations (6) and (7), the value of m is a function of β and the polydispersity correction factor p. As p gives only a rough estimate of the polydispersity correction, the results obtained for the intrinsic shear resistance represent only the minimum values.

The earlier investigations of Stock[20] on polystyrene ($M_w = 9.35 \times 10^6\,\text{g mol}^{-1}$) in decalin(FL) and in a mixture of 22.1 wt% oligostyrene in toluene (oligo20), both at 20°C, yield qualitatively the same results (*Figure 9*) as this investigation. Although the shear rate dependence of m appears to be stronger, the intrinsic values of the shear resistance are confirmed by the results of the present investigation obtained for the same polymer–solvent systems. Stock's data give $m_0 = 3.20$ for decalin(FL) and $m_0 = 1.94$ for oligo20. The difference in shear dependence may be related to the difference in evaluation procedure. Nevertheless, the results are widely consistent, and finally coincident values of the intrinsic shear resistance are obtained.

Before we compare our results to the flow birefringence results, we should discuss the light-scattering results of Cottrell *et al.*[4], obtained from rheooptical investigations of high molar mass polyisobutene (PIB) in decalin. The experimental χ values the authors obtained by investigation of this thermodynamically good system ($a = 0.70$)

are believed to be in good agreement with the experimental results obtained by flow birefringence for the same polymer–solvent pair, and also with the theoretical prediction. In practice, Cottrell *et al.* took m as an adjustable constant in equation (5b), which they found to fit best to the experimental χ data for $m = 2.5 \pm 0.5$. A comparison with the limiting relations according to Kuhn and Zimm was not drawn. However, if the experimental data of Cottrell *et al.* are plotted in orientation diagrams (χ *versus* β) and in diagrams of m *versus* β, a large scatter of data around the Rouse-type line is clearly seen in both diagrams. Even here, an increase in shear resistance with shear rate is obvious. Estimation of the intrinsic value, which incidentally is rather uncertain, gives $m_0 = 2.5 \pm 0.5$ for solutions of PIB when $M_w = 16.8 \times 10^6\,\mathrm{g\,mol^{-1}}$ and $m_0 = 2.0 \pm 0.5$ when $M_w = 10.5 \times 10^6\,\mathrm{g\,mol^{-1}}$, so that even here the intrinsic values below $m = 2.5$ (Rouse) are experimentally preserved.

For comparison to the flow birefringence results, the data for the extinction angle χ of polystyrene ($M_w = 1.14 \times 10^6\,\mathrm{g\,mol^{-1}}$) in the thermodynamically good solvent monobromobenzene have been taken from a paper by Janeschitz-Kriegl[21]. Owing to the lower molar mass of the polystyrene sample and the very low solvent viscosity, and despite the relatively high values of the shear rate G, only very low values of the reduced shear rate β were achieved. Nevertheless, the extinction angle data, which were corrected for the influence of the solvent birefringence by Janeschitz-Kriegl, clearly show the expected dependence on concentration and on shear rate, and are easily extrapolated to zero concentration behaviour (*Figure 10a*). In harmony with the flow birefringence theory, the zero concentration data are in the region between the Zimm-type and Rouse-type limits. The intrinsic shear resistance $m_0 = 2.79$ (*Figure 10b*), which in correspondence with theory describes good solution properties.

In contrast to the light scattering data, the flow birefringence measurements display clear and correct orientational behaviour even at relatively low reduced shear rates. On the other hand, in terms of the shear resistance m the birefringence results also show that this quantity increases quasi-linearly with shear rate. However, the intrinsic value m_0 obtained from the flow birefringence data is larger than the values obtained by light scattering measurements, while the light scattering results of the present investigation are in good agreement with those of Cottrell *et al.* The deviations may originate from differences in the molar masses of the investigated polymers, or may be traced back to an insufficient polydispersity correction in the evaluation of the light scattering data. However, since the two orientation angles obtained independently from flow birefringence and from flow light scattering are related to different optical methods and to different optical properties of the polymer, there is the further possibility that the observable deviation in the degree of orientation is related to the difference in optical technique.

CONCLUSIONS

In addition to earlier papers[5,6], the present investigation demonstrates that the new rheooptical light scattering photometer allows the detection of the shear-induced orientation of polymers in dilute solution. The investigation of high molar mass polystyrene in good and poor solvents shows that the degree of orientation in shear flow depends on solvent viscosity, polymer concentration, coil expansion and chain rigidity. An increase in one of these parameters leads to a stronger orientation of the polymer coil.

While the measurements for the good solvents (oligo solutions) do not show a distinct influence of polymer

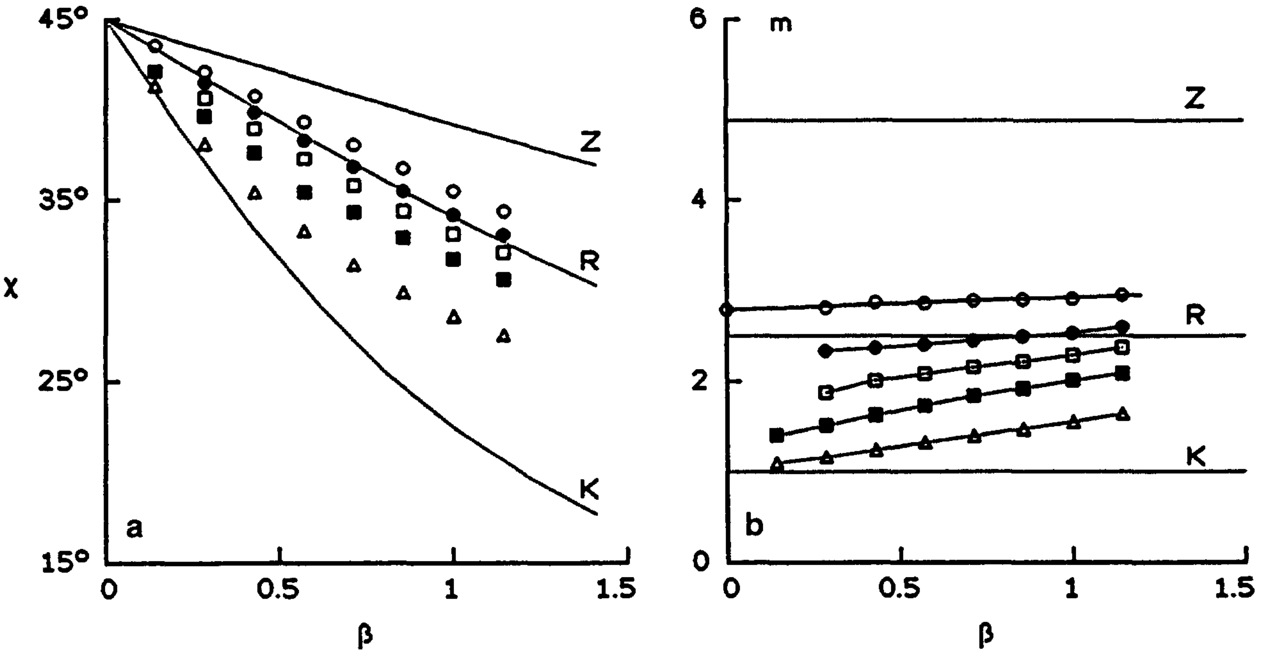

Figure 10 (a) Extinction angles obtained by flow birefringence[21] for polystyrene ($M_w = 1.14 \times 10^6\,\mathrm{g\,mol^{-1}}$) in monobromobenzene in comparison to the theoretical values: (●) $c_a = 2.0\,\mathrm{g\,l^{-1}}$; (□) $c_b = 3.5\,\mathrm{g\,l^{-1}}$; (■) $c_c = 5.0\,\mathrm{g\,l^{-1}}$; (△) $c_d = 10.0\,\mathrm{g\,l^{-1}}$; (○) zero concentration values. (b) Same data set recalculated to shear resistance m in comparison to the theoretical values

concentration, for the poor solvents (decalin) an extrapolation of the observed orientation angles to zero concentration behaviour is easily performed. In the range of very low shear rates, i.e. $\beta < 1$, where Brownian motion is dominant, the obtained orientational behaviour deviates from the general linear behaviour at higher shear rates. In opposition to theory and experimental results given in the literature, the limiting orientation at zero shear rate obtained by the present light scattering investigation is smaller than $\chi = 45°$. This deviation may be related to the evaluation procedure, or to the viscoelasticity of the high molar mass polystyrene.

Compared to another rheooptical light scattering method[4], the Springer–Wölfle rheophotometer turns out to be more sensitive and gives quantitatively better results. However, the results for the intrinsic shear resistance in good solvents obtained by the two light scattering methods are in good agreement. Nevertheless, the values are smaller than predicted by theory. This deviation may be traced back to the high molar masses of the polymer samples, to an insufficient consideration of the polydispersity or to partial chain rigidity with increasing solvent power. It may also originate from the difference between the flow birefringence and light scattering techniques in principle. Further theoretical and experimental investigations of this problem are in progress.

In summary, the Springer–Wölfle rheophotometer is a suitable tool for the detection of molecular orientation phenomena, and therefore can be employed for its main objective, the quantitative determination of coil deformation in shear flow according to the theory of Peterlin. The investigation of the strange orientational behaviour observed in the low shear range certainly remains a subject for further experimental work.

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