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Light-scattering studies on the dynamics of long-chain macromolecules in shear flow

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By use of the Springer–Wölfle rheophotometer, the shear-induced orientation of high-molar-mass polystyrene ($M_w = 10.3 \times 10^6\,\mathrm{g\,mol^{-1}}$) is investigated in dilute solution. It is known that the degree of molecular orientation in extremely good and poor solvents is significantly different and, furthermore, that its dependence on shear rate is a function of solvent power. For this reason, the present investigation deals with polystyrene in solvents of intermediate quality, represented by binary mixtures of poly(methylvinylether) (PMVE) and toluene. Owing to the variation of the PMVE fraction, which builds an isorefractive pair with toluene, a variation of both solvent quality and viscosity is realized. This investigation proves that the degree of orientation is induced not only by hydrodynamic interaction but also by thermodynamic interaction, and therefore describes a non-linear function of solvent power. The observed dependence of the rheo-optically detected molecular orientation on solution properties is interpreted and discussed in the light of various theoretical predictions.

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

INTRODUCTION

Orientation phenomena in simple shear flow, e.g. in a Couette- or Searle-type flow, are known to be a function only of mechanical and dimensional parameters[1]. In the case of chain macromolecules, these parameters are described by the molar mass, the intrinsic viscosity and the solvent viscosity. When the number of macromolecules is large enough to enable intermolecular interaction, the orientation behaviour is also influenced by polymer concentration. For a long time the application of flow birefringence techniques[2,3] was the method of favour in the optical study of polymeric solutions subjected to shear flow. Later on, light-scattering techniques[4,5] were developed for the same purpose, and it is widely believed that the shear-induced orientation obtained by these two methods is in good agreement. However, recent rheo-optical light-scattering investigations[6,7] on high-molar-mass polystyrene in good and poor solvents have revealed that there may be differences in the results, which can be traced back to differences in the related optical mechanisms.

The intention of the present paper is to prove these results in principle, and to find a relation between solvent power and the orientability of the polymer coil in shear flow. For this purpose, the orientation behaviour of high-molar-mass polystyrene is investigated in two composite solvents consisting of poly(methylvinylether) (PMVE) and toluene, which differ in viscosity and in solvent quality with regard to polystyrene. In comparison to formerly used oligostyrene–toluene solvent compositions[6], the present polystyrene–solvent systems exhibit a larger scattering contrast, because PMVE and toluene represent an isorefractive pair, while oligostyrene lowers the scattering contrast.

THEORY

It is well known[8,9] that flexible polymer chains in solution are in the form of anisotropic ellipsoidal coils, and anisotropy grows with chain length and excluded volume. In solution at rest, owing to diffusive motion of the solvent and of the chain segments, the polymer coils reveal an average spherical shape and their radius of gyration can be determined by classical static light scattering. When subjected to shear flow, the macromolecules become oriented in the direction of flow when the hydrodynamic shear force 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:

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

Taking the rheologically relevant rotatory relaxation time τ_r, the reduced shear rate for macromolecules in dilute solution is given by[1]:

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

where $[\eta]$ is the intrinsic viscosity of the polymer, M is the molar mass, and η_s is the solvent viscosity. R and T have their usual meanings.

With increasing shear rate, the longitudinal axis of the

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polymer coil is oriented to the direction of flow and the average ellipsoidal shape of the coil becomes deformed. Both orientation and deformation of the coil in shear flow cause the gyration space of the macromolecules to change from the spherical shape at rest to a shear-dependent anisotropic form. At that time, conventional static light scattering is not applicable any more and the evaluation of light-scattering data has to be performed according to the theoretical work of Peterlin *et al.*[10,11]

If only molecular orientation is to be determined, the scattered light intensity has to be measured within the flow-plane, which is defined by the vectors of shear gradient, $\vec{G}$, and flow velocity $\vec{v}$, as can be seen from the inset of *Figure 1*. Normally, the detection angle is varied in the range $40° \leq \omega \leq 140°$ with respect to the direction of flow, and the incident beam is normal to the flow-plane and polarized parallel to the flow.

As in the case of the Peterlin[10] scattering function (see ref. 6) and typically for all of the rheo-optical measurements, *Figure 1* demonstrates how the angular distribution of the scattered light intensity in the flow-plane is correlated to the orientation of the molecules. At a constant rate of shear, the intensity 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. With increasing shear rate, $\omega_{\max}$ approaches 90° while the longitudinal axis of the coil, which is perpendicular to the minor axis, moves to the direction of flow. The angle between the direction of the longitudinal axis and the direction of flow is called the orientation angle χ, defined by:

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

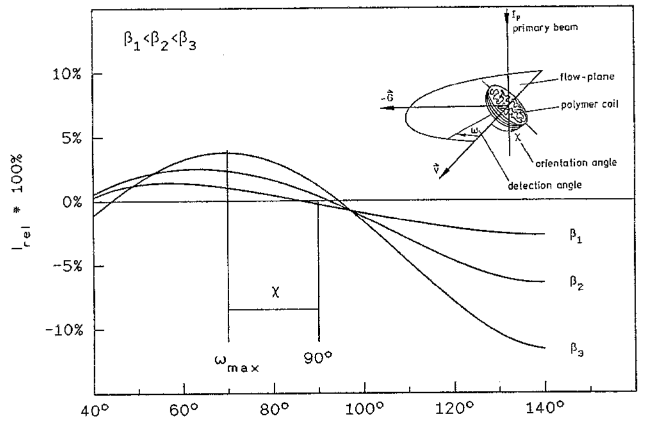

Figure 1 Schematic drawing of the orientation geometry and of the changes of the relative scattering intensity I_{rel} as a function of detection angle ω at different reduced shear rates β. While the polymer coil is oriented in the flow-plane, defined by the vectors of shear gradient $\vec{G}$ and flow velocity $\vec{v}$, the orientation angle χ is obtained as the difference between the detection angle showing maximum intensity, $\omega_{\max}$, and $\omega = 90°$

Table 1 List of solvents

Designation	Solvent
decalin	*trans*-decalin
Oligo30	30 wt% oligostyrene, $M_w = 1.3\,\text{kg}\,\text{mol}^{-1}$, in toluene
PMVE4	4 wt% poly(methylvinylether), $M_w = 130\,\text{kg}\,\text{mol}^{-1}$, in toluene
PMVE17	17 wt% poly(methylvinylether), $M_w = 130\,\text{kg}\,\text{mol}^{-1}$, in toluene

EXPERIMENTAL

Samples

The present investigation was performed on a high-molar-mass polystyrene sample (PS10) purchased from Polymer Laboratories Ltd, UK, with a weight-averaged molar mass of $M_w = 10.3 \times 10^6\,\text{g}\,\text{mol}^{-1}$ and a polydispersity of $M_w/M_n = 1.25$. For the rheological characterization of the solution properties, further polystyrene standards of lower molar mass, down to $M_w = 1.86 \times 10^6\,\text{g}\,\text{mol}^{-1}$, were used.

The composite solvents were established by adding a fraction of 4 wt% (PMVE4) or 17 wt% (PMVE17) of a commercial sample of PMVE (Gantrez M-556, GAF GmbH, Germany) to toluene. The average molar mass of the polydisperse PMVE sample is about $M_w = 1.3 \times 10^5\,\text{g}\,\text{mol}^{-1}$. As the commercial product contains 50 wt% of toluene, the absolute fraction of PMVE is 2 and 8.5 wt%, respectively. A summary of solvent designations and compositions is given in *Table 1*.

Rheology

Viscometric measurements were performed with a Couette-type rotational viscometer (CV100, Haake, Germany) which provides a continuous range of shear rate of $0 \leq G \leq 1000\,\text{s}^{-1}$. Newtonian fluid properties were proved for PMVE–toluene compositions up to 21 wt% of the commercial sample. The viscometric measurements were performed on dilute solutions up to a maximum polystyrene concentration of about double the overlap concentration c^*, defined by $c^* = 1/[\eta]$. In order to obtain intrinsic viscosities, the shear-dependent reduced viscosity was extrapolated to zero concentration and zero shear rate.

Finally, the solution properties are characterized by the parameters a and K of the Mark–Houwink relation:

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

and by the parameters A and B of the two-parameter theory, where A is the short-range interaction parameter which provides information about the local conformation of the chain owing to steric and/or thermodynamic interaction with the solvent, and B is the long-range interaction parameter which is related to the excluded volume effect owing to thermodynamic interaction of the polymer–solvent pair. Generally these parameters are evaluated by application of the Burchard–Stockmayer–Fixman equation[12,13], which relates $[\eta]/M^{0.5}$ to $M^{0.5}$. Because this evaluation fails when excluded volume effects are too large[14], the evaluation of A and B has to be performed with the modified equation suggested by Tanaka[15]:

$$([\eta]/M^{0.5})^{5/3} = K_\theta^{5/3} + 0.627\Phi_0^{5/3}A^2BM^{0.5} \tag{5}$$

where $K_\theta = \Phi_0 A^3$ is the unperturbed dimensions parameter, and $\Phi_0 = 2.862 \times 10^{23}\,\text{mol}^{-1}$ is the universal Flory constant. Plotting $([\eta]/M^{0.5})^{5/3}$ *versus* $M^{0.5}$, a linear relationship ensues and K_θ, A and B are obtained from the values of the ordinate intercept and the slope. The results of the rheological characterization of polystyrene in PMVE4 and PMVE17 at 20°C are given in *Table 2*.

Table 2 Solvent viscosity η_s, Mark–Houwink parameters a and K, short-range interaction parameter A and long-range interaction parameter B for polystyrene in different solvents

Solvent	T (°C)	η_s (mPa s)	a	K (ml g^{-1})	A (cm mol$^{0.5}$ g$^{-0.5}$)	B (ml mol^2 g^{-2})
Oligo30	20	2.4	0.747	5.61×10^{-3}	6.56×10^{-9}	1.09×10^{-27}
PMVE4	20	2.2	0.714	6.75×10^{-3}	6.28×10^{-9}	5.27×10^{-28}
PMVE17	20	40	0.647	12.2×10^{-3}	6.45×10^{-9}	1.60×10^{-28}
decalin	20	2.4	0.523	56.8×10^{-3}	6.45×10^{-9}	1.16×10^{-29}

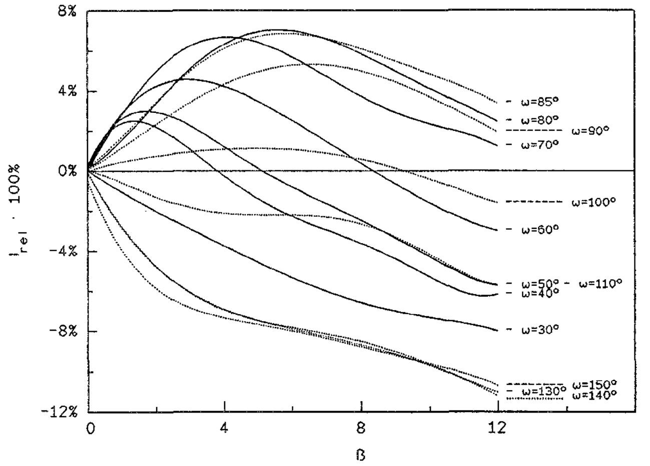

Figure 2 Orientation of PS10 in PMVE4, $c = 0.060\,\mathrm{g\,l^{-1}}$: relative scattering intensity $I_{rel} = (I_\beta - I_{\beta=0})/I_{\beta=0}$ as a function of reduced shear rate β at different detection positions ω

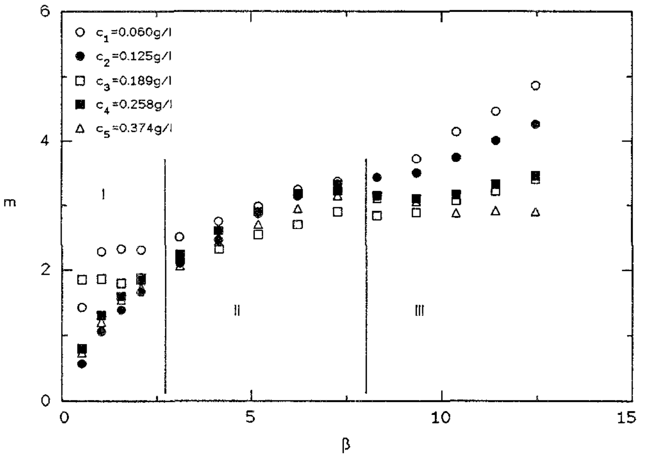

Figure 3 PS10 in PMVE4: orientation resistance m as a function of reduced shear rate β for different concentrations c. Part I is related to the onset of orientation, part II describes the pure orientation process, and part III is related to the formation of laminar Taylor vortex flow

Light scattering

The laser light-scattering measurements were performed with the Springer–Wölfle rheophotometer[16], which has been described in detail in a recent paper[6]. As optical and rheological preconditions of the solutions and first measurements have already been discussed in previous papers[6,7,17], only a short summary of the experimental set-up and the evaluation procedure will be given here.

The solution is placed in a small gap between two concentric cylinders, the inner of which is rotating while the outer one is fixed (Searle-type arrangement). The gap is passed by a vertically polarized argon-ion laser beam ($\lambda_0 = 514$ nm) parallel to the rotor axis, i.e. normal to the flow-plane. Through a window made of optical glass, the scattered light is detected in the flow-plane in the range of $40° \leq \omega \leq 140°$ with respect to the direction of flow. The angular distribution of the scattered light is detected once while the solution is at rest (I_0) and as a function of shear rate (I_β). When the relative scattering intensity $I_{rel} = (I_\beta - I_0)/I_0$ is plotted against β as a function of ω (*Figure 2*), the orientation process becomes rather evident. Looking at the shear-dependent variation of I_{rel} in the range $40° \leq \omega \leq 90°$, at first an increase of intensity with increasing shear rate is seen, followed by a maximum, and finally a decrease of intensity. Compared to the orientation process, it is seen that the polymer coil turns round with respect to the chosen position, and while doing so a maximum of intensity is observed when the smallest axis of the ellipsoid is turned to the detection position. If the molecule is looked upon from a position $\omega > 90°$, the orienting coil turns away from the detection position, and therefore the scattered intensity only decreases with β. A better view of the orientation process is achieved when I_{rel} is plotted against ω as a function of β, as shown in *Figure 1*, where the curves represent polynomial fits to measurements on polystyrene in decalin[6]. Again, the maximum of the curves (ω_{max}) gives the orientation of the minor ellipsoid axis and, with equation (3), the orientation angle χ is obtained from experimental data. Usually, the orientation angle is determined from the maximum of such polynomial fits[17].

As can be seen from *Figure 2*, the shear-dependent scattering intensity diminishes rather uniformly for all values of ω when a certain shear rate ($\beta \cong 8$) is exceeded. Experimental experience and calculations show that this is caused by the appearance of laminar shear instabilities, particularly Taylor vortex flow[18,19], which are due to the Searle-type flow and the low viscosity of the solutions.

In this investigation, the polystyrene concentration is in the relatively low range of $0.04c^*(c_1)$ to $0.25c^*(c_5)$ in PMVE4, and less than $0.7c^*$ in PMVE17. Owing to the differences in solvent viscosity (*Table 2*), lower values of the reduced shear rate β occur in PMVE4 and higher values in PMVE17. For that reason, low-shear behaviour is detectable in PMVE4 and high-shear behaviour is observed in PMVE17.

RESULTS AND DISCUSSION

Orientation

Figure 3 shows the shear-dependent orientation of PS10 in PMVE4 in terms of the orientation resistance parameter m, defined as:

$$m = \beta \tan(2\chi) \tag{6}$$

In theory, $m = 1$ is predicted for the elastic dumb-bell (Kuhn), $m = 2.5$ for the Rouse chain, representing the free-draining coil, and $m = 4.88$ for the Rouse chain with hydrodynamic interaction (Zimm), which represents the impermeable coil. Although these models are relatively simple, they are rather convenient and are often used for comparison to experiment[1] because they are well known and represent the theoretical limits. The validity of these 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 to the theoretical behaviour can at least be qualitative. While in theory the value of m is independent of β, light-scattering experiments[6,7] prove that m increases nearly proportionally with shear rate. Therefore, both the intercept at zero shear rate, m_0, and the slope $b = \mathrm{d}m/\mathrm{d}\beta$ are characteristic numbers describing the influence of solution properties on the orientation behaviour.

The orientation curves obtained for PS10 in PMVE4 (*Figure 3*) can be subdivided into three regions: up to $\beta \cong 2.7$ (part I) and above $\beta \cong 8$ (part III) m changes with concentration, while in between (part II) there is no dependence on concentration within the range of experimental error, which is about $m \pm 0.3$. The three observable regions may be associated with the onset of orientation (I), the pure orientation (II), and the superimposed Taylor vortices (III). Theory only describes the orientation behaviour displayed in II which, extrapolated to zero shear rate, exceeds an orientation angle of $\chi_0 = 45°$ at the onset of shear flow. The light-scattering experiments[6,20], however, show that orientation at rather low shear rates is different from the theoretical predictions. In the limit of zero shear rate, $m_0 = 0$, and with increasing shear force, m quite rapidly increases following the empirically developed series:

$$m(\mathrm{I}) = k_1\beta \pm k_2\beta^2 \mp k_3\beta^3 \tag{7}$$

which fully describes the variation of m at the onset of orientation until at a certain critical shear rate, β_{crit}, the orientation turns to the pure orientation behaviour approximately described by:

$$m(\mathrm{II}) = m_0 + b\beta \tag{8}$$

In poor solvents, the described onset of orientation $(k_1, k_2 > 0; k_3 < 0)$ and its dependence on concentration is very pronounced[20]. With increasing solvent power β_{crit} increases, while the onset behaviour $(k_1, k_3 > 0; k_2 < 0)$ and the concentration dependence become less pronounced. The measurements on PS10 in the solvent PMVE4 (*Figure 3*) represent the intermediate state: while some of the data in part I exhibit the described onset behaviour (c_2, c_4, c_5), the others (c_1, c_3) tend to follow the orientation given in part II.

The origin of the observed orientational behaviour at low shear rates is not at all clear now, but the effect may be traced back[20,21] to the formation of supramolecular domains which are orientable at low shear rates and destroyed with increasing shear force.

The results obtained for PS10 in PMVE4 are suitable for comparison with recent results[6] obtained on the same polystyrene standard in *trans*-decalin and in a composite solvent consisting of 30 wt% oligostyrene in toluene (Oligo30). As molar mass, solvent viscosity ($\eta_s \cong 2.2$ mPa s) and temperature are almost equal, the only variable parameter of solution properties remaining in equation (2) is the intrinsic viscosity, which characterizes the solution quality. Therefore, the different orientational behaviour of polystyrene in these solvents (*Figure 4*) is only a function of solvent power. As already mentioned, the concentration dependence of orientation is clearly seen in poor solvents (e.g. *trans*-decalin) and diminishes with increasing solvent power. For this reason, the data shown in *Figure 4* consist of values extrapolated to zero concentration for PS10 in *trans*-decalin, and mean values that are assumed to represent zero concentration behaviour for PS10 in PMVE4 and Oligo30, where no concentration dependence was observable. Furthermore, only data representing the pure orientational state (see *Figure 3*, part II) are shown, together with a linear approximation calculated from equation (8). *Figure 4* evidently demonstrates how, with increasing solvent power, the orientation resistance m falls both in terms of the intrinsic value m_0 and its shear dependence parameter $\mathrm{d}m/\mathrm{d}\beta$. The following relations are for PS10 in the given solvents at 20°C:

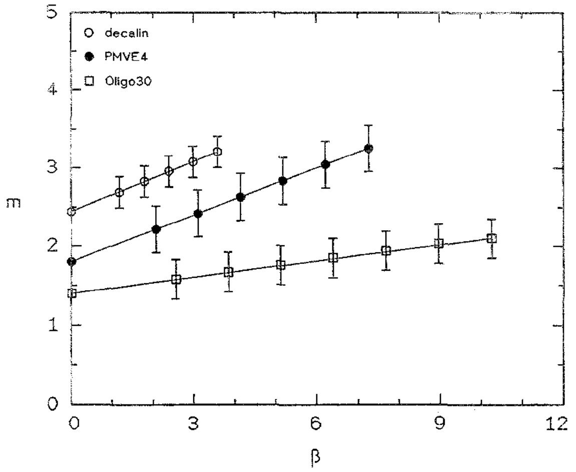

Figure 4 Orientation resistance m for $c \to 0$ as a function of reduced shear rate β in the pure orientational state (part II in *Figure 3*) and extrapolation to zero shear rate: comparison of the behaviour of PS10 in different solvents of equal viscosity $\eta_s = 2.3$ mPa s at $T = 293$ K. Increasing solvent power: decalin < PMVE4 < Oligo30

$$m_{\mathrm{Oligo30}} = 1.4(\pm 0.3) + 0.07\beta \tag{9}$$

$$m_{\mathrm{PMVE4}} = 1.8(\pm 0.3) + 0.21\beta \tag{10}$$

$$m_{\mathrm{PMVE17}} = 2.2(\pm 0.5) + 0.08\beta \tag{11}$$

$$m_{\mathrm{decalin}} = 2.44(\pm 0.05) + 0.22\beta \tag{12}$$

The solution properties of polymers are generally described by the Mark–Houwink exponent a which, however, represents the influence of both hydrodynamic and thermodynamic interactions. In practice, the contribution of thermodynamic interaction is expressed by means of the excluded volume parameter B, which is dependent on chain length and therefore, using equations (4) and (5), may be written as a function of M and a:

$$B_{(M)} = \frac{K^{5/3}5/3(2a-1)}{0.627\Phi_0 K_\theta^{2/3}} M^{5/3(a-0.8)} \tag{13}$$

Although this equation predicts the relation

$B \sim M^{5/3(a-0.8)}$, experimental evaluation[14] on the basis of Tanaka's[15] equation (5) proves that variation in B through molar mass is within the limits of experimental accuracy. At last, for a given polymer solvent pair B may be taken as constant over the entire range of molar mass.

According to Hsu and Schümmer[22], the contribution of hydrodynamic interaction to solution properties is described through the interaction parameter h^* as:

$$h^* = 8.87 \times 10^{-2}(a^{-2} - 1.10) \qquad (14)$$

This relation was achieved by regression of eigenvalue data obtained through computation and analysis of exact Zimm's eigenvalues, and was proved for a number of polymer–solvent systems as well as for the theoretical limits. When for flexible polymer molecules the Mark–Houwink exponent is between the limits of $a = 0.5$ at θ temperature and $a = 0.775$ in very good solution[20], $0.25 \leq h^* \leq 0.05$. The theoretically lowest value, $h^* = 0$, corresponds to $a = 1$ and the free-draining flexible polymer coil according to Rouse theory.

Theory, as well as evaluation of the rheo-optical measurements, proves that m_0 is a function of solution properties and declines with increasing solvent power. In theory, however, this decline is attributed solely to the diminution of hydrodynamic interaction, leading to the limits given by Zimm and Rouse based on the impermeable coil with strong and negligible hydrodynamic interaction, respectively. However, the comparison of m_0 with characteristic hydrodynamic (h^*) and thermodynamic (B) parameters (*Figure 5*) underlines the importance of excluded volume effects on the orientation dynamics of the polymer coil. Only in rather poor solvents, i.e. when $0.5 \leq a \leq 0.65$, is the hydrodynamic interaction predominant and m_0 is only dependent on h^*. With the assumptions $h^*_\theta = 0.25$ and $m_{0\theta} = 2.5$ (extrapolated value), the linear relation

$$m_0 = 2.5 - 2.25(0.25 - h^*) \qquad (15)$$

is obtained. In extremely good solvents, i.e. $0.73 \leq a \leq 0.775$, where thermodynamic interaction is predominant and hydrodynamic interaction is rather negligible, the relation

$$m_0 = 1 + 0.04(20 - B/(10^{-28}\,\mathrm{cm^3\,mol^2\,g^{-2}})) \qquad (16)$$

reveals, when the limiting values ($a \rightarrow 0.775$) $m_0 = 1$ and $B = 20 \times 10^{-28}\,\mathrm{cm^3\,mol^2\,g^{-2}}$ (calculated for PS10 in toluene) are assumed. In the intermediate range the orientation dynamics of the polymer coil is affected by both hydrodynamic and thermodynamic interaction.

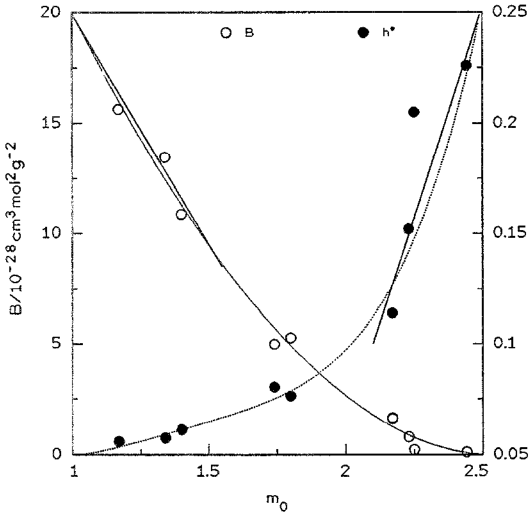

Figure 5 Changes of the intrinsic orientation resistance m_0 with variation of hydrodynamic (h^*) and thermodynamic (B) parameters. Curves represent polynominal fits, and straight lines demonstrate the linear approximations for dominant hydrodynamic and thermodynamic interaction, respectively

While the influence of solvent power on the intrinsic value m_0 is quite obvious, its contribution to the shear dependence parameter $\mathrm{d}m/\mathrm{d}\beta$ is more complicated. As already seen in the discussion of *Figure 4*, $\mathrm{d}m/\mathrm{d}\beta$ is slightly smaller for better solvents. Additionally, however, $\mathrm{d}m/\mathrm{d}\beta$ is smaller for higher solvent viscosity and molar mass[20]. Furthermore, changes due to solvent viscosity and molar mass are larger the better the solvent. Basicly, contributions of η_s and M to the shear-induced orientation should be covered by use of the reduced shear rate β. The experiment, however, proves that the influence of these parameters, which may be traced back to additional changes in chain and coil flexibility, is not negligible.

Basic theories relating to the viscoelasticity[23] and flow birefringence[2] of polymer solutions predict $m_0 = 4.88$ in the case of predominating hydrodynamic interaction (Zimm model) and $m_0 = 2.50$ in the absence of hydrodynamic interaction (Rouse model). Additionally, the agreement of the extinction angle obtained in flow birefringence experiments and the orientation angle obtained by flow light-scattering methods has been postulated[10,24] and experimentally proved[5], and the limiting values are believed to be valid both for flow birefringence and flow light scattering.

However, recent results[6], as well as the results obtained in the present investigation, show that in discrepancy with theory, $2.5 \leq m_0 \leq 1$ is determined by application of the rheo-optical measurement. Usually[1,25] the deviation of experimental results from theoretical prediction is related to polydispersity, especially to the contribution of the high-molar-mass tail. For correction of experimental data the relation[26]:

$$\beta^2_{\mathrm{cor}} = \frac{(z+2+2a)!}{(z+1)^{2+2a}z!}\beta^2 = p\beta^2 \qquad (17)$$

is suggested, where p is a function of polydispersity ($(z+2)/(z+1) = M_w/M_n$) and the Mark–Houwink exponent a. With $m \sim \beta$ (equation (6)), the correction of m and m_0 is given by $m_{\mathrm{cor}} = m\sqrt{p}$ and $m_{0,\mathrm{cor}} = m_0\sqrt{p}$, respectively. In fact, implementation of the polydispersity correction raises m_0 for $\Delta m_0 \approx 0.9$ and, therefore, even to values larger than 2.5 (*Figure 6*). The reliability of the polydispersity correction will be discussed in the following, together with further theoretical approaches.

In the case of flow birefringence, a link between mechanical and optical properties is formed by the so-called linear stress-optical rule[2], i.e. proportionality of the deviatoric components of the respective tensors and, as a consequence, coaxiality of these tensors. The stress-optical rule was originally derived for rubber-like networks and then generalized to temporary networks, the dumb-bell model and the bead-spring models. Assuming its validity, which is restricted to the ideally flexible chain, the orientation resistance parameter may be expressed by means of the steady-state shear

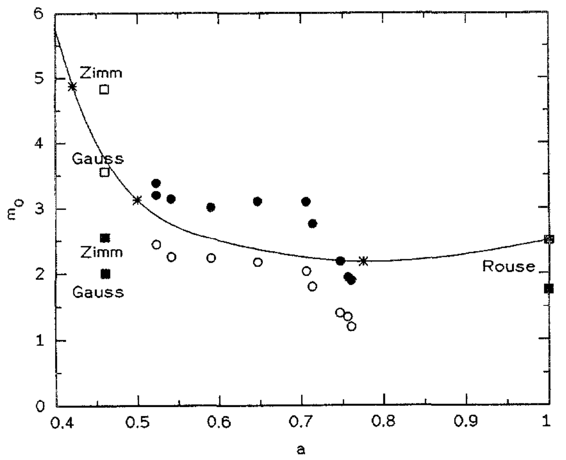

Figure 6 Comparison of experimental m_0 values (○) and m_0 data corrected for the influence of polydispersity (●) (equation (17)) to theoretical values calculated[27] for the orientation of the gyration tensor (■) and the stress tensor (□), and to values obtained for the inverse reduced shear compliance[20,22] (——)

compliance, $m_0 = 1/J_{eR}$. The dependence of this quantity on a and h^* is given[22] by:

$$J_{eR} = E7.82^{2a}/1.60^2 \qquad (18)$$

with

$$E = 0.105 - 0.0938\exp(-11.65h^*) \qquad (19)$$

Following this theory, $h^* = 0.4$ and $a = 0.421$ in the limit of the Zimm model, where $J_{eR} = 0.205$, and $h^* = 0$ and $a = 1$ in the Rouse limit, where $J_{eR} = 0.4$. The value at θ temperature, $J_{eR} = 0.32$, is defined by $a = 0.5$ and $h^* = 0.25$, while the limiting value for polymers in very good solvents, $J_{eR} = 0.46$, is characterized by a maximum in J_{eR} when $h^* = 0.05$ and $a = 0.775$. The main experience following from these data is that, on the one hand, the values obtained for the Zimm model do not coincide with those obtained for the θ state, and, on the other hand, there is no continuous change in J_{eR} but a certain maximum with quantities exceeding the Rouse limit. Accordingly it reveals, in terms of the orientation resistance parameter, $2.174 \leq m_0 \leq 3.125$ from the good to the poor solution, and therefore even values lower than the Rouse limit appear to be reasonable.

A comparison with the rheo-optical results (*Figure 6*) shows that the relation between $m_0 = 1/J_{eR}$ and a, determined by use of equations (18) and (19), coincides with the data obtained after polydispersity correction in the limit of very good and very poor solution properties. In the intermediate state, however, there are large discrepancies and the curve fits better to the original data. However, the influence of thermodynamic interaction (excluded volume) is not included in this theory. The deduction of relation (18), although containing a as parameter, only considers the contribution of hydrodynamic interaction (h^*) to changes in J_{eR}, that is, through a transformation of equation (14), a can be substituted by h^*. Therefore a comparison of the theoretical curve to experimental data in the range of very good solution properties, where the experiments reveal a strong influence on the excluded volume effect, is meaningless. Finally, the theoretical curve can be considered as a representation of the changes in m_0 as a function of h^*, and a good qualitative agreement to experimental data in the range where orientation is dominated by hydrodynamic interaction ($0.5 \leq a \leq 0.7$) may be concluded.

The question of whether the extinction angle determined with flow birefringence methods and the orientation angle obtained by rheo-optical measurements are comparable has also been the subject of recent theoretical work. Bossart[27] and Öttinger and Rabin[28] describe the shear-induced orientation of the polymer coil by means of gyration and stress tensors, where the gyration tensor correlates with light-scattering theory and the stress tensor with flow-birefringence theory. The result of their calculation is that values of the intrinsic orientation resistance m_0, determined for the Rouse and Zimm models as well as for Gaussian approximations[28], are, as widely believed, $2.50 \leq m_0 \leq 4.83$ for the stress tensor but, unexpectedly, $1.75 \leq m_0 \leq 2.553$ for the gyration tensor. A comparison of the rheo-optical data with these calculations (*Figure 6*) proves that the original data indeed coincide with the range given for the gyration tensor. With increasing solvent power, i.e. decreasing hydrodynamic interaction, the data range from the Zimm value to the Rouse value. The deviations seen for very good solution properties ($a \geq 0.7$) are attributed to the neglect of excluded volume effects in the theoretical treatment. The Gauss approximation, although accounting for the inhomogeneity of hydrodynamic interaction within the polymer coil, represents no good correlation with the experimental data in the case of strong hydrodynamic interaction.

This is different from the corrected data, which in general coincide with the range given for the stress tensor; strictly speaking they are between the limits of the Gauss and the Rouse values. However, the fact that polydispersity correction by use of equation (17) raises the light-scattering data to the range predicted for the stress tensor is confusing to some extent. It is understandable, bearing in mind that the task of this semiempirical equation is just to shift experimental results to the given range, as outlined by Peterlin[26].

SUMMARY

In a simple shear flow where the coil is oriented and deformed through the shear field, the orientational behaviour of the polymer coil in dilute solution is dependent on molar mass, solvent viscosity and solvent power. The influence of these parameters should be eliminated by introduction of the reduced shear rate β; however, additional changes of the dynamic behaviour of the polymer chain, dependent on these parameters, are not comprehended by β. The consideration of hydrodynamic interaction between chain segments leads to the well known theoretical results of Zimm and Rouse and, in practice, to the discussion of Rouse-like and Zimm-like behaviour in good and poor solutions, respectively. While the influence of thermodynamic interaction, i.e. the excluded volume effect, is generally neglected, the present investigation demonstrates that, especially in very good solutions where excluded volume strongly increases but hydrodynamic interaction is negligible, this is the dominant parameter. Owing to increasing polymer–solvent interaction in better solvents, hydrodynamic interaction between chain segments and the flexibility of the chain and the coil itself diminish[29], the latter leading to an easier orientation of the coil.

In *Figure 5*, the variation of the orientation parameter m_0 in correlation with changes of parameters characterizing hydro- and thermodynamic solution properties is proved. Furthermore, equations (15) and (16) give limiting approximations in the case of predominant hydrodynamic and thermodynamic interaction, respectively.

The intrinsic orientation resistance parameters obtained through rheo-optical light-scattering measurements do not coincide with the range predicted by flow birefringence theory, although the two methods have hitherto been believed to be comparable. However, recent theoretical work dealing with the calculation of gyration and stress tensors describing the orientational behaviour of macromolecules in shear flow, reveals very different results. With the assumption that the gyration tensor is observed in light-scattering experiments while the stress tensor is correlated with the flow birefringence method, different predictions are related to the different methods. Finally, most of the data obtained by rheo-optical measurement coincide with the predicted range given for the gyration tensor.

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