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A modified rheometer for in-situ radial and tangential SAXS studies on shear-induced alignment

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Abstract A tooth rheometer de-
signed to investigate the influence of
large amplitude oscillatory shear on
the macroscopic orientation of
complex fluids is described. The
rheometer allows in-situ two-direc-
tional small-angle scattering mea-
surements, making it possible to
observe in particular the orientation
process of hierarchically structured
block copolymers in dynamics.
Experiments performed with a linear
poly(vinyl methyl ether) show that,
despite a considerable gap/width
ratio, the rheometer can be used for
adequate rheological measurements.
In addition we found an unexpected
dependence of the dynamic param-
eters on the rheometer gap. The
small amount of sample required
favors the use of this rheometer for
measuring the rheological charac-
teristics of new compounds.

Keywords Tooth rheometer ·
In-situ two-directional rheo-optic
measurements · Gap-dependent
behavior

Introduction

The rheological properties of "complex fluids" is to a
great extent determined by their supramolecular structure
and therefore a combination of rheometry with other
experimental methods, that can characterize any flow-
induced structural changes, is often the most useful way to
study new materials (Larson 1999). Polymers and in
particular block-copolymers are good examples of com-
plex fluids. Viscoelastic properties of linear polymers are
thoroughly reviewed in a number of books (e.g., Ferry
1980; Vinogradov and Malkin 1980; Macosko 1994;
Larson 1999) and the main experimental findings can be
quite well explained on the basis of theoretical models (de
Gennes 1979; Doi and Edwards 1986). However, not all
aspects of polymer rheology are fully understood at

present and the viscoelastic behavior of linear polymers
remains a subject of experimental and theoretical studies
(Larson 2000; Groisman and Steinberg 2000; Archer et al.
1997; McLeish 1997; Ianniruberto and Marrucci 2001;
Likhtman and McLeish 2002; McLeish 2002).

The rheology of block-copolymers is a branch of
polymer rheology, that has been developed since the
1970s when styrene-butadiene-styrene triblock copoly-
mers attracted a lot of attention due to their interesting
mechanical properties. Later an increasing interest in
nanotechnology resulted in the intensive study of di-
block-copolymers, including their rheological properties
(Bates and Fredrickson 1990; Koppi et al. 1992; Larson
et al. 1993; Winey et al. 1993; Kannan and Kornfield
1994; Patel et al. 1995; Zhang et al. 1995; Zhang and
Wiesner 1995; Han et al. 1995; Gupta et al. 1996).

It is well known that, due to microphase separation, block-copolymers tend to form a multi-domain morphology, which is normally macroscopically isotropic. In rheological measurements this multi-domain structure can be easily changed, making the experimental data somewhat ambiguous, if not supported by additional structural investigations (Scott et al. 1992). On the other hand, imposing shear is the most straightforward way to get such microphase-separated materials macroscopically aligned. An effective technique for block-copolymer alignment is the use of large-amplitude oscillatory shear (LAOS) (Hadziioannou et al. 1979, 1982; Winter et al. 1993; Maring and Wiesner 1997; Wiesner 1997; Chen and Kornfield 1998; Leist et al. 1999; Langela et al. 2002). Despite considerable progress achieved in this field, the mechanism of shear-induced alignment is still not completely clear. Depending on the four most important parameters, which are the frequency, strain amplitude, temperature and duration of shear, a LAOS imposed on lamellar diblock-copolymers can give rise to either parallel or perpendicular orientation of lamellae with respect to the shear plane (Wiesner 1997). However, the alignment is usually not perfect, no matter how long the shear procedure has been applied, and a mixed parallel and perpendicular orientation of lamellae is often observed (see, e.g., Larson 1999). Moreover, a transverse alignment in a combination with the parallel one has been reported as well (Okamoto et al. 1994; Zhang and Wiesner 1995; Pinheiro et al. 1996).

In most studies, the morphological investigations of shear-oriented block-copolymers were performed ex-situ. A number of in-situ rheooptical methods, including birefringence, SANS and SAXS have also been reported in the literature (Balsara et al. 1994; Kannan and Kornfield 1994; Okamoto et al. 1994; Gupta et al. 1996; Chen et al. 1997; Polis et al. 1999; Vigild et al. 2001). Birefringence is known to be a good method to follow the overall dynamics of fast orientation processes, while small angle scattering techniques using either neutrons (SANS) or X-rays (SAXS) are more suitable to study a nano-scale orientation in detail. The devices reported in the literature for in-situ small angle scattering investigations are unique but also rather complex and not very flexible for a series of routine measurements, especially at elevated temperatures. Except for the set-up reported by Polis et al. (1999), a considerable amount of sample is usually required for such in-situ experiments. Besides, most of the shearing devices can be used for one-directional scattering measurements only. A few in-situ two directional SAXS and SANS investigations have been carried out with block-copolymer solutions and gels (Balsara et al. 1994; Hamley et al. 1998; Pople et al. 1999). Unfortunately, it is hardly possible to use the circular Couette geometry reported in these studies in the case of polymer melts. Still, *two directional* rheooptic measurements appear to be a powerful method to elucidate the orientation behavior of "conventional" di- and triblock copolymers in bulk. Moreover, the synthesis of new compounds with a more complex molecular structure is an additional stimulus to propose new approaches to nano-scale structure investigations. During recent years, for instance, a concept to prepare *hierarchically structured* block-copolymer materials has been introduced (Ikkala and ten Brinke 2002). Composed of diblock-copolymers and low molecular weight amphiphile-like compounds, these materials are characterized by self-organization at two different length scales, giving rise to, for example, lamellar-*within*-lamellar or cylinder-*within*-lamellar structures. Almost all applications, such as functional membranes, anisotropic proton conductivity, etc., require the hierarchically structured materials to be macroscopically aligned. Motivated by this we developed a new tool that can be readily used for two-directional monitoring of the shear-induced changes in the nano-structure during rheological measurements.

In this paper we describe the tooth rheometer constructed to perform in-situ radial and tangential small-angle scattering measurements during LAOS alignment. Recently, this rheometer was successfully used in SAXS experiments as a shear device (Polushkin et al. 2003). It has turned out, however, that the designed geometry can be employed for adequate rheological measurements as well. The results of dynamic measurements of a linear polymer, which was measured to examine the rheometer, are presented below.

Calibration sample and rheometer description

The material utilized in this work as a calibration sample was a linear poly(vinyl methyl ether), PVME, with $M_w = 80,000$ g/mol. Viscoelastic characteristics of the sample were preliminary determined with two customary cone-plate rheometers at two shear strain amplitudes γ equal to 5 and 50% and at temperatures 25, 35, and 50 °C. One of the devices was a shear stress controlled AR 1000 N rheometer (TA Instruments), exploited in the constant deformation mode, and the other was a shear strain (or rate) controlled Bohlin VOR rheometer (Bohlin Reologi AB). The measurements have been performed using an aluminum cone-and-plate fixture of 4.0° and 20 mm in diameter for the AR rheometer and a stainless steel fixture of 2.5° and 25 mm in diameter for the Bohlin rheometer. The frequency range used was from 0.01 to 20 Hz, since the latter is the maximal frequency of the Bohlin rheometer. Figure 1 shows the frequency dependences of the storage G' and loss G'' moduli and the phase angle ϕ, measured with $\gamma = 5\%$ at two temperatures, 25 and 50 °C. As seen from the figure, the frequency dependencies obtained from these two rheometers, are rather similar but not the same. At low
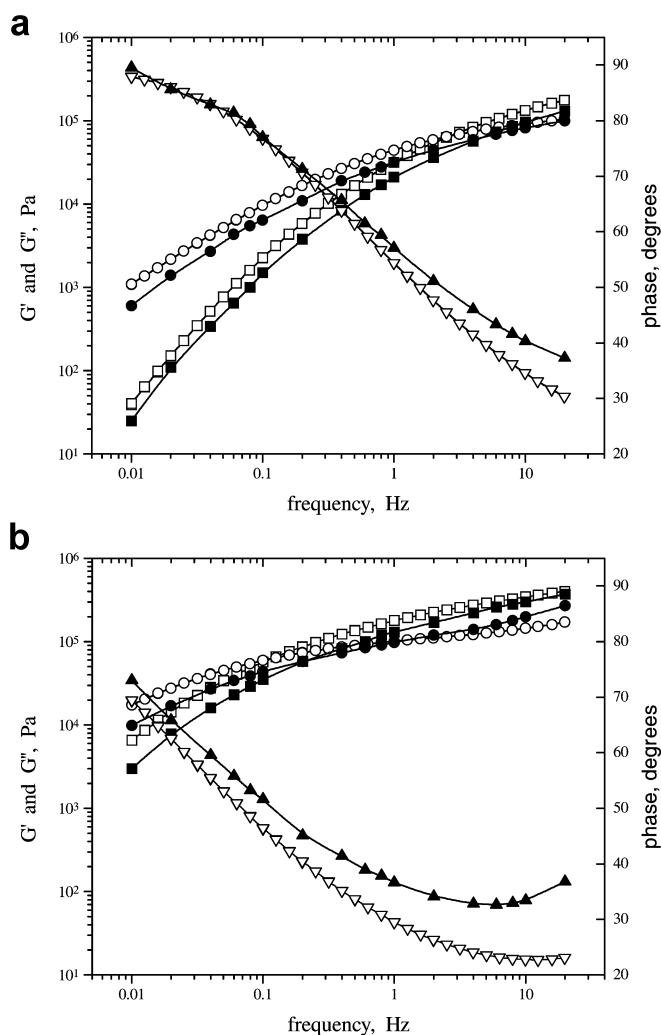
Fig. 1a,b The dynamic characteristics G′ (*squares*), G″ (*circles*), and ϕ (*triangles*) of PVME at $\gamma = 5\%$, measured by two cone-and-plate rheometers—the AR rheometer (*open*) and the Bohlin rheometer (*solid*)—at: **a** 50 °C; **b** 25 °C

frequencies, i.e., up to ca. 1 Hz, G′ and G″ of the Bohlin rheometer are somewhat lower than those measured by the AR rheometer. At 50 °C the discrepancy in the dynamic moduli is probably just due to a difference in the initial tuning of the rheometers, since the values of ϕ obtained for both rheometers are practically the same (Fig. 1a). At 25 °C, however, a difference in ϕ is already well observed and the discrepancy in measurements of G′ and G″ becomes more evident (Fig. 1b). When the frequency increases, the measurements reveal that the difference in measured values of ϕ is also increasing, especially at 25 °C. For instance, at this temperature the values of ϕ at 10 Hz are 23° and 34° for the Bohlin and AR rheometers, respectively. Interestingly, at $\gamma = 50\%$ both rheometers show practically the same values of ϕ in the whole frequency region at 50 °C while there is a

difference in G′ and G″ at high frequencies. At 35 °C a small difference in ϕ becomes already noticeable in the high frequency region. At 25 °C such a comparison of the experimental data obtained at high frequencies was not possible, since the AR rheometer at $\gamma = 50\%$ was exploited up to 0.2 Hz only where the shear torque limit was reached. As for the Bohlin rheometer, the high frequency dependencies of ϕ as well as G′ and G″ are not quite smooth, most likely indicating a stick-slip behavior of the PVME sample. At low frequencies, however, a good agreement in the measurements was observed.

Thus, for the same polymer the experimental data obtained using these two cone-plate rheometers are slightly different. We believe that the discrepancy in the dynamic parameters is due to a difference in the rheological conditions, which were applied to the polymer. The AR rheometer is a shear stress controlled rheometer whereas the Bohlin was operated in a shear strain mode. The geometry, material and probably the surface roughness of the cone-plane pairs of the rheometers were also different. In general, however, these data seem quite reliable to use this linear PVME as a calibration sample for the tooth rheometer described below.

In order to allow in-situ two-directional small angle scattering investigations during dynamic measurements, a new measuring cell adjustable for the Bohlin rheometer mentioned above was designed. Instead of the conventionally used cone-and-plate or plate-and-plate fixtures, two stainless steel disks of 56 mm in diameter have been exploited. The disks were thinned down in such a fashion that, at a distance of 25 mm from their center, five teeth of 3 mm in width and 2, 3, 4, 5, and 8 mm in length were left. The disks can be easily mounted on the rheometer so that the teethed sides are facing each other. A sample is then placed between two opposing teeth of the same size and subjected to oscillatory shear, driven by the bottom plate. As usual, the upper plate is firmly connected with a torque and normal force transducer. At this configuration of the Bohlin rheometer, a free tangential (along the shear vector 1) and radial (along the vertex vector 3) access to the sample is provided for an X-ray beam (Fig. 2). When a homemade oven, having windows transparent for X-rays, surrounds the measuring cell rheo-optic measurements can be performed in an inert atmosphere at temperatures up to 250 °C. A thermocouple inserted in the upper plate allows an accuracy of temperature measurements within 0.5 °C.

The chosen, rather large, diameter of the tooth disks was mostly aimed to decrease the uncertainty in shear conditions along the radial direction. When the inner and outer rims of the rheometer teeth are of 23.5 and 26.5 mm from the disk center, respectively, such an uncertainty is within 13%. Compared with conventionally used plate-plate geometry, where the shear condi-
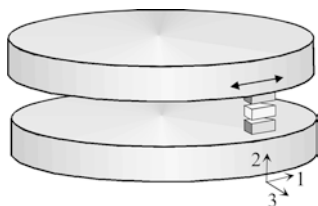
Fig. 2 A sketch of the tooth rheometer constructed to perform in-situ radial (along the vertex vector 3) and tangential (along the shear vector 1) small-angle scattering measurements during a large amplitude oscillatory shear alignment

Fig. 3 A scheme for the passing of an optic beam through a plate-and-plate fixture. The orientation uncertainty along the beam is determined by the intersection angle α at the edge of the fixture

tions are known to be inhomogeneous, this value is relatively small. Restricted by the configuration of the Bohlin rheometer, further increase of the disk diameter, which would result in an even smaller experimental error, was not possible. Another reason for the diameter to be large is the existence of an orientation uncertainty along the tangential direction. As shown in Fig. 3, if an optical beam goes through a plate-plate (or cone-plate) shear cell next to its edge, then the intersection angle between the beam and tangent trajectories of the shear vector, represented in the figure by circular lines, varies from $-\alpha$ to $+\alpha$, where α is the angle at the edge of the shear cell. It is obvious that when the diameter of a measuring cell increases the orientation uncertainty determined by such an angle range becomes smaller, provided the path length of the optical beam within the cell is the same. For a given diameter, using a tooth geometry instead of a conventional plate-plate one, allows further reduction of the orientation uncertainty. Besides, the large diameter of the tooth rheometer disks was favorable to facilitate sample loading and trimming, as well as to increase the measuring system sensitivity.

Despite an evident drawback mentioned below, the tooth rheometer has a number of advantages if compared to conventional rheological tools. First of all, because of a small working area of the rheometer teeth, a low force is needed to squeeze a sample at its loading. As a consequence, the gap between the teeth can be readily adjusted in the range of 1.5 to 0.15 mm, though smaller gaps are also possible. Secondly, no special alignment is required for the designed geometry in contrast to the procedure reported elsewhere (Mhetar and Archer 1996; Dhinojwala and Granick 1997). Finally, the amount of sample measured by the tooth rheometer is very small, of the order of 0.03 g or less, which can be very crucial for the study of new compounds. On the other hand, the designed measuring system is a kind of plate-plate geometry with a considerable gap/width ratio, which implies that the accuracy of the measurements can be aversely affected by edge effects. However, the experimental data presented below show that the influence of edge effects is not dramatic.

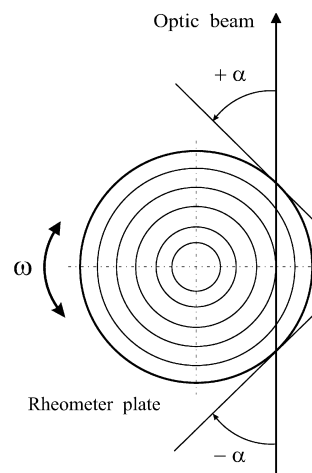In order to determine the dynamic moduli $G' = G^*\cos(\phi)$ and $G'' = G^*\sin(\phi)$, where $G^* = \sigma/\gamma$ is the complex modulus and ϕ is the phase angle, the following expressions for the shear stress amplitude σ and the shear strain amplitude γ have been used:

$$\sigma = a \cdot T/(100 \cdot S \cdot R) \tag{1}$$

$$\gamma = b \cdot R \cdot D/(100 \cdot h), \tag{2}$$

where $R = 25$ mm is the mean distance from the disk center to the rheometer teeth, h is the gap between the teeth, S is the working surface area of the teeth, $a = 5\times10^{-2}$ N·m is the maximal load of the torque transducer, and $b = 20$ mrad is the maximal angular deflection of the bottom disk. T and D are the measured value of the torque and the set value of the deformation amplitude, respectively, in % of the maximal values.

The experimental data reported below have been obtained with a tooth pair of 8 mm length and 3 mm width (i.e., $S = 24$ mm^2); however, similar dependencies were observed for a 4×3 mm^2 pair. The dynamic characteristics of the PVME sample were examined in the region of 0.04 to 20 Hz, since at lower frequencies the measured torque values were within 0.5% of the whole range. Similar to the cone-plate experiments discussed above, the measurements with the tooth geometry were carried out with $\gamma = 5$ and 50% at temperatures of 25, 35, and 50 °C. A freshly loaded sample was tested at each of these temperatures.

Experimental results and discussion

Figure 4 shows the frequency dependencies of G', G'', and ϕ measured by the tooth rheometer with a gap $h = 1$ mm at $\gamma = 5\%$ and temperatures 25 and 50 °C. The corresponding data of the Bohlin cone-plate rheometer are also presented in this figure for comparison. As seen
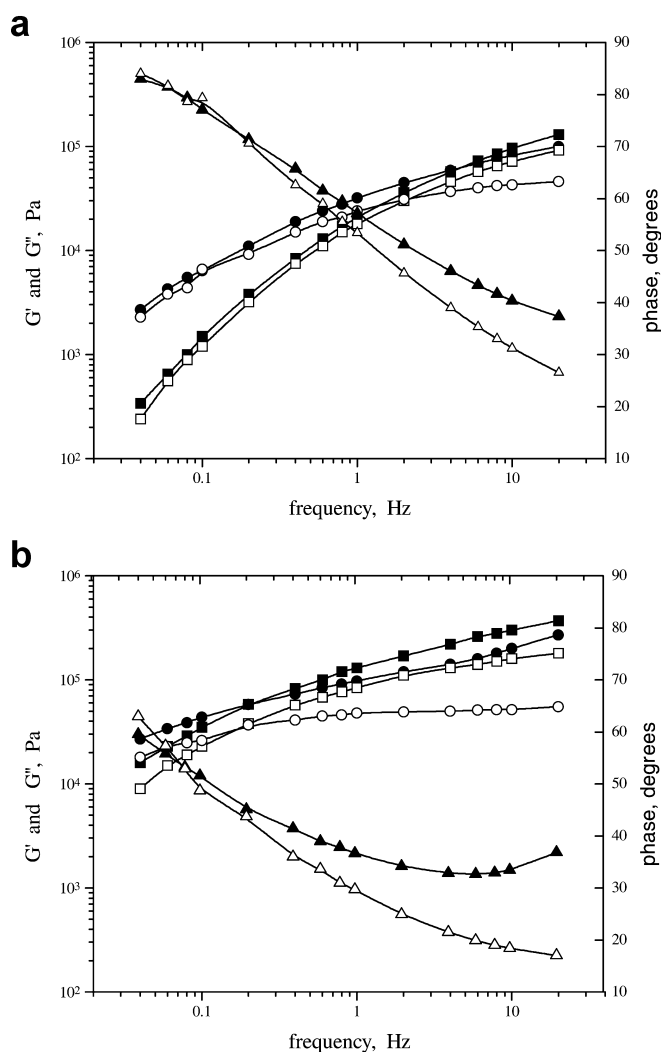
a

b

Fig. 4a,b The dynamic characteristics G′ (*squares*), G″ (*circles*), and ϕ (*triangles*) of PVME at $\gamma = 5\%$, measured by the tooth rheometer at a gap h = 1 mm (*open*) and the Bohlin rheometer (*solid*) at temperatures of: **a** 50 °C; **b** 25 °C

from Fig. 4a, at 50 °C the values of G′ and G″ obtained with these two rheometers are in good agreement, although an evident discrepancy in G″ is observed at high frequencies. At 20 Hz, when the discrepancy is largest, the measured values of G″ are 4.6×10^4 and 1.1×10^5 Pa for the tooth and cone-plate rheometers, respectively. Apart from G″, the values of ϕ measured by the tooth rheometer at 50 °C, are also noticeably lower than those of the cone-plate rheometer. In contrast, at $\gamma = 50\%$ both rheometers show quite similar frequency dependencies of ϕ. When the temperature is decreased down to 25 °C, the difference in ϕ revealed at $\gamma = 5\%$ in the high frequency region becomes more prominent (Fig. 4b). Moreover, lower values of ϕ are also observed for the tooth rheometer at $\gamma = 50\%$. For example, at 6 Hz and 25 °C the tooth and cone-plate rheometer

values of ϕ are 19 and 33° at $\gamma = 5\%$, and 20 and 28° at $\gamma = 50\%$, respectively. Interestingly, the phase angle dependencies obtained by the tooth rheometer are in much better agreement with those presented in Fig. 1 for the AR rheometer than with the Bohlin rheometer data. Nevertheless, the tooth rheometer values of ϕ measured at $\gamma = 5\%$ at high frequencies are somewhat less than those for the AR rheometer. For instance, at 25 °C the tooth rheometer shows $\phi = 17°$ at 20 Hz whereas the value of $\phi = 23°$ was obtained with the AR rheometer. As for the dynamic moduli measured at 25 °C, in comparison with the Bohlin rheometer, the tooth rheometer shows lower values of both G′ and G″ already at low frequencies (Fig. 4b). The difference in the dynamic moduli, especially G″, becomes more considerable as frequency increases. Since the gap/width ratio of the tooth rheometer is quite high, this can in principle be explained by an influence of edge effects, increasing with frequency and/or decreasing temperature. However, it turns out that the tooth rheometer shows even lower values of G′ and G″ when the gap between the teeth is reduced. The opposite result might be expected if the observed discrepancy is primarily caused by edge effects. Figure 5 presents the data obtained with the tooth rheometer for gaps h of 1.0, 0.5, 0.3, and 0.15 mm. It is important to note that apart from the influence on the dynamic moduli G′ and G″, especially at high frequencies, the rheometer reveals a decrease in values of the phase angle ϕ when the gap is decreased. Trimming the rheometer teeth after changing the gap slightly decreased G′ and G″ but it did not affect the measured values of ϕ at all. As seen from Fig. 5, the frequency dependencies of G′, G″, and ϕ on the gap width are practically indifferent to the shear strain amplitude γ, which was either 5 or 50%. However, the influence of temperature on the dependencies is quite strong. At 25 °C, changes in ϕ on varying the gap width are already observed at 0.04 Hz (Fig. 5c,d) while at 50 °C the measured values are practically the same up to 0.2 Hz (Fig. 5a,b). A similar shift in the onset frequency as a function of temperature is revealed for the dependencies of G′ and G″. Compared at one frequency, a decrease of the dynamic moduli with decreasing gap width is more prominent at the lower temperature. For instance, at 20 Hz the values of G″ measured at $\gamma = 5\%$ and gaps h = 1.0 and 0.15 mm are 3.3×10^4 and 1.0×10^4 Pa at 50 °C, while they are 4.2×10^4 and 0.9×10^4 Pa at 25 °C, respectively (cf. Fig. 5a,c).

The experimental data of the linear PVME presented in Fig. 5 are rather unexpected, since we are not aware of any other examples of such a gap-dependent dynamic behavior of linear polymers described in the literature. A few studies, however, are known where an influence of the gap width on the rheological properties of polymer melts was observed at a steady shear flow. Burton et al. (1983) were probably the first who reported on appre-
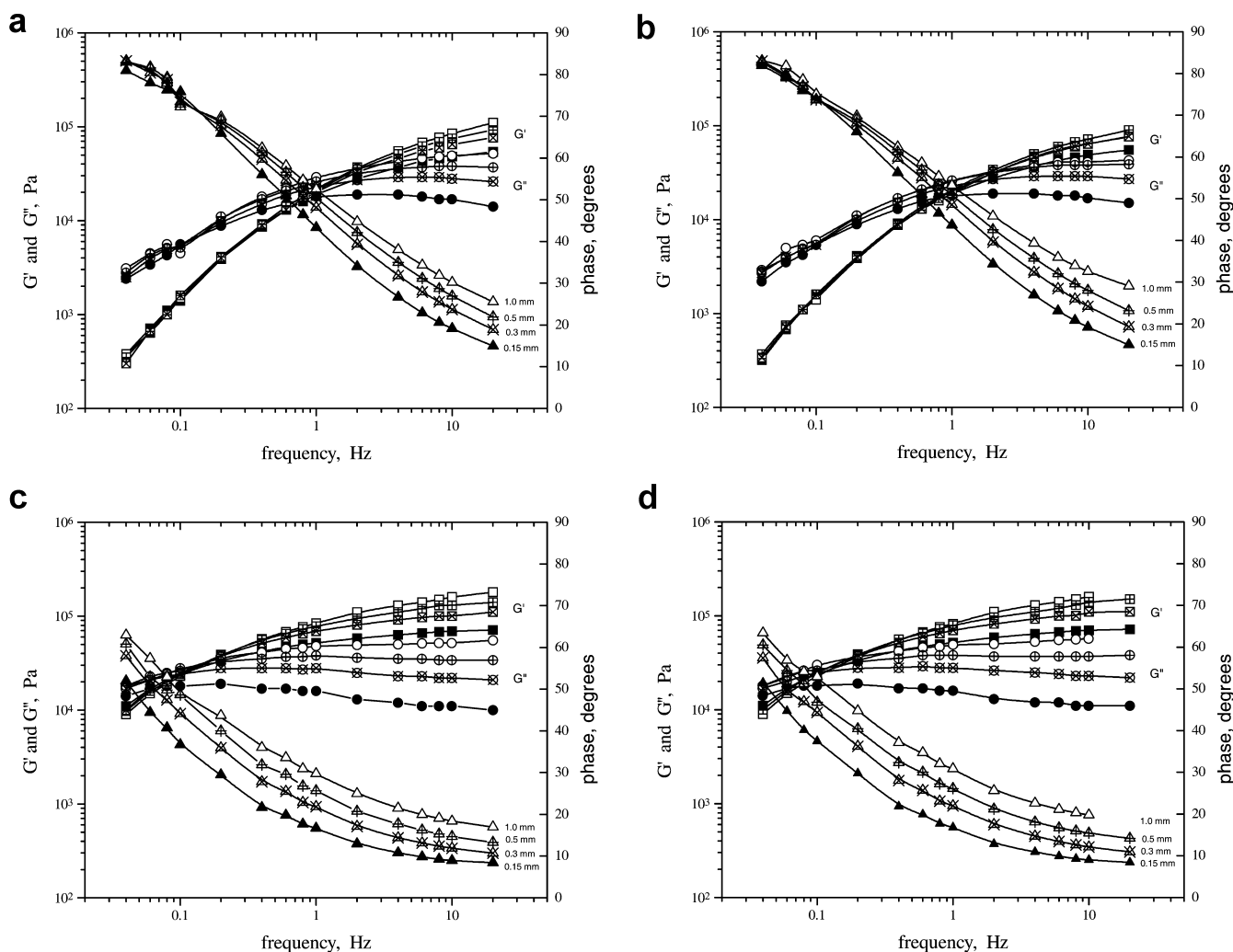
Fig. 5a–d The dynamic characteristics G′ (*squares*), G″ (*circles*), and φ (*triangles*) of PVME measured by the tooth rheometer at gaps h = 1 (*open*), 0.5 (+), 0.3 (x) and 0.15 mm (*solid*): **a,c** at γ = 5%; **b,d** at γ = 50%; **a,b** at a temperature of 50 °C; **c,d** at a temperature of 25 °C

ciable dependencies of the torque on the gap between the parallel plates of a Weissenberg Rheogoniometer, ranging from 500 down to 25 μm, which were obtained for a series of polystyrenes (PSs). Then, Hatzikiriakos and Dealy (1991) observed a gap-dependent behavior of a high density polyethylene which, on varying the gap from 500 to 250 μm, was quite moderate. Later, Henson and Mackay (1995), again for a series of linear PSs, found a considerable decrease of the apparent viscosity with decreasing the rheometer gap below 100 μm. In both latter cases such a gap-dependent behavior was explained by slip at the walls. Recently, Dao and Archer (2002) investigated the stick-slip dynamics of a series of 1,4-polybutadienes (PBDs) subjected to steady shear flow in a planar-Couette cell, the gap of which was varied from 750 to 50 μm. Among other findings, the

authors observed a slowing down of stress relaxation in the PBDs when the shear cell gap was reduced. Polymer slip was also put forward as a possible explanation for the relaxation retardation. Believing that the gap-dependent behavior of the PVME sample observed in this study might be of the same origin with that described in the above-mentioned papers, we took into account the possibility of slip in our experiments, although polymer slippage is usually considered as the phenomenon of a steady state flow (Denn 1990, 2001). Depending on the magnitude of the slip velocity, three regimes—the apparent or weak slip, the intermediate stick-slip regime and the strong slip mode—have been distinguished (Mhetar and Archer 1998b; Dao and Archer 2002). It is known that weak slip can occur in polymers at shear stresses of the order of 0.1 G_e, where G_e is the elastic modulus. As seen from Fig. 5, the dependence of the dynamic parameters on the gap width is most pronounced in the high frequency region, which happens to correspond to a shear induced transition of the PVME to a "high-elastic" state (Vinogradov et al.

1972). In this state, polymers show lower values of G'' compared to G', which approaches a plateau value of G_e, indicating thus enhanced viscoelasticity. Therefore, slippage of the PVME being in the "high-elastic" state seems in principle possible, especially at $\gamma = 50\%$. However, we still have to conclude that slip can not be the prime cause of the gap-dependent behavior observed in this study. First of all, as mentioned above, the frequency dependencies of G', G'', and ϕ are practically independent of γ, whereas a strong non-linear behavior should be expected at $\gamma = 50\%$ if slip already occurs at $\gamma = 5\%$. Secondly, at 25 °C the high frequency values of ϕ are found to be extremely small. For example, at $\gamma = 5\%$ and 20 Hz the phase angle ϕ is 17° at h = 1.0 mm and 8° at h = 0.15 mm. Such low values of ϕ provide additional evidence against wall slip, since they are thought to be possible only when a good contact between the polymer and the rheometer teeth takes place. Finally, as the gap is varied a difference in ϕ measured at 25 °C is clearly observed already at 0.04 Hz, which is the lowest frequency used. The gap-dependent values of ϕ found at this frequency are in the range of 52–63°, which suggests a fluid-like behavior of the PVME sample where slip is unlikely.

As a tentative explanation of the observed behavior we propose a model of skin-core flow which allows a non-uniform gradient of the shear deformation across a polymer sample, even if that is quite thin. A velocity profile of the flow, which does not necessarily have to be symmetrical, is presented in Fig. 6. It should be noted that such a skin-core profile, along with slip and a decrease of the effective gap due to a stagnant adsorption layer formed along the walls, has already been assumed by Burton et al. (1983) to explain their gap-dependent data mentioned above. So actually, considering the model of non-uniform flow, we in some extent follow these authors.

In line with the relaxation mechanism suggested for apparent weak slip (see, e.g., Mhetar and Archer 1998a), it is assumed that in the vicinity of the rheometer walls, skin layers are formed at flow where macromolecules are more oriented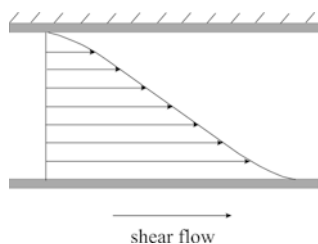 along the shear direction than those in the core layer. Such local molecular orientation implies an increase of elasticity within the skin layers and, on the other hand, facilitates the flow there. The latter is thought to occur either by the flow mechanism developed by Ianniruberto and Marrucci (2001) or just as the result of a decrease in the orientation entropy of the molecules in the skin layers under flow. Assume that a relatively thick sample, compared to the thickness of skin layers, which is in turn large in comparison with the size of polymer chains, is tested in an oscillatory flow mode. In this case, in order to provide a certain shear deformation the macromolecules of the skin layers should be stretched considerably stronger than those in the core layer, resistant to flow. As a consequence, high values of the dynamic moduli G' and G'' are observed at high frequencies simultaneously with enhanced values of the phase angle ϕ, mostly determined by the thick core layer. When the sample thickness is decreased, applying the same shear strain results in a more uniform profile of shear deformation, since the thickness of the core layer is also decreased. The skin layers become dominant and the macromolecular overstretching within these layers decreases. This should give rise to a lowering of G' and G'' together with a decrease in the values of ϕ, as revealed in this study. In our opinion, the skin-core model proposed is also consistent with the above-mentioned data by Dao and Archer (2002) on the slowing down of relaxation with decreasing the gap. The main moot point of the model is the thickness of skin layers, which compared to the size of macromolecules, was assumed to be very large, of the order of several micrometers or higher. More studies on polymer flow at small gaps would be useful to verify this model.

Conclusions

In order to investigate the influence of large amplitude oscillatory shear on the morphology of hierarchically structured block copolymers and in particular to study the pathways toward their macroscopic orientation, a tooth rheometer was recently constructed. The rheometer design enables us to observe the dynamics of the shear-induced alignment in two directional SAXS experiments performed in-situ. Namely, tangential and radial SAXS patterns with respect to the imposed shear can be obtained for a sample subjected to a large amplitude oscillatory shear.

Dynamic measurements of a linear poly(vinyl methyl ether) carried out to calibrate the tooth rheometer have shown that at a gap width h = 1 mm a good agreement with the experimental data obtained using two cone-plate rheometers is observed. Although the gap/width ratio of the measuring cell used in the tooth rheometer is considerable, the influence of edge effects on the data is not dramatic, at least if the latter are plotted in a con-

Fig. 6 A velocity profile of the skin-core flow proposed to explain the gap-dependent behavior of PVME. The profile is characterized by a non-uniform gradient of the shear deformation across the sample

ventional log-log scale. The rheometer is straightforward in use and requires a very small amount of sample, which makes it favorable for the dynamic measurements of new compounds.

With decreasing the gap width between the rheometer teeth, a gap-dependent behavior of the linear PVME has been observed at high frequencies at 50 °C and in the whole frequency range used at 25 °C. From our point of view, it is unlikely that the obtained frequency dependencies are due to any artifacts of the tooth rheometer or caused by slip at the tooth surface. It appears that the decrease of G', G'', and ϕ found on decreasing the gap width is an inherent response of the polymer to the varying flow conditions. A model of flow with a non-uniform gradient of the shear deformation is proposed to explain the experimental data obtained.

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