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Communications to the Editor

Simultaneous Measurement of Shear Viscosity and Director Orientation of a Side-Chain Liquid-Crystalline Polymer by Rheo-NMR

D. A. Grabowski and C. Schmidt*

Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

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Introduction. Many theoretical attempts have been made to describe the relation between rheological properties of polymer solutions and melts and the corresponding shear-induced chain configuration.[1] In contrast only a few experiments have been performed to measure molecular orientations and configurations under the influence of shearing forces. Typical experiments to obtain such information under shear conditions are rheooptical measurements, e.g., flow birefringence or infrared dichroism. The use of NMR to detect the deformation of polymer chains under shear has been introduced by Samulski and collaborators.[2–4] These authors designed a cone and plate sample cell for an electromagnet and used both deuterium[3] and proton NMR[4] to detect shear-induced orientation effects in polymer melts and solutions. In this paper, we describe a cone and plate NMR viscometer, which is integrated into a NMR probe for a wide-bore superconducting magnet. While for the sample cell described in ref 4 the angle between the cone and plate axis and the external field can be varied, the axis of our cone and plate is fixed parallel to the magnetic field. In contrast to the previous cell, our design allows the simultaneous measurement of both the NMR spectrum and the sample shear viscosity. To demonstrate the use of this NMR viscometer, first experiments were performed on a side-chain liquid-crystalline polysiloxane, since the reorientation effects expected for such a liquid-crystalline system are particularly large.

NMR Viscometer. A cone and plate geometry was chosen as it provides an approximately constant shear rate throughout the sample.[1] For the NMR part of the experiment, we selected to observe deuterium because the electric quadrupole coupling of this nucleus allows us to measure molecular orientations with high angular resolution.[5] Furthermore, the isotopic labeling of the samples provides high selectivity.

The construction of the viscometer is affected both by restrictions on the material which can be used in an NMR probe and by the small volume in the probe. To preserve the homogeneity of the magnetic field in the NMR spectrometer, poly(ether ether ketone) was used for the main constituents. The cone and plate assembly has a diameter of 15 mm and the sample gap has an angle of 5° to get acceptable conditions for both NMR and rheological measurements.

The top of the NMR probe with the viscometer is shown schematically in Figure 1. The axis of the cone and plate is parallel to the external magnetic field. The plate is driven by a motor outside of the NMR magnet. Two different gear units for shear rates between 1×10^{-3} and $100\ \mathrm{s}^{-1}$ have been used. To ensure a minimum of frictional resistance, the cone rests on an air bearing, which was machined from a block of a special condensed carbon material provided by Haake Mess-Technik.

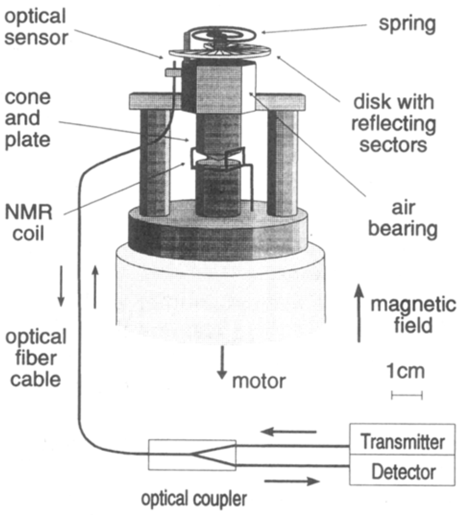

Figure 1. Scheme of the NMR viscometer.

The spring together with the optical scanner enables us to determine the torque transmitted from the rotating plate through the viscous sample to the cone. The optical scanner consists of an optical fiber cable with a coupling unit and a glass disk with narrow reflecting sectors. The optical scanner allows us to measure the angular displacement of the cone which is proportional to the torque.

The shape of the NMR coil is adjusted to the sample volume to obtain an optimum filling factor. The temperature can be controlled in the range of 5–100 °C with a modified Bruker temperature regulator.

The NMR viscometer is calibrated with a commercial silicone oil which shows Newtonian viscosity. The proportionality between torque and shear rate, i.e., the independence of the viscosity on the shear rate, was verified for shear rates up to $100\ \mathrm{s}^{-1}$. With a commercial rheometer the absolute values of the viscosity of the silicone oil were measured at two different temperatures, 21.8 and 50.0 °C. These values were used for the calibration of the NMR viscometer. The calibration error was estimated to be less than 10%.

Flow Alignment and Shear Viscosity of a Side-Chain Liquid-Crystalline Polymer. First measurements with the new NMR viscometer were performed on a side-chain liquid-crystalline polysiloxane, obtained by the addition of 2,3,5,6-tetradeuterio-4-methoxyphenyl 4′-butenyloxybenzoate to poly(hydrogen methylsiloxane).[6,7] The polymer has a nematic phase extending from the glass transition at 4 °C to the clearing point at 97 °C. The number-average degree of polymerization is approximately 70.[7] The rheological properties of this type of liquid-crystalline polymer have been studied before.[8–10]

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* Address for correspondence: Institut für Makromolekulare Chemie, Universität Freiburg, Sonnenstrasse 5, D-79104 Freiburg, Germany.

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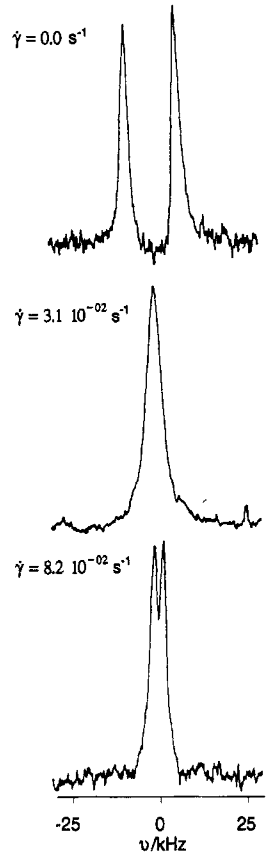

Figure 2. ^{2}H NMR spectra of the liquid-crystalline polysiloxane measured at different shear rates $\dot\gamma$. For each spectrum 1024 scans were accumulated using the quadrupole echo technique.

Our measurements were performed at 75 °C. At this temperature the nematic director is readily aligned within several minutes by the external magnetic field of 7.05 T, resulting in a uniform director orientation parallel to the magnetic field, i.e., parallel to the cone and plate axis. A comparison of the width of the individual NMR lines of the magnetically aligned linear liquid-crystalline polymer studied here and a mechanically aligned liquid-crystalline elastomer[7] shows that the director order parameter is almost 1 in both cases. For the mechanically aligned elastomer the orientational distribution of the director was obtained from an analysis of the NMR line shapes as a function of the sample orientation with respect to the magnetic field. This method of measuring the width of the orientational distribution function is very sensitive but cannot be applied in the case of the linear liquid-crystalline polymer because of the magnetic-field-induced director realignment.

Shearing the sample forces the director to realign under an angle θ to the axis of the magnetic field, with the angle depending on the shear rate. The deuterium NMR spectra open insight into the functional dependence of the director orientation on the shear rate. Some spectra at different shear rates are shown in Figure 2. The quadrupole splitting of the two satellite peaks allows us to determine θ according to[5,11]

$$\Delta\nu = \delta(3\cos^2\theta - 1) \qquad (1)$$

The value of the constant δ is obtained from the spectrum for zero shear rate, that is, for the angle $\theta = 0$. With this value of δ, the angles for nonvanishing shear rates can be obtained from the measured splittings $\Delta\nu$ according to eq 1.

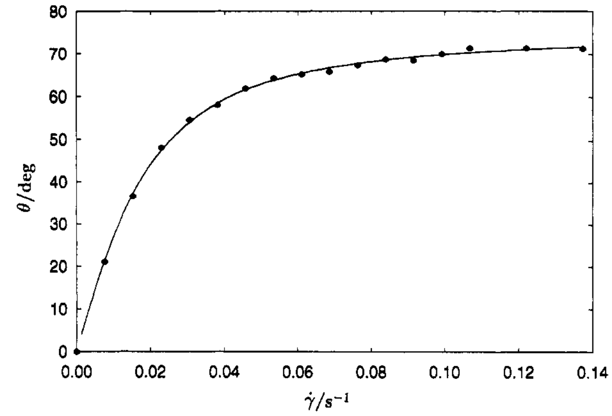

Figure 3. Director orientation θ obtained from the NMR spectra as a function of the shear rate $\dot\gamma$. The line represents the fit according to the Ericksen–Leslie–Parodi theory (eq 3).

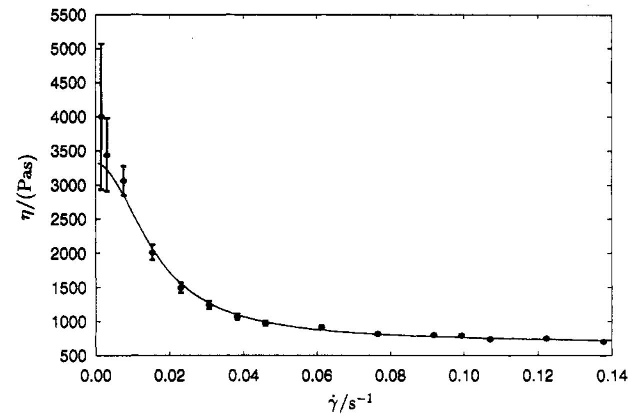

Figure 4. Measured values of the steady-state shear viscosity η as a function of the shear rate $\dot\gamma$. The line represents the fit (eq 4) with the three Miesowicz viscosities as fit parameters.

Assuming a constant shear rate $\dot\gamma$ and a unique orientation of the director throughout the sample, the orientation as a function of the shear rate can be calculated according to the Ericksen–Leslie–Parodi theory.[12] Neglecting the elastic part, the torque balance leads to

$$(\alpha_3 \sin^2\theta - \alpha_2 \cos^2\theta)\dot\gamma - \mu_0\chi_a H^2 \sin\theta\cos\theta = 0 \qquad (2)$$

where H is the external magnetic field, χ_a is the anisotropy of the magnetic susceptibility, μ_0 is the vacuum permeability, and α_2 and α_3 are Leslie coefficients.[12] Thus the orientation θ is given by

$$\tan\theta = \frac{1}{q_1\dot\gamma} + \left[\frac{1}{(q_1\dot\gamma)^2} + q_2\right]^{1/2} \qquad (3)$$

with $q_1 = 2\alpha_3/\mu_0\chi_a H^2$ and $q_2 = \alpha_2/\alpha_3$.

Using q_1 and q_2 as fit parameters, a good fit on the data could be received as illustrated in Figure 3. The values obtained for the fit parameters are $q_1 = -6.5 \pm 0.3$ s and $q_2 = 15.8 \pm 0.6$.

With the assumptions above, the steady-state viscosity η as a function of the orientation is given by three Miesowicz viscosities η_1, η_2, and η_{12}:[13]

$$\eta = \eta_1 \sin^2\theta + \eta_2 \cos^2\theta + \eta_{12} \sin^2\theta\cos^2\theta \qquad (4)$$

Figure 4 depicts the steady-state viscosities measured in the magnetic field as a function of the shear rate. For comparison, we also measured the shear viscosities in the absence of a magnetic field. In this case no shear thinning was observed; the steady-state viscosity has a value of approximately 650 Pa s, independent of the shear rate. The line in Figure 4 shows the fit of eq 4 with the three Miesowicz viscosities as fit parameters. The values of these parameters resulting from the fit are $\eta_1 = 530 \pm 30$ Pa s, $\eta_2 = 3300 \pm 200$ Pa s, and $\eta_{12} = -960 \pm 400$ Pa s. Within the experimental errors, which are largest for the viscosities at low shear rates, the fit agrees with the measured data. Thus, for our liquid-crystalline side-chain polymer shear alignment and shear viscosity as a function of the shear rate are in agreement with the Ericksen–Leslie–Parodi theory.

Conclusion. The results presented above demonstrate that rheo-NMR is an appropriate tool to study the interplay of shear-induced orientation and rheological behavior. Therefore, we believe that further measurements with the NMR viscometer will give insight into the relation between molecular orientation and rheology not only for liquid crystals but also for polymers in melt or solution and other complex fluids.

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