# Shear-Induced Orientational Order in a Polystyrene/Benzene-$d_6$ Solution As Observed by $^2$H NMR

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ABSTRACT: Using a home-built Couette-type shear cell we studied the behavior of a concentrated solution of polystyrene in benzene-$d_6$ under shear. Deuterium NMR revealed a shear-dependent splitting of the benzene-$d_6$ signal, indicating partial orientation of the polystyrene due to shear forces. Our preliminary results show a linear relationship between the order parameter $S_{zz}$ of the benzene molecule and the shear rate $\dot{\gamma}$ for the interval $0\ s^{-1} \leq \dot{\gamma} < 400\ s^{-1}$.

## Introduction

Flow-induced structures in polymeric systems have received interest from both academia and industry. The examination of the effects of shear on polymer solutions is particularly of interest to the food industry and provides a unique probe into the physical chemistry of polymers. Multiphase polymeric systems are susceptible to shear, which may cause orientation, morphological changes, phase transitions, and several other phenomena effecting the properties of the end product.[1,2] It is known that the introduction of additives into polymeric systems affects the rheological behavior, but as yet there is no real understanding how this affects the microstructure of these system.[3] There is clearly a requirement to further pursue the relation of microstructure and rheology to sensory experiences such as mouth feel. A possible link between rheological properties and mouth feel[4] with the microstructure of the material would be of particular importance from a fundamental point of view. Furthermore, with the aid of this knowledge, new products with unique properties could be designed. In this light, there exists a definite need for suitable methods for characterizing the structure of multiphase polymeric materials under flow.

Although reports of flow-induced structure formation date back several decades,[5] recent advances in experimental techniques for probing the alignment of polymers under external shear forces have stimulated several researchers in the field of polymer science to regain interest.[2] Shear-induced orientation effects have been probed by small-angle neutron scattering of polystyrene coils in dilute solution,[6] by X-ray scattering of hydroxypropylcellulose solutions,[7] and with fluorescence anisotropy measurements of polymer melts.[8]

Nuclear magnetic resonance spectroscopy (NMR) has proven to be an excellent technique for gaining knowledge of the behavior of molecules. It provides structural, orientational, and dynamic information on the molecular level and to some degree fingerprinting of mixtures. Several papers on the study of velocity profiles of flowing high-polymer melts, solutions, and fiber suspensions using dynamic NMR microscopy have been published.[9−15] More recently, NMR has been used for the measurement of molecular orientation as induced by the application of external mechanical fields[16] or of shear flow in Couette and cone/plate geometry.[17,18]

As the cone/plate geometry described in refs 17 and 18 requires a fairly elaborate modification to a standard NMR spectrometer, we chose the Couette geometry for our shear NMR measurements. In contrast to ref 18, we did not observe the ordering of the polystyrene directly but measured the ordering of the solvent (benzene), induced by the ordering of the solute (PS). The drawback of the indirect observation of polymer order is counterbalanced by the savings in experimental costs due to lack of isotopic labeling of the polymer.

In this paper, we present a relatively easy modification to a conventional NMR spectrometer which allows the measurement of rheological (macroscopic) and spectroscopic molecular properties of a sample in a Couette-type shear field.

The polystyrene/benzene solution used has no inherent anisotropy (such as that found in liquid crystal polymers where oriented domains will align under shear) and is therefore suitable for measuring the order induced by a shear field itself.

## Materials and Methods

**Materials.** Atactic polystyrene with a molecular weight of 1 000 000 and a polydispersity of 1.04 was purchased from Polymer Standards Service (Mainz, Germany). Deuterated benzene (benzene-$d_6$) was obtained from Aldrich Chemical Co. (St. Louis, MO). Both chemicals were used without further purification.

**Sample Preparation.** We prepared the PS sample by dissolving 400 mg of PS in 8 mL of benzene-$d_6$. The resulting solution was stirred with a magnetic stirrer overnight to achieve a homogeneous mixture. Using Pasteur pipets, the mixture was transferred into a 10-mm NMR tube. The viscosity of the mixture was adjusted by evaporating a defined amount of benzene-$d_6$ under vacuum and subsequently stirring to homogenize the mixture again. The last step was performed to obtain a very viscous PS/benzene solution of a concentration of 125 mg/mL, which is too viscous for a direct transfer into the NMR tube.

**Experimental Setup.** The construction of a shear cell is dictated by the restrictions imposed by the NMR setup, notably

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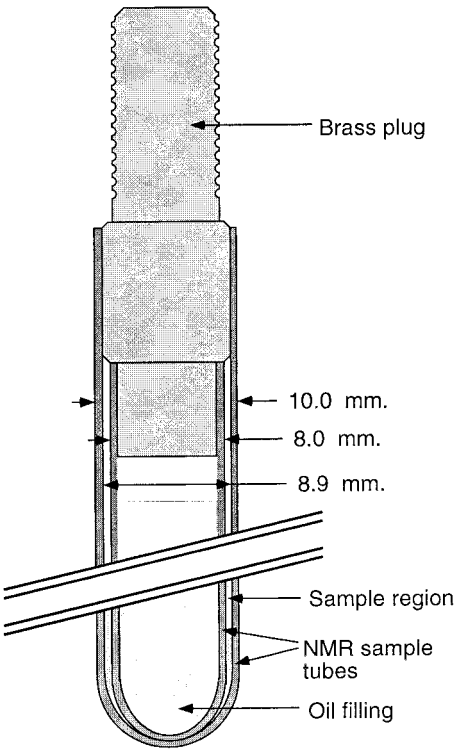


**Figure 1.** Schematic picture of the sample cell.

the presence of a strong static magnetic field. Our shear cell can be used in most NMR setups and can be modified easily.

Figure 1 shows a schematic overview of our home-built NMR shear cell. We used two standard thin-wall high-resolution NMR sample tubes (outer diameters 8.0 and 10.0 mm, length 7 in., Ultra-Imperial Quality, Wilmad Glass, Buena, NJ) as a starting point for our sample cell. The 8.0-mm sample tube contained mineral oil to prevent it from floating upward on filling the intertube spacing (annular region) with our sample. A custom-made brass insert served both as a connection to the nylon drive shaft (via a short piece of rubber tubing) and as a bearing, centering the upper part of the inner tube with respect to the outer one. The lower part was centered automatically due to the spherical shape of the ends of both sample tubes and the presence of a slight pressure of the outer end of the inner tube on the inner end of the outer one.

Figure 2 shows an overview of the whole shear setup. The actual shear cell was inserted into a homemade 25.0-mm diameter holder, and the inner tube was connected to a nylon drive shaft (0.32-cm diameter). The drive shaft itself was held concentric in the magnet bore by an outer brass sleeve (outer diameter 0.65 cm, inner diameter 0.45 cm) which in turn was attached to the upper end of the magnet bore for the experiment. To prevent rotation of the holder and with it the outer shear tube, we increased the friction between holder and stator (stationary in magnet) by introducing an O-ring and applying pressure (using a brass rod) on the holder. The inner sample tube was rotated via the nylon drive shaft, which in turn was rotated by a modified $5^1/_4$-in floppy disk motor, which rested on a support platform (see Figure 2 on top of the magnet dewar.

The rotational frequency of the modified Tandon $5^1/_4$-in. floppy disk drive was measured via the frequency output of its speed feedback loop. We used a Hewlett-Packard HP5326B timer−counter unit to measure this frequency to an accuracy of 1%. The rotation speed could be varied with a 10-turn potentiometer and was stable within 1% during the experiment.

With the present setup, the limits on the rotation speed are 3.2−6.8 Hz, corresponding to shear rates of 180−380 $s^{-1}$ for our 8-mm/8.9-mm (outer/inner diameter) shear cell setup. Using a gear box, the range of rotation speeds could be

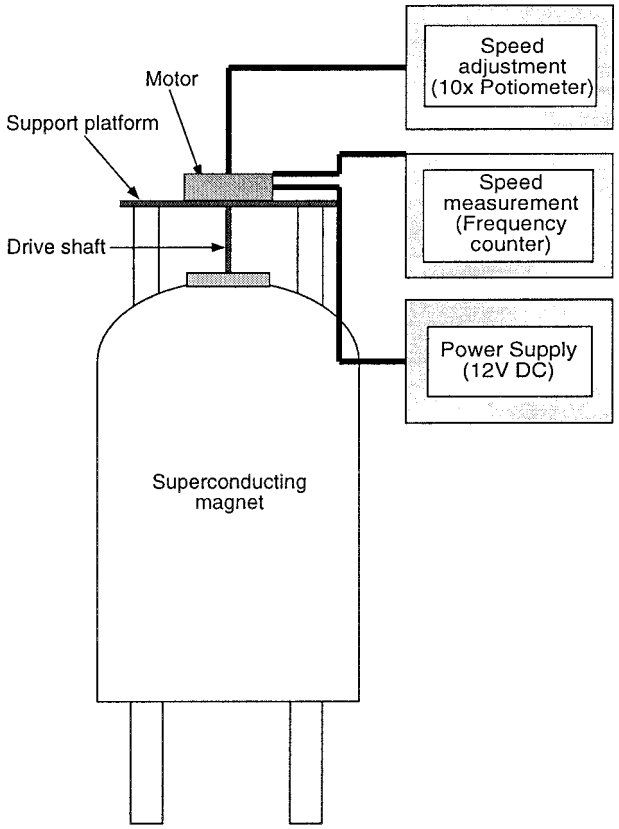


**Figure 2.** Schematic picture of the experimental setup.

increased to cover the region from a few millihertz to tens of hertz. The lower limit will be determined by the jerkiness of the motion produced by the individual teeth of the gear wheels. One limit for the maximum drive speed is the torque supplied by the drive motor; the other limit is posed by the onset of non-Newtonian behavior at high shear rates (e.g., slip near the wall) as described in ref 14. The best line width obtainable with the described shear cell is fwhm 0.4 Hz (for pure benzene-$d_6$ in the shear cell).

**NMR Experiment.** All experiments were performed on a Bruker AM400 using the homemade 25.0-mm holder and a 10-mm Bruker 400-MHz triple-resonance probe ($^1H$, $^2H$, BB). The pulse sequence was 90° acquire with a 90° pulse length of $t_{90}° = 8\ \mu s$. The sample temperature was controlled using a Bruker BVT1000 air flow temperature controller and was kept at 300 K for all experiments.

## Results and Discussion

The sample in the annular region experiences an almost constant shear rate when the gap between the two concentric cylinders is small enough, i.e., when the ratio of the inner ($r_i$) and outer ($r_o$) radii is greater than 0.97.[19] The shear rate can then be derived from the radii and angular velocity $\omega$ as

$$\dot{\gamma} = r_i\omega/(r_o - r_i) \qquad (1)$$

We assume constant shear rate although we do not meet the above requirement ($r_i/r_o = 0.90$ in our case). This assumption turned out to be reasonable since the liquid is not shear-thinning in our interval of shear rates, as reflected by our results. We also assume a no-slip situation, i.e., no relative motion between the tube walls and the immediately adjacent PS/benzene-$d_6$ solution.

If shear preferentially orients the PS (similar to that discussed for oil droplets under shear[20,21]), the benzene

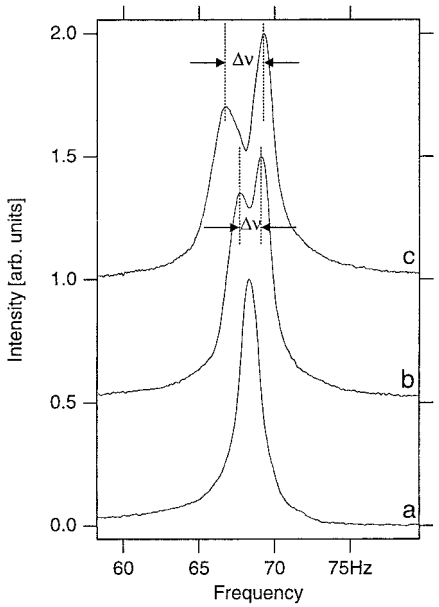


**Figure 3.** Deuterium NMR signal for different shear rates: (a) $\dot{\gamma} = 0.0\ s^{-1}$; (b) $\dot{\gamma} = 195.5\ s^{-1}$; (c) $\dot{\gamma} = 379.5\ s^{-1}$.

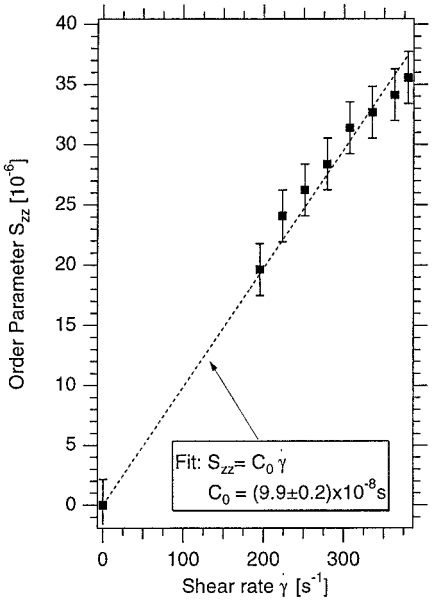


**Figure 4.** Absolute value of the order parameter $S_{zz}$ of the benzene molecule versus the shear rate $\dot{\gamma}$ at 300 K. The dashed line represents the fit of the data to a straight line without offset.

should report this deviation from isotropy via a nonzero-order parameter. This would lead to a splitting in the $^2$H NMR line.

Figure 3 shows some examples for the deuterium NMR signal of the benzene as observed at different shear rates. In quiescent solution ($\dot{\gamma} = 0\ s^{-1}$), we observed a single resonance line with a line width of 1.70 Hz (Figure 3, spectrum a). The application of shear splits this line into a doublet, with the splitting of the doublet being dependent on the shear rate (Figure 3, spectra b and c). The observed splittings $\Delta\nu_q$ were in the range of 1.4−2.6 Hz for the shear rates used.

The static quadrupolar splitting is given by (assuming the asymmetry parameter $\eta$ to be zero)

$$\Delta\nu_q = \frac{3}{2}\frac{e^2qQ}{h}P_2(\cos\alpha) \qquad (2)$$

with $\alpha$ being the angle between the C−D direction and the magnetic field $B_o$. In the case of benzene-$d_6$ we have rapid axially symmetric reorientation of the benzene ring around its $C_6$ symmetry axis, which effectively reduces the observed splitting by a factor of $-1/2$ and leads to (ref 22, p 374, eq 45)

$$\Delta\nu_q = \frac{3}{4}\frac{e^2qQ}{h}P_2(\cos\beta) \qquad (3)$$

where $\beta$ is the angle between the $C_6$ axis of the benzene ring and the magnetic field direction $B_o$. The application of shear to the PS/benzene-$d_6$ solution leads to an anisotropy in the orientational distribution of the PS molecules. On the basis of refs 18 and 20, we assume that the PS molecules tend to align in the plane formed by the velocity vector and the gradient of the velocity vector. The benzene molecules are sampling this axially symmetric anisotropic environment, which leads to the following form of the observed quadrupolar splitting:

$$\Delta\nu_q = \frac{3}{8}\frac{e^2qQ}{h}S_{zz} \quad \text{with} \quad S_{zz} = \langle P_2(\cos\theta)\rangle \qquad (4)$$

with $\theta$ being the angle between the anisotropy direction (the alignment direction of the PS, being perpendicular to the magnetic field) and the $C_6$ symmetry axis if the benzene molecules. The additional reduction by a factor of $-1/2$ (compared to eq 3) is due to the 90° angle between the direction of anisotropy and the direction of the magnetic field. We used a value of 279 kHz for the static quadrupolar coupling constant $(3/2)(e^2qQ/h)$ of the C−D bond in benzene[23,24] for the conversion of our observed splittings to values of the orientational order parameter $S_{zz}$.

It should be noted here that we are measuring the order parameter of the benzene, induced by the shear-induced ordering of the PS. We expect the order parameter of the PS to be significantly higher than that of the benzene. Unfortunately a quantitative estimate for the relation between the PS and benzene order parameters requires very detailed knowledge about both PS and benzene and has therefore not been attempted.

Figure 4 shows the results of our experiments, plotted as order parameter value $|S_{zz}|$ versus shear rate $\dot{\gamma}$, together with a linear fit

$$|S_{zz}| = (9.9 \pm 0.2) \times 10^{-8}\ \text{s} \times \dot{\gamma}$$

The error bars give estimates for the standard deviation for each measurement point. The small value of $\chi^2 = 4.32$ corresponds to a probability of 83% for observing a $\chi^2$ value larger than the observed one, assuming the correctness of our linear model.[25] A fit allowing for a possible offset gives

$$|S_{zz}| = (1.4 \pm 1.6) \times 10^{-6} + (9.4 \pm 0.5) \times 10^{-8}\ \text{s} \times \dot{\gamma}$$

with $\chi^2 = 3.61$ and a corresponding probability value of 82% for observing a $\chi^2$ value larger than the observed one. As the error for the offset of $1.6 \times 10^{-6}$ is larger than its determined value of $1.4 \times 10^{-6}$, our data contain no detectable offset at 0 Hz.

The good representation of our data by a straight line suggests Newtonian behavior for this regime of shear rates. The slight deviation from linearity at high shear

rates (still within the error bars) could stem from the onset of non-Newtonian behavior (see ref 14).

Our observation of increasing order with increasing shear rate are in qualitative agreement with those described in refs 6−8, where other techniques were used to observe the polymers themselves. For example, the SANS results of a dilute PS solution[6] show that the experimental root-mean-square radius as a measure of the overall coil size clearly increases in the direction parallel to the flow, whereas the value perpendicular to the flow slightly decreases in comparison with the value in the solution at rest. This qualitative agreement between our results (obtained by observing the solvent) and the results stemming from measurements on the polymers themselves suggest that one might hope to determine an "*order reduction ratio*" (ORR), given by the ratio of the order parameter of the solvent (benzene) to the order parameter of the solute (PS). Although it is to be expected that these ORRs are fairly system dependent, they would be useful in providing an inexpensive way for researchers to determine approximate values for shear-induced polymer order parameters by measuring the solvent order parameters.

## Summary

With our experiments we have shown that it is possible to simultaneously apply a shear stress and to measure the changes induced by this stress. This is a promising result as it unveils a directly observable link between rheological properties and molecular orientation induced by shear forces.

The next step in pursuing the shear orientation of PS would be to perform an $^2$H NMR experiment on partly deuterated PS dissolved in protonated benzene under shear. Knowing the CD bond order parameter for the polymer as a function of shear rate one could determine the ORR, which would enable fast and fairly inexpensive shear NMR experiments on PS solutions. Furthermore, the concept of ORRs should be applicable to other polymer systems as well.

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