*Macromolecules* **1993,** *26,* 7095–7096

# Shear Rheology of Semidilute Poly(methyl methacrylate) Solutions

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*Received April 26, 1993*
*Revised Manuscript Received September 28, 1993*

**Introduction.** Very high molecular weight, low polydispersity, linear chain samples of poly(methyl methacrylate) have recently been prepared by plasma-induced polymerization.[1] They constitute an ideal material for testing rheological theories since solutions in various solvents can easily be obtained at concentrations large enough to be well into the entangled state. The rheology of such semidilute solutions has not been widely investigated, due to the lack of very high molecular weight polymers. Magda et al.[2] investigated the shear rheology of polystyrene solutions and found a qualitative agreement with the Doi–Edwards theory.

In a recent paper, Cates, McLeish, and Marrucci[3] suggested a new mechanism for removing the unrealistic continuous decrease of the shear stress with shear rate which occurs in the Doi–Edwards model for entangled polymers. This mechanism is based on the fact that, in the tube model, the chains have a finite transverse dimension. The consequence of this is that different parts of the chain will experience different shear rates, causing extension of the chain. The result of this approach is that three regions will occur in steady-state shear, depending on shear rate. There is a stable shear flow at low shear rates followed by an unstable region where the stress and the first normal stress difference are leveling. A second stable region is recovered at higher shear rates due to this tube stretching mechanism. This theory shows that the tube stretching occurs at very high shear rates for polymer melts, in a region where probably no measurement of normal stresses can be performed. Cates et al. suggested in their paper that there is one favorable case where this mechanism could be seen. It is when the polymer is in a semidiluted state. This ensures that the unstable region can still be investigated in a cone-and-plate rheometer without expelling the material from the gap. Another important point is that the shear rate at which the tube stretching occurs is strongly decreasing with molecular weight and very high molecular weight must be used.

The aim of this Communication is to report evidence that very high molecular weight polymer solutions have a shear behavior which has some of the features predicted by the above theory.

**Experimental Section.** Poly(methyl methacrylate) (PMMA) samples were prepared by plasma-induced polymerization. The detailed description of the method is given in ref 1. The molecular weight of PMMA which was used is $23.8 \times 10^6$. The molecular weight determinations, given elsewhere,[4] were performed by light scattering and viscometry.

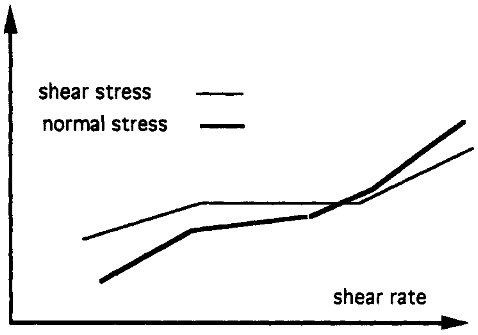

**Figure 1.** Schematic drawing of the shear stress and first normal stress difference versus shear rate as predicted by ref 3.

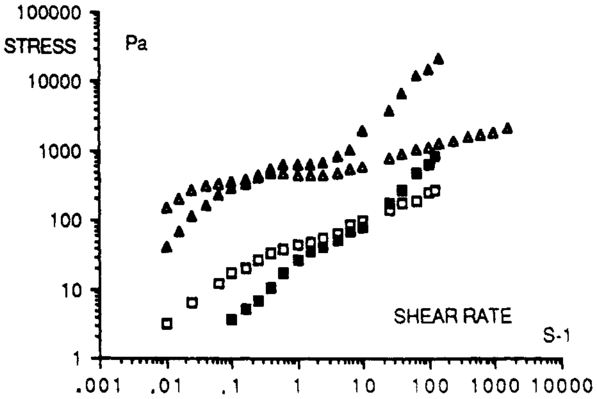

**Figure 2.** Shear stress and first normal stress difference versus shear rate for two solutions of PMMA in toluene. PMMA concentration 2 g/dL: (□) shear stress; (■) normal stress. PMMA concentration 6 g/dL: (△) shear stress; (▲) normal stress.

Solutions of PMMA in toluene were prepared by gently mixing the polymer and the solvent, keeping the mixture at 50 °C for 10 days and then centrifuging at 1000 rpm. Two polymer concentrations were used, 2 and 6 g/dL.

The viscosity and first normal stress difference were measured in steady-state shear at room temperature (23 °C) with a cone-and-plate Instron 3250 rheometer fitted with a 6° cone and a system to prevent solvent evaporation. The shear rate range which was investigated is between $10^{-2}$ and $10^3$ $s^{-1}$.

**Results and Discussion.** The critical concentration $C_e$ above which chain interpenetration occurs can be estimated to be $C_e = 0.03$ g/dL from intrinsic viscosity measurements.[4] The two solutions are thus deep into the entangled state since the lowest concentration is 2 g/dL.

Figure 1 gives the schematic prediction of Cates et al.[3] for the plot of the shear stress and the first normal stress difference as a function of the shear rate. The normal stress is predicted to have four regimes (quadratic, constant, linear, and quadratic again) and the shear stress has three regimes (linear, constant, and linear). The two intermediate regimes for the normal stress occupy the same range of shear rates as the single intermediate regime in shear stress. Figure 2 shows the measured values for the two solutions. It is clear that there are a lot of qualitative similarities between the two figures. The relative position along the shear rate axis of the viscosity and first normal stress difference curves is the same as in the theory.

The most striking effect is the three-stage region of the first normal stress difference. This was observed for five molecular weights ranging from $12.9 \times 10^6$ to $23.8 \times 10^6$ in three solvents, toluene, dimethylformamide, and methyl ethyl ketone.[4] Observed during flow, the rim of the gap between the cone and the plate did not present any particular instability.

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0024-9297/93/2226-7095$04.00/0

A closer comparison of the predictions of the Cates et al. theory with the experiments gives the following results. According to the theory, the beginning of the flow instability (which corresponds to the beginning of the stress plateau) should occur at a shear rate $\dot{\gamma}_d = 1/t_d$ with $t_d$ proportional to $C^a$, $C$ being the concentration and $a$ being in the range 1.6–2. It is indeed what is found for the dependence of $\dot{\gamma}_d$ on concentration (−1.6 for the reported solution). The slope of the first normal stress difference versus shear rate at high shear rates in the second stable region is about 1, as predicted. Another possible quantitative comparison is that the ratio between $\dot{\gamma}_d$ and $\dot{\gamma}_r$ (the shear rate at the end of the flow instability) is a constant for a given polymer solution. This is verified within 15%.

Several differences can be observed with the theory. First, the first normal stress difference has only three regions and not four. This may be due to the very high shear rates needed to see the fourth region. Second, the relative values of the shear stress and normal stress should be the same for all solutions, as predicted by the theory. This is not the case. Finally, the shear stress does not have the constant regime, its value in this region increasing slightly with the shear rate.

The occurrence of this first normal stress difference plateau seems to be due to the very high molecular weight of the polymer. To our knowledge, such a behavior has never been explicitly reported, one reason being that the PMMA molecular weight was lower than $2 \times 10^6$ in previously published papers.[5–7] Another reason can be that such a phenomenon was not noticed. For example, Magda et al. studied the viscosity and first normal stress difference of a 2% solution of a polystyrene sample with a molecular weight of $20 \times 10^6$.[2] Figure 7 of their paper clearly shows a behavior very similar to that for PMMA, with an upturn of the first normal stress difference far in the nonlinear region, and this for two solvents. The qualitative agreement between the theory and the experiments is a first indication that stretching of the chains as considered in this theory may occur during shear.

**Acknowledgment.** We are grateful to Prof. G. Marrucci for valuable discussions and for making a preprint of ref 3 available for us. We thank the referees for making useful comments.

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