NOTES

Viscometry of Anisotropic Solutions of Poly-p-Phenyleneterephthalamide in Sulfuric Acid

INTRODUCTION

In recent years there has been considerable interest in the processing of high-strength–high-modulus fibers from anisotropic solutions* of rigid aromatic polyamides in strong acid and dialkylamide solvents.[1,2] Solutions of poly-p-phenyleneterephthalamide (PPPT) and poly-p-benzamide (PBA) in concentrated sulfuric acid and dimethylacetamide (DMAC)/LiCl, respectively, have received the most attention.

Although there is a voluminous literature concerned with the rheology of low-molecular-weight organic liquid crystals,[3] there is apparently very little information available on the rheology of anisotropic polymer fluids.[4] The most frequently published data consist of the concentration dependence of the viscosity (η) measured in the low shear rate ($\dot{\gamma}$) range.[4] η has been reported to increase with increasing polymer concentration (c) until reaching a critical concentration (c^*) at which the solution becomes anisotropic, and with further increases in c, η decreases until the solubility limit of the polymer in the given solvent is exceeded. This behavior has been observed for both the synthetic polypeptides in various helicogenic solvents[5] and the rigid aromatic polyamides[1,2,6] and is believed to be characteristic of polymer systems existing in either the nematic or cholesteric mesophase.

In addition to the optical properties of these solutions, the characteristic concentration dependence of η is used to identify the onset of liquid crystalline order with changes in other variables such as molecular weight, temperature, and nature of the solvent. However, it appears that some care must be taken in selecting the shear rate range over which η is measured. At high $\dot{\gamma}$ (i.e., $\dot{\gamma} > 10$–100 sec^{-1}), η no longer shows the characteristic concentration dependence as the difference between anisotropic and isotropic phase tends to disappear.[5,7] At low $\dot{\gamma}$ there are two phenomena which could also disguise this characteristic behavior of η. The first of these is the occurrence of a yield shear stress which has been observed by Papkov et al.[7] in the $\dot{\gamma}$ range from 0.001 to 1.0 sec^{-1} for solutions of PBA and DMAC/LiCl. The other phenomenon is that of a boundary layer effect which could lead to η depending not only $\dot{\gamma}$ but on the geometry of the viscometer. The calculations of Leslie[8] and Ericksen[9] based on constitutive theories derived for low-molecular-weight liquid crystals (but probably general enough to be applicable to polymeric systems) led to the conclusion that η would be a function of not only $\dot{\gamma}$ but the gap separation (h) between two parallel plates, i.e., $\eta = f(\dot{\gamma}h^2)$. There is some experimental confirmation of this effect for organic liquid crystals.[10,11] However, it is not known whether the geometry of the rheometer is an important factor in the viscometry of polymer systems with liquid crystalline order.

The purpose of this note is to investigate the rheometry of anisotropic solutions of PPPT in 100% H_2SO_4 with particular attention given to the phenomena of yield shear stresses and the dependence of η on the rheometer geometry. The rheometer geometries studied here include the cone-and-plate and the plate-plate. In addition, the complex viscosity (η^*) is determined from dynamic mechanical measurements and compared with the steady-state viscosity.

EXPERIMENTAL

Solutions were prepared by blending chopped PPPT fiber (intrinsic viscosity $[\eta] = 5.9$ dl/g in 96.6% H_2SO_4) or polymer flake ($[\eta] = 3.8$ dl/g in 96.6% H_2SO_4), polymerized by procedures given elsewhere,[2] with 100% H_2SO_4 in a Helicone Mixer (Model 2CV) at 60°C for 4 to 6 hr. Mixing was carried out in a dry nitrogen atmosphere, and solutions were extruded from the mixing bowl directly into bottles which were kept well sealed until being used. Solutions of 3.5%, 7.5%, 12.0%, 14.0%, and 16.0% by

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* The term anisotropic has been used to describe these solutions because they transmit polarized light and diffract x rays. These solutions are thought to exist in the nematic mesophase, one of three liquid crystalline types.
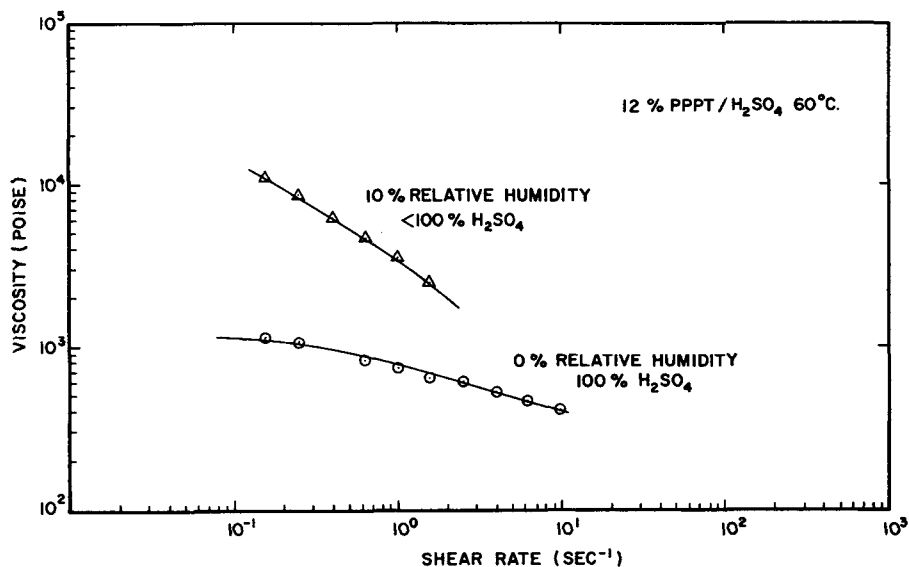
Fig. 1. Effect of moisture on the steady shear viscosity of an anisotropic solution of 12.0% PPPT in 100% H_2SO_4 ($[\eta]$ = 3.8 dl/g). Viscosity data were obtained by means of the cone-and-plate mode of the RMS.

weight were prepared. The 12.0%, 14.0% and 16.0% solutions were determined to be anisotropic since they exhibited stir opalescence and transmitted polarized light.

Viscosity measurements were carried out using various modes of the Rheometrics Mechanical Spectrometer (RMS). For the plate-and-plate mode (5 cm diameter plates), gap settings of 0.05, 0.1, 0.2, and 0.4 mm were used. The diameter of the cone-and-plate was 5 cm, while the cone angle was 0.04 rad. The complex viscosity was also obtained from the cone-and-plate system used in the oscillatory mode. Viscosity data was obtained by reducing the torque measurements and angular velocity or frequency of the two geometries by well known methods described in the Rheometrics operation manual. These methods have been derived many places (e.g., Lodge[12]) and summarized
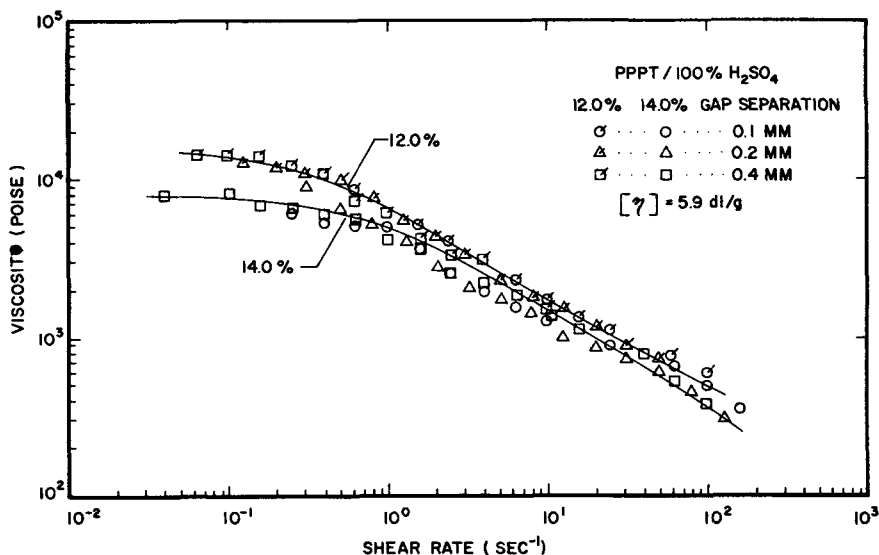

Fig. 2. Steady shear viscosity data vs shear rate for 12.0% and 14.0% anisotropic solutions measured in a plate-plate rheometer for various plate separations ($[\eta]$ = 5.9 dl/g).
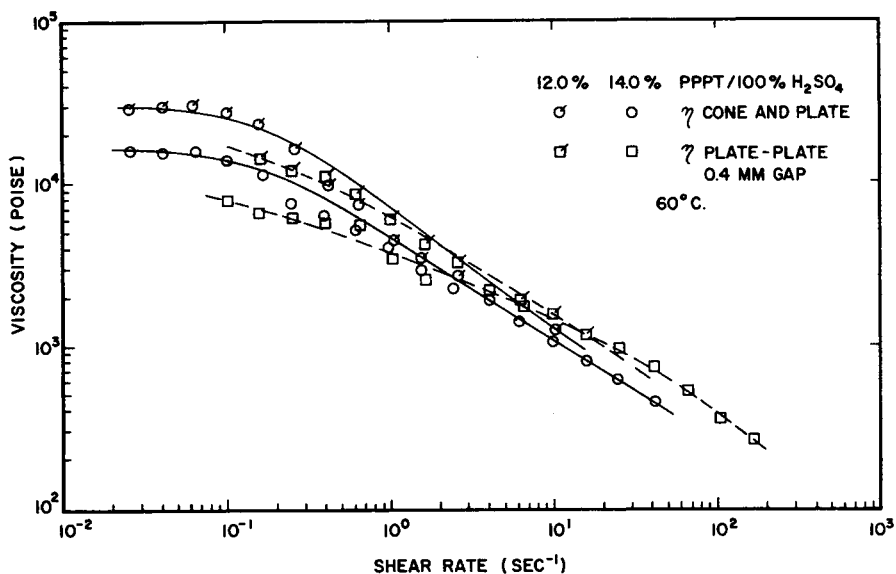
Fig. 3. Comparison of steady shear viscosity data measured in the cone-and-plate with the steady shear viscosity measured in the plate-plate viscometer with a gap separation of 0.4 mm ($[\eta] = 5.9$ dl/g).

more recently by Bird and co-workers.[13]   In the case of the dynamic data, torque and phase loss values had to be corrected for frequencies greater than 1 Hz because of phase losses due to the inertia of the cone.   A suitable procedure consisted of developing a calibration curve which gave the phase lag and amplitude loss of the cone with no sample between the cone and plate as a function of frequency.
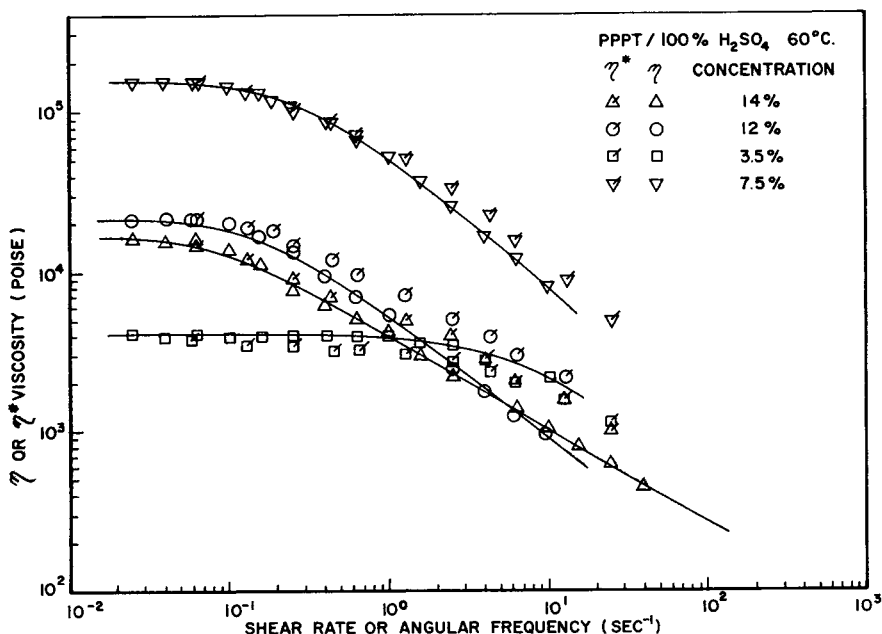

Fig. 4. Steady shear and complex viscosity measured in the cone-and-plate viscometer vs shear rate and angular frequency, respectively, for solutions of PPPT in 100% H_2SO_4: 3.5% and 7.5% solutions are isotropic while 12.0% and 14.0% solutions are anisotropic ($[\eta] = 5.9$ dl/g).

Because of the sensitivity of the anisotropic phase to moisture, two methods were used to minimize the effects of moisture. A dry box was constructed which covered the entire test chamber of the RMS allowing us to keep a dry nitrogen atmosphere. Another equally effective method consisted of using a plate with a baffle. In this way the free surface of the test fluid could be covered with a low viscosity mineral oil (see the Acknowledgments).

RESULTS AND DISCUSSION

Viscosity measurements were complicated by the sensitivity of this system to moisture. The low viscosity anisotropic phase changed to a much higher viscosity solid plus anisotropic phase with only small changes in the acid concentration. As the concentration of polymer increased the sensitivity to moisture increased (see ref. 1 for a phase diagram of a similar polymer/solvent system). To illustrate this behavior η values vs. $\dot{\gamma}$ for a solution of 12.0% PPPT ($[\eta]$ = 3.8 dl/g) in 100% H_2SO_4 measured under anhydrous conditions are compared with values for the same solution exposed to moisture (about 10% relative humidity) in Figure 1. For a $\dot{\gamma} \approx 0.2$ sec^{-1}, we see that η of the solution exposed to moisture is about an order of magnitude higher than that of the protected solution. Furthermore, the protected solution exhibits a region in which η is apparently becoming independent of $\dot{\gamma}$, whereas the solution exposed to moisture is highly non-Newtonian over the same $\dot{\gamma}$ range. Thus, the lack of proper care to eliminate moisture in either the solution preparation or viscosity measurements can lead to large viscosity increases at low $\dot{\gamma}$.

Taking proper care to minimize the amount of moisture which could be absorbed into the fluid samples, η values were measured in the plate-plate viscometer using various plate separations. Data are presented in Figure 2 for a 12% and 14% solution. For these two solutions, there is apparently no systematic dependence of η on the gap separation. However, we have observed that data obtained from the cone-and-plate is always greater in magnitude at low $\dot{\gamma}$ than data obtained from the plate-plate (see Fig. 3). (This phenomenon is apparently a peculiarity of the fluid since viscosity measurements made on National Bureau of Standards test fluid No. 1 using the cone-and-plate and plate-plate system are in excellent agreement.) Thus, there is some dependence of η on the rheometer geometry but possibly not of the form envisioned by Leslie and Ericksen. Although we can not account for this behavior directly, data presented later for a 16.0% anisotropic solution point to the presence of small amounts of moisture as a possible cause.

Although there is apparently some dependence of η on the rheometer geometry, we note that there is evidence that η becomes independent of $\dot{\gamma}$ for $\dot{\gamma} < 0.1$ sec^{-1}, and there is no evidence of a yield stress. This is illustrated further by the data in Figure 4 in which values of η^* and η have been plotted as
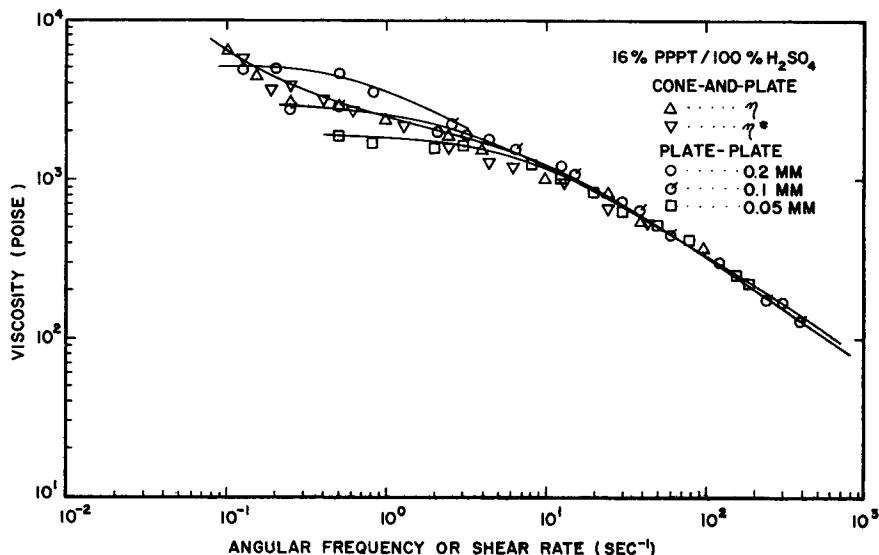

Fig. 5. Steady shear viscosity obtained from the cone-and-plate and the plate-plate viscometer vs $\dot{\gamma}$ and complex viscosity vs angular frequency for a 16.0% PPPT/100% H_2SO_4 anisotropic solution ($[\eta]$ = 5.9 dl/g).
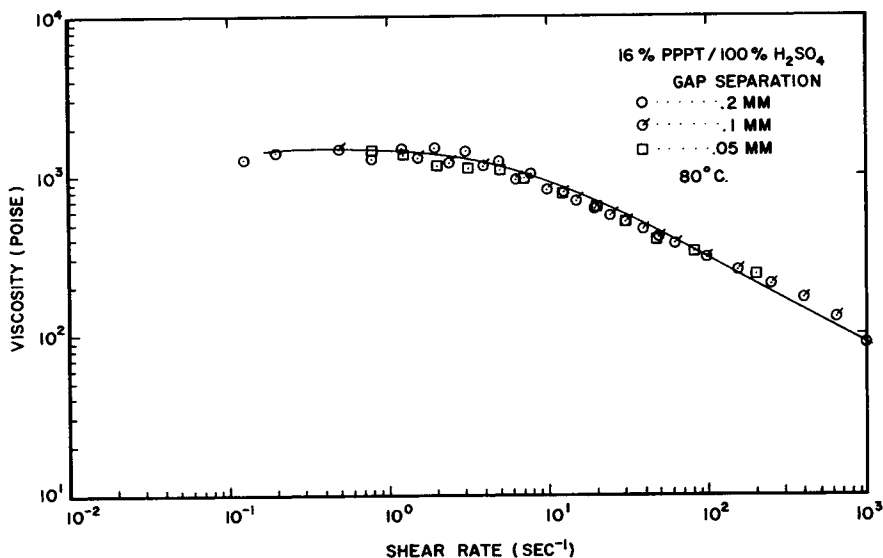
Fig. 6. Viscosity data obtained from the plate-plate viscometer at 80°C for a 16% PPPT/100% H_2SO_4 solution ($[\eta]$ = 5.9 dl/g).

a function of angular frequency (ω) and $\dot\gamma$, respectively, for solutions of various concentration. We observe that for both the isotropic and anisotropic solutions there is a range of $\dot\gamma$ over which η is independent of $\dot\gamma$ (in this region we use η_0 to represent η values). There appears to be no tendency for η values to rise at low $\dot\gamma$.

Of further interest in Figure 4 is the comparison of the steady state viscosity η and the complex viscosity. Except for the 3.5% solution, η eventually falls below η^* which is contrary to behavior observed for nearly all other polymer systems.[14] However, this behavior can not be associated with anisotropic solution behavior alone, since the 7.5% solution also exhibits this same behavior. We suspect that this is due to the break down of the gel-like structure of these solutions which arises as a result of the ionization of the PPPT molecules in H_2SO_4 (ref. 15) and the subsequent intermolecular attraction.

Viscosity data for the 16.0% solution have been presented separately from the other anisotropic solution data because of their peculiar behavior. In Figure 5, η data measured in the cone-and-plate and the plate-plate viscometer are presented. In this case we see that both η and η^* exhibit no Newtonian flow region and rise sharply at low $\dot\gamma$ which is indicative of a yield stress. Furthermore, η depends on the plate separation with η decreasing with decreasing plate separation.

We feel that this behavior is an artifact which is caused by the extreme sensitivity of the 16.0% anisotropic solution to moisture. According to phase diagrams given by Kwolek[1] for solutions of PBA and PPPT in H_2SO_4 the minimum acid concentration required for the formation of an anisotropic phase increased with polymer concentration and decreased with polymer molecular weight. The 16.0%/100% H_2SO_4 solution is on the verge of forming a solid phase at 60°C. Even though extreme precautions are taken to eliminate moisture, an increase in water by as little as 0.1% could cause a phase change to the solid plus anisotropic phase at the free surface of the test fluid. Since a slight color change of the test fluid occurred at the free surface, we suspect this to be the case.

To check this hypothesis, viscosity measurements were made at 80°C in the plate-plate system and data are presented in Figure 6. We observe that the dependence of η on the gap separation disappears and there is a Newtonian flow region. In addition we observed no change in color at the free surface. At 80°C we believe that a lower acid concentration can be tolerated before a phase change occurs.

CONCLUSIONS

Provided proper precautions are taken to eliminate moisture during viscosity measurements of solutions of PPPT in 100% H_2SO_4 no yield stresses are observed. A region in which η is independent of $\dot\gamma$ is observed and this value of η_0 can be used to determine c^*. There is some evidence that η is

dependent on the geometry of the rheometer. Although we can not account for this phenomenon directly, we feel that it may be associated with diffusion of moisture into the test fluids resulting in a phase change at the free surface. This dependence of η on the rheometer geometry can lead to large discrepancies in viscosity data and make it difficult to determine c^*.

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Donald G. Baird

Technical Center
Monsanto Textiles Company
Pensacola, Florida 32575