NOTES

Concentrated Solutions of Poly(p-phenylene-1,3,4-oxadiazole) in Sulfuric Acid

INTRODUCTION

The spinning of high-strength, high-modulus fibers from optically anisotropic polymer solutions has been a topic of both commercial and scientific interest in recent years.[1,2] Optically anisotropic polymer solutions are systems considered to possess liquid crystalline order. Two systems of commercial interest are poly-*p*-benzamide (PBA) and poly(*p*-phenyleneterephthalamide) (PPT), both in sulfuric acid. Both polymers are thought to be highly extended, rod-like molecules in H_2SO_4. (There is, however, some question as to the degree of extension.[3-5]) These solutions are characterized by their ability to transmit polarized light under static conditions and a significant decrease in viscosity of the anisotropic phase with increasing polymer concentration.[2,6]

High-strength, high-modulus fibers have also been produced from concentrated solutions of poly(*p*-phenylene-1,3,4-oxadiazole) (POD), although the physical properties of fibers are somewhat lower than those for PPT.[7] POD molecules are also thought to be highly extended in H_2SO_4 but apparently less extended than those of PPT.[8] Because of the similarities of the POD system with those of PPT, the question has been raised as to whether solutions of POD in H_2SO_4 are anisotropic.[9] Although claims of high-strength, high-modulus fibers spun from highly concentrated solutions (i.e., 17.5 wt-%) were made in a patent issued to Inventa,[7] no claims of optical anisotropy were made. On the other hand, Eftimova and co-workers[9] reported that solutions of POD in H_2SO_4 were reminiscent of anisotropic solutions of PPT and hence anisotropic.

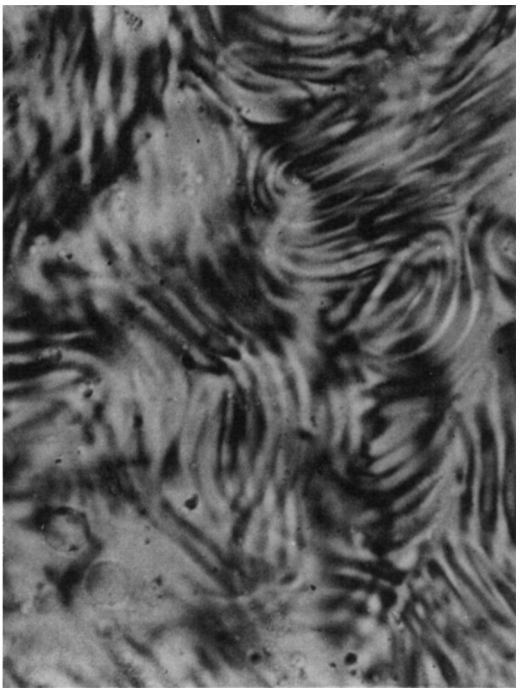

Fig. 1. Photograph of polarized light transmitted from a thin layer of a 20% solution of poly(γ-benzyl-L-glutamate) in dimethylformamide; 23°C. 185×.

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Fig. 2. Photograph of polarized light transmitted from a thin layer of a 12% solution poly(*p*-phenyleneterephthalamide) in 100% H_2SO_4; 23°C. 185×.

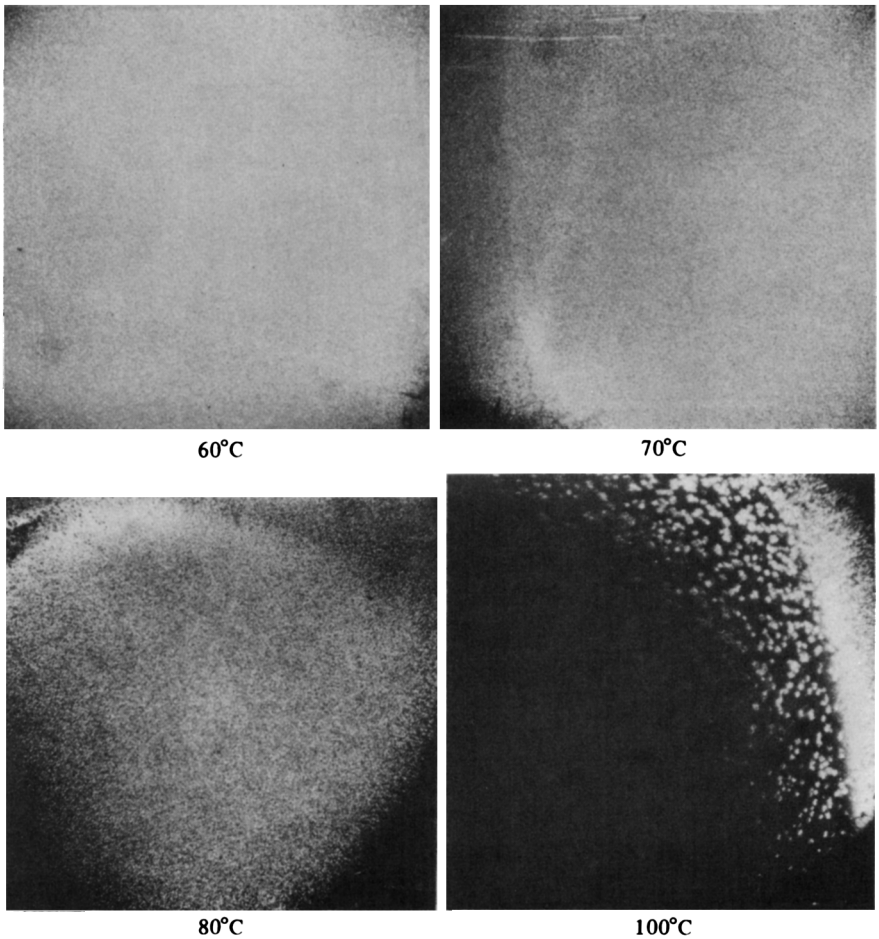

Fig. 3. Photographs of polarized light transmitted from a thin film of 25% poly(*p*-phenylene-1,3,4-oxadiazole) in 100% H_2SO_4 at various temperatures; η_{inh} = 1.66. 185×.

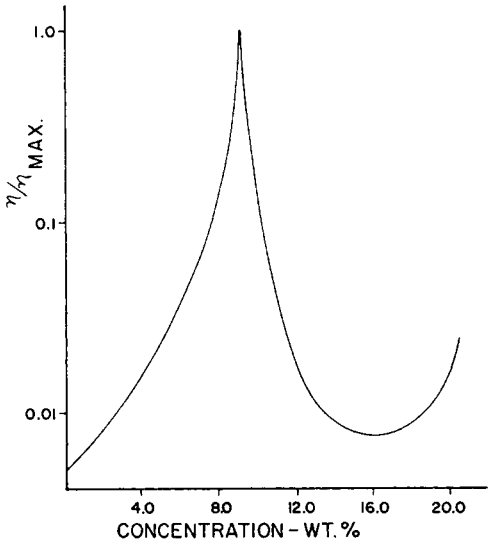

Fig. 4. Schematic drawing of the concentration dependence of viscosity of solutions of PPT in 100% H_2SO_4 and other systems which form the nematic or cholesteric mesophase.

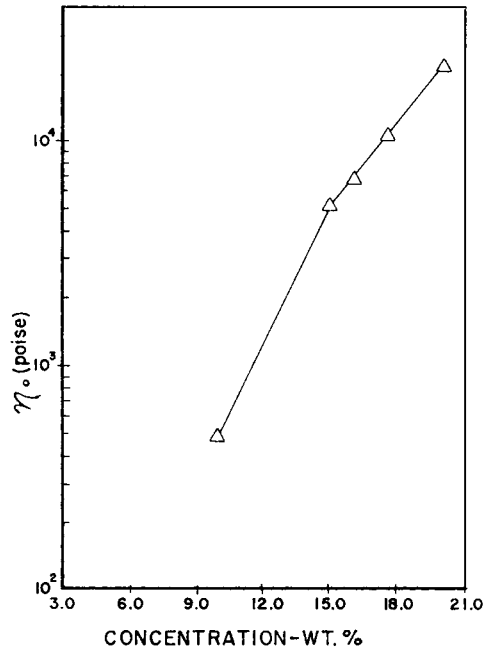

Fig. 5. Viscosity vs concentration for POD in 100% H_2SO_4 at 100°C; η_{inh} = 1.66.

The results of Eftimova and co-workers[9] are not only vague but incomplete. To support their claim, they cited the optical appearance of POD solutions under polarized light and the fact that the concentration dependence of the temperature of transition from the solid state to the isotropic state was similar to that for PPT solutions. They however have apparently overlooked the clearest and most direct method for establishing the formation of an anisotropic phase. This is to determine the concentration and temperature dependence of viscosity, which is apparently characteristic of anisotropic polymer solutions.[10] The purpose of this note then is to use less ambiguous data to determine whether solutions of POD in H_2SO_4 exhibit the form of anisotropy observed for PPT.

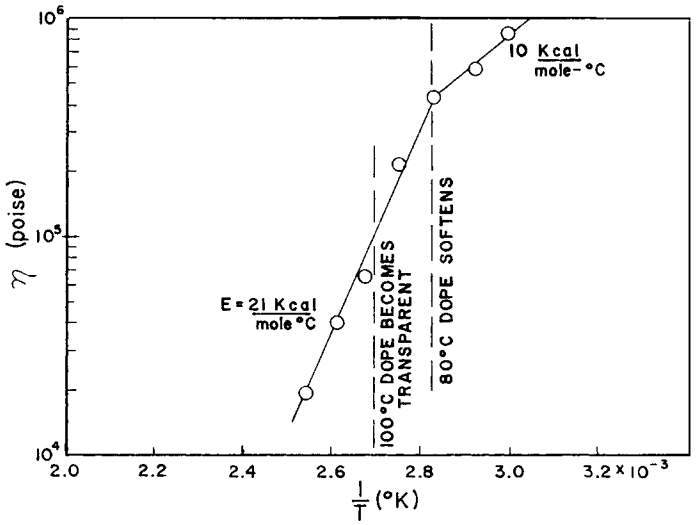

Fig. 6. Viscosity vs reciprocal of temperature for a solution of 25% POD in 100% H_2SO_4; η_{inh} = 0.66.

EXPERIMENTAL

Polymers of two different inherent viscosities (η_{inh}), 0.66 and 1.66, determined at a concentration of 0.2 g/dl in 96% H_2SO_4 at 25°C were prepared by reacting terephthalic acid and hydrazine in fuming sulfuric acid (oleum) at elevated temperatures. Details of this polymerization process are given elsewhere.[7,8,11] The final product consisted of a polymer solution containing 20% by weight of POD in about 100% H_2SO_4. The polymer concentration of the solutions was then adjusted by either adding coagulated polymer or diluting with 100% H_2SO_4. Concentrations in the range of 9.0% to 35.0% were prepared.

Two solutions were employed as models of optically anisotropic solutions. A 20% solution of poly(γ-benzyl-L-glutamate) (PBLG) of 150,000 molecular weight (purchased from Sigma Chemical Co.) in dimethylformamide (DMF) was chosen because it was representative of a solution existing in the cholesteric mesophase.[12] A 12% solution of PPT in 100% H_2SO_4 was prepared by dissolving chopped fiber in H_2SO_4. This solution served as a model of a system existing in the nematic mesophase.[2]

The POD solutions and model systems were first studied under the polarizing microscope with a Mettler hot-stage attachment. A thin layer of fluid (0.0015 in. thick) was mounted on a glass slide according to procedures given elsewhere.[2] The patterns of transmitted polarized light were then compared in a qualitative fashion (see Figs. 1–3). Rheological properties of the POD solutions were measured in steady shear using the cone-and-plate mode of the Rheometrics Mechanical Spectrometer.

RESULTS AND DISCUSSION

The concentration range of primary interest is that of $15 < C < 25$ wt-%. Above 25%, the solid-like masses would not melt but only decompose on heating. Below 15%, the solutions were translucent and hence optically isotropic. It is our experience with anisotropic solutions of PPT and PBLG that they are opaque but become translucent on passing into the isotropic state. Hence, it is not necessary to study solutions below a concentration of 15% or above 25%. However, solutions in the concentration range of 15% to 25% are white, solid-like masses at room temperature which melt at about 100°C. Since these solutions in the concentration range of 15% to 25% resemble to some degree those of PPT in H_2SO_4, the question which has arisen is whether POD solutions exhibit the anisotropic phase which is intermediate between the solid and isotropic liquid state. To answer this question, it is necessary to investigate both the birefringent and rheological properties of these solutions over the range of concentrations and temperatures for which POD solutions exhibit a change from the solid to liquid state.

Under static conditions, anisotropic solutions of PBLG in DMF[12] and PPT in 100% H_2SO_4[2]

transmit polarized light, as illustrated by the photographs in Figures 1 and 2. Periodic lines which arise from light interference are observed in both cases, but they seem to be more distinct for PBLG in DMF. A more detailed description of the optical properties of PBLG in various solvents is given by Robinson.[12] The photographs presented here serve only as a means by which to compare the optical properties of solutions of POD with those which exist in either the cholesteric or nematic mesophase.

A thin film of POD in 100% H_2SO_4 was observed under the polarizing microscope at various temperatures (see Fig. 3). As is observed in Figures 3(a), 3(b), and 3(c), the film transmitted polarized light. At 100°C, the film has nearly completely melted, and, except for some microscopic regions of birefringence, polarized light is no longer transmitted. The birefringent pattern for POD is different from that of PBLG or PPT in that no periodic lines of extinction are observed. In fact, the birefringent regions are granular in nature and more reminiscent of crystallites than an anisotropic fluid.

The concentration and temperature dependence of the zero shear viscosity (η_0) are both unique and characteristic for anisotropic solutions of PBLG in DMF and PPT in 100% H_2SO_4.[10] In particular, η_0 increases with C until reaching a critical concentration C^* at which the anisotropic phase forms. At this C, η_0 passes through a maximum and begins to decrease. This behavior is shown in schematic form in Figure 4. For an anisotropic solution, η_0 decreases with increasing temperature until reaching a temperature at which the solution becomes isotropic. At this temperature, η_0 begins to increase over a small but significant temperature range. On the contrary, η_0 is observed in Figure 5 to increase monotonically with C for solutions of POD in 100% H_2SO_4. Furthermore, η_0 increases monotonically with the reciprocal of temperature ($1/T$), as is observed in Figure 6.

Although the optical results are not completely conclusive, the temperature and concentration dependence of viscosity indicate more specifically that POD in 100% H_2SO_4 does not form an anisotropic solution of the nematic or cholesteric type over the polymer concentration range studied here. It is believed that there is only negligible chance of POD solutions being anisotropic over any concentration range since below 15.0% solids the solutions were translucent and above 25.0% solids the solutions decomposed before melting.

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