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Phase Relationship of Rodlike Polymer, Poly(p-phenyleneterephthalamide), in Sulfuric Acid-Water System

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Abstract: The phase equilibrium was quantitatively investigated by using a typical rodlike polymer, poly(p-phenyleneterephthalamide), in mixed solvent system. The experimental results may afford a basis on the formation of liquid crystal of the polymer.

Introduction

As a consequence of particle assymmetry, the solution of rodlike polymer separates into two phases, an isotropic phase and a more concentrated anisotropic phase. Previously, we have determined the phase relationship of α-helical poly-(γ-benzyl-L-glutamate) in dimethyl formamide-methanol, and in dimethyl formamide-water systems, and reported that the experimental results were in semiquantitative agreement with the prediction of Flory's theory(FLORY,1956). Investigations so far(ROBINSON,1958; WEE,1971) have been carried out mainly with polypeptides, as rodlike polymer sample. In the case of polypeptides, the flexibility of side chains led to some modifications of the original Flory's theory(FLORY,1965;Rai, 1972). In this respect, this communication concerns with poly(p-phenyleneterephthalamide), which is more well-defined rodlike polymer and moreover has no branch at all.

Experimental

Materials- Poly(p-phenyleneterephthalamide)(PPTA) was obtained from Unitica Co., and was vacuum dried for 24 hr at room temperature before use. Three samples of PPTA different in molecular weights were used for the experiments. Their weight-average molecular weight M_w was estimated from the limiting viscosity number $[\eta]$ in sulfuric acid at 30°C according to the viscosity-molecular weight relationship obtained by Schaefgen et al.(1976). Table I includes M_w and the axial ratio x.

TABLE I. Characterization of PPTA Samples

Code	$[\eta]$(dl/g)	M_w	Axial ratio, x
PPTA-1	3.7	24,000	240
PPTA-2	5.6	32,000	290
PPTA-3	7.6	40,000	350

Sulfuric acid (97%) of extra-puregrade was purchased from Nakarai Chemicals Co. 100 % sulfuric acid was prepared by mixing the 97 % sulfuric acid with necessary amount of fuming sulfuric acid. Water distilled and purified by the ion-exchange resin was used for the experiment.

Measurements- The phase separation measurements were carried out as follows: a measured amount of PPTA was dissolved in a given volume of 100% sulfuric acid. The solution was then kept at 30°C for two or three days. To this solution, the nonsolvent, water, was added under agitation through a microsyringe at 30°C until the solution showed turbidity. Near the end-point, addition of the nonsolvent was carried out carefully to permit the precipitation point to be detected thermodynamically. A slight increase in temperature resulted in a clear solution. Turbidity appeared upon cooling the solution again to the original temperature. Thus, the boundary point was determined and the concentrations of the three components at this point were indicated by the volume fractions, v_1, v_2, and v_3 for solvent, nonsolvent, and polymer, respectively. To obtain the volume fraction v_3, the density of PPTA was determined, assuming no volume change upon mixing, from the specific weight measurement on solution of PPTA in sulfuric acid. Thus obtained value of PPTA density was 1.61 g/cm^3.

The phase equilibria were also investigated by polarizing microscope. A Nikon microscope having a temperature controlled stage was employed. These studies were carried out within a week after the solutions were prepared.

Results and Discussion

For a binary system composed of v_1 solvent and v_2 rodlike polymer with an axial ratio x, the chemical potentials μ_1 of the solvent and μ_2 of the polymer derived by Flory (1956) are indicated as

$$(\mu_1 - \mu_1^0)/RT = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi v_2^2 \tag{1}$$

$$(\mu_2 - \mu_2^0)/RT = \ln(v_2/x) + (x-1)v_2 - \ln x^2 + \chi x(1-v_2)^2 \tag{2}$$

for isotropic phase, and

$$(\mu_1 - \mu_1^0)/RT = \ln(1 - v_2) + [(y-1)/x]v_2 + 2/y + \chi v_2^2 \tag{3}$$

$$(\mu_2 - \mu_2^0)/RT = \ln(v_2/x) + (y-1)v_2 - 2 - \ln y^2 + \chi x(1-v_2)^2 \tag{4}$$

for anisotropic solution. In which y is a disorientation parameter which varies from 1 for perfect order to x for complete disorder, and its equilibrium value is given by the lower solution of

$$v_2 = [x/(x-y)][1 - \exp(-2/y)] \tag{5}$$

The calculated phase equilibria between the isotropic and anisotropic phases for rodlike polymers of x=150, 200, 250, 300, and 350 are shown in Figure 1, in which the interaction parameter χ was plotted against v_2. The boundary curve of isotropic solution is on the left, that of anisotropic solution is on the right, and the heterogeneous region is in between. Flory's theory predicts that the polymer concentration v_2'(A-point) of the isotropic phase and that v_2'' of the conjugated anisotropic phase at $\chi=0$, are related to x by

$$v_2' = 8/x, \text{ and } \quad v_2'' = 12.5/x \qquad (6)$$

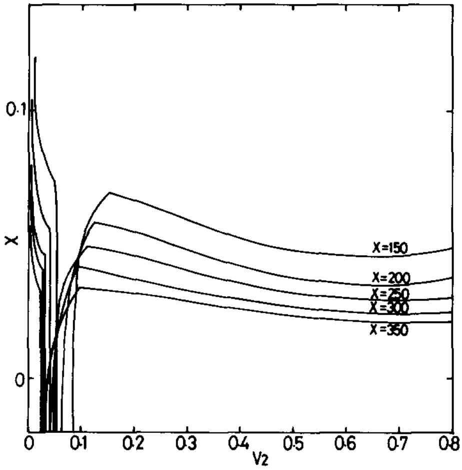

Figure 1 Theoretical phase diagrams

In Figure 2, the experimental results for ternary systems consisting sulfuric acid(v_1), water(v_2), and PPTA(v_3) are shown by circles. The axial ratios of PPTA's used, x=250, 300, and 350 lead to v_3'=0.032, 0.027, and 0.023, respectively. These values calculated from eq(6) closely agree with the experimental values shown in Figure 2. The boundary curve for anisotropic solution was not possible to obtain experimentally.

To discuss the results of Figure 2 qualitatively, the change of χ with solvent composition for PPTA in sulfuric acid-water mixture is necessary, However, nothing has been

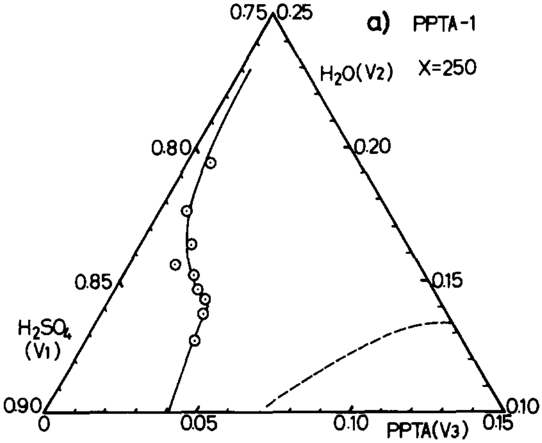

Figure 2 Phase diagrams for H_2SO_4-H_2O-PPTA systems.

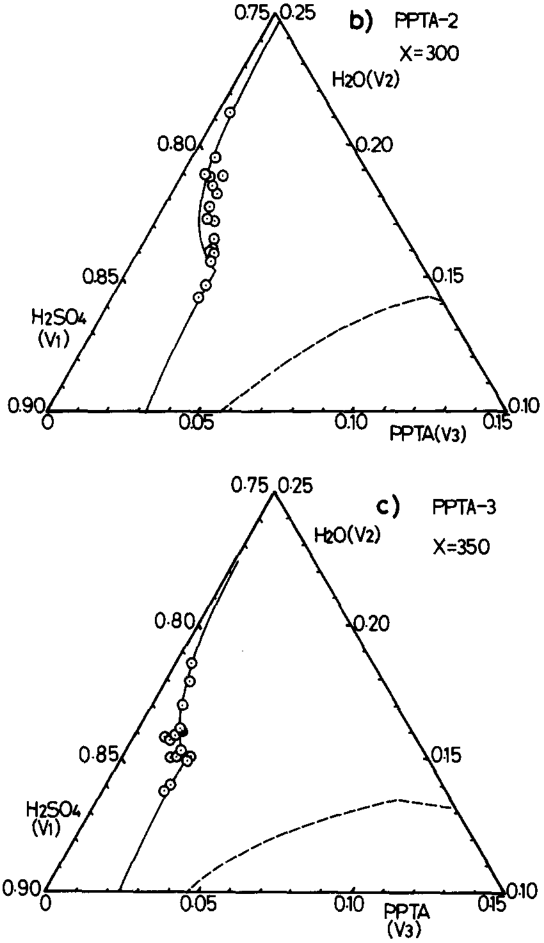

Figure 2 (continued)

reported on this polymer. Therefore, here we assume that the χ value at the break point on the isotropic boundary curve in Figure 1 corresponds to the solvent composition at the corresponding point in Figure 2, and adopt the single liquid approximation for sulfuric acid-water mixture. Thus we have linear relationship between χ and $v_2/(v_1+v_2)$, the solvent composition.

After trial-and-error, we arrived at the χ vs. solvent composition relationships as shown in Figure 3, which fit the experimental values represented in Figure 2. The solid curves in Figure 2 are theoretical ones based on Figure 3. The broken curves in Figure 2 are also theoretical ones which concern with the conjugated anisotropic boundary.

It is pointed out that the system is characterized by

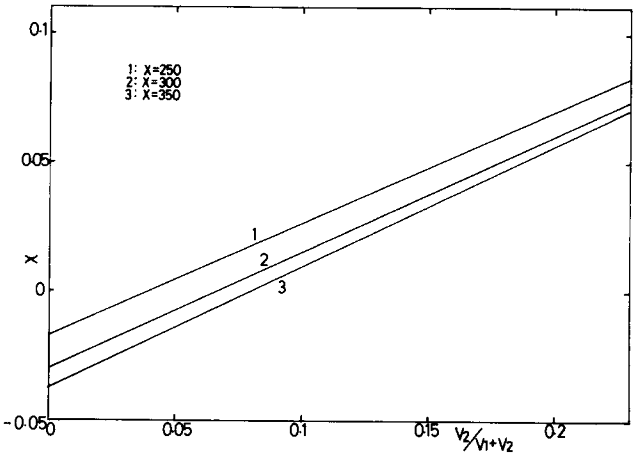

Figure 3 Relation between χ and solvent composition for PPTA in H_2SO_4-H_2O mixture.

marked effect with orientation of rodlike molecules and is quantitatively interpreted on the theoretical background given by Flory.

Polarizing microscope studies were carried out with the isotropic phase(A-point), heterogeneous region, and the anisotropic phase. The isotropic phase placed between crossed polars does not transmit light. In the heterogeneous biphasic region, some areas of the sample transmit light when placed between crossed polars, but others do not. In the anisotropic phase, assemblies of oriented particles were observed just like brocken pieces of glass in the dark isotropic background. These results support the phase diagram obtained in this paper.

References

FLORY,P.J.: Proc. Roy. Soc.(London), A234, 73 (1956)
FLORY,P.J. and W.J.LEONARD,Jr.: J. Am. Chem. Soc., 87, 2102 (1965)
NAKAJIMA,A. et al.: Biopolymers, 6, 973 (1968)
RAI,J.H. and W.G.MILLER: Macromolecules, 5, 45 (1972)
ROBINSON,C., et al.: Disc. Faraday Soc., 25, 29 (1958)
SCHAEFGEN,J.R.: Polymer Preprints, 17, 69 (1976)
WEE,E.L. and W.G.MILLER: J. Phys. Chem., 75, 1446 (1971)

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