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Takashi Inoue,* Shin-ichi Ogata, Masa-aki Kakimoto, and Yoshio Imai
Department of Textile and Polymeric Materials
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan

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Triphase Equilibrium in Aqueous Solutions of the Rodlike Polysaccharide Schizophyllan

It is well established experimentally[1-5] and theoretically[6-9] that a solution of a rodlike polymer separates into two phases, isotropic and anisotropic, above some critical concentration. The solution becomes completely anisotropic above another critical concentration. From the pioneering theories on this phenomenon of Onsager[6] and of Flory,[7] who treated monodisperse solutes, we can draw one common conclusion that the long asymmetric shape of the molecule is of primary importance for the formation of the anisotropic phase; no specific intermolecular interaction needs to be involved.

Subsequently Flory and Abe[8] extended the original Flory theory to polymers polydisperse in molecular weight neglecting polymer–solvent interactions. As the simplest case of polydisperse polymers, Abe and Flory[9] treated mixtures of two monodisperse polymers of different axial ratios, paying particular attention to phase behavior for different combinations of polymer molecular weights. We here quote two important predictions from their theory: (1) Phase separation of such a ternary mixture is accompanied by pronounced fractionation according to molecular weight; the higher molecular weight species is almost excluded from the isotropic phase, especially when the mixture contains the lower molecular weight species in excess. (2) When the difference in axial ratio between the two polymers is large, the binodal contains a relatively wide region in which two anisotropic phases and an isotropic phase coexist at triphase equilibrium. Figure 1 shows a ternary phase diagram calculated according to Abe and Flory for the system containing two polymers with axial ratios x of 18.3 and 223, where ξ stands for the weight fraction of the smaller x component in the polymer mixture and ϕ_i (i = 1, 2) for the volume fraction of polymer component i. The hatched triangle IA_1A_2 indicates the region for the three-phase separation. So far no experimental evidence for these important predictions, especially prediction 2, has been reported in the literature.[10]

In our recent work,[11-14] we have been concerned with a polysaccharide called schizophyllan. This is because schizophyllan can be taken as an appropriate model polymer for investigating solution properties of rodlike polymers. In fact, schizophyllan exists in aqueous solution as a triple helix, forming a rigid cylindrical rod at low molecular weights, at least up to an axial ratio x of 100, and being essentially rodlike up to x of 250.[15,16] We found that an aqueous solution of this polysaccharide becomes birefringent at high concentrations, forming a cholesteric mesophase.[11,12] The critical concentrations for the incipience of the cholesteric phase and disappearance of the isotropic phase decrease with increasing axial ratio.[13] This is essentially the same trend found in polypeptide solutions[2,3] and naturally expected from the rodlike shape of this polysaccharide. However, the molecular weight dependence of the critical concentrations cannot be described precisely by either of the existing theories for rodlike polymers.[13]

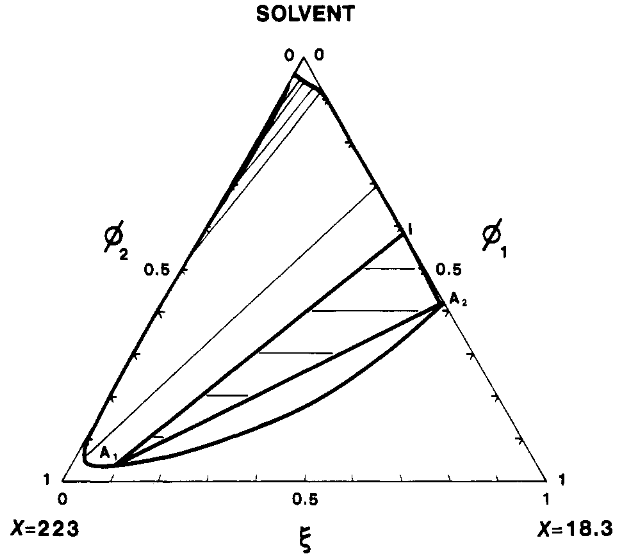

Figure 1. Theoretical phase diagram for an athermal system of two monodisperse polymers with axial ratios x of 18.3 and 223 + a single solvent calculated according to Abe and Flory.[9] The hatched triangle IA_1A_2 shows the region of three-phase separation.

This paper describes a preliminary experiment performed on the same polysaccharide in water to test the prediction by Abe and Flory[9] on the ternary mixture mentioned above.

We used two reasonably well fractionated samples of schizophyllan designated T-3 ($M_w = 80.0 \times 10^4$, $x = 223$) and U-110 ($M_w = 6.58 \times 10^4$, $x = 18.3$); they are characterized by M_z/M_w ratios smaller than 1.3. Appropriate amounts of the two samples and water were mixed in a calibrated stoppered tube (about 1-mL capacity), stirred by a magnetic stirrer bar at room temperature for about 2 days, kept in an air bath thermostated at 25 °C with occasional stirring, and finally kept standing for 1–2 days to attain an equilibrium state. Since no macroscopic phase separation took place within an accessible period of time less than a week, the solution was centrifuged at ca. 2100g to obtain phase separation.[17] The volume ratio of each separated phase was determined from its column height. Then an aliquot of each phase was taken to analyze for the total concentration by differential refractometry and average molecular weight by viscometry. Each phase was also analyzed by gel permeation chromatography. The weight fraction ξ of U-110 in a given polymer mixture was estimated both from the average molecular weight and from the GPC data, yielding essentially the same result.

Figure 2 shows a typical photograph of a phase-separated solution, where three different phases are clearly distinguished. Observation between crossed polars indicated that the uppermost phase was isotropic and the bottom two phases were anisotropic. Usually, the upper two phases were clear but the bottom one was more or less turbid, reflecting its very high viscosity. The results from such phase separation experiments are summarized in a ternary phase diagram in Figure 3. Here a given solution with the composition expressed by a cross separated into two or three phases indicated by circles. The solid curves connecting the circles represent the phase boundaries. As predicted by Abe and Flory (1), the biphase equilibrium accompanies pronounced molecular weight fractionation.

In any case with the three-phase separation, it was not easy to determine the composition of the smallest volume

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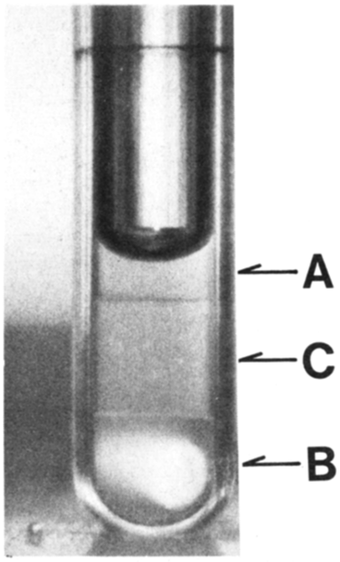

Figure 2. Photograph of coexisting phases at triphase equilibrium. Weight fraction ξ of the lower molecular weight component U-110 in the original polymer mixture, 0.841; total polymer weight fraction, 0.317. A, isotropic; B and C, anisotropic.

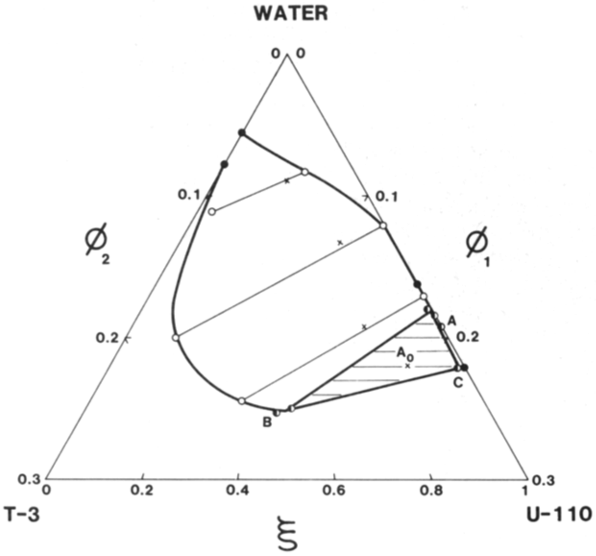

Figure 3. Phase diagram for the system schizophyllan U-110 and T-3 + water: crosses, original mixtures; open circles, solutions separated from biphasic mixtures; half-filled circles, those from triphase mixtures; filled circles, those from binary mixtures. The hatched triangle shows the region of the three-phase separation (A, B, and C are the three conjugated phases separated from A_0 corresponding to the experiment shown in Figure 2). Note that the phase diagram in Figure 1 is for an athermal solution of strictly monodisperse solutes of different axial ratios; the present system is nonathermal[13] and contains two polydisperse solutes.

phase, but those of the rest were determined with reasonable accuracy. Therefore, the corresponding portion of the phase diagram has been constructed on the basis of the latter data. The hatched triangle indicates the region of the three-phase separation, with the compositions of the coexisting phases held approximately constant. For example, one of the mixtures inside this region, A_0, separated into three phases A, B, and C. It should be noted that with respect to composition, the isotropic phase resembles those separated from pure U-110 (lower molecular weight component) solutions, namely, the corresponding binary mixtures. Precisely speaking, there is a slight composition difference among the isotropic solutions separated, which may be ascribed mostly to the polydispersity of the samples used. The concentration of the middle anisotropic phase is rather close to that of the bottom phase, but the average molecular weight of the polymer mixture contained is substantially the same as that in the isotropic phase. On the other hand, the average molecular weight of the polymer mixture in the most concentrated phase is always far greater than that of the others.

This pronounced molecular weight fractionation together with the presence of the three-phase separation is consistent with the predictions (1) and (2) of Abe and Flory mentioned above. However, comparison of Figure 3 with Figure 1 shows that the experimental results are greatly different in quantitative terms from the theoretical predictions; the experimental triphasic region as well as the biphasic region is much narrower than the corresponding theoretical ones. This may be correlated with the disagreement between theory and experiment in the phase behavior of binary systems pointed out previously.[13] Further discussion of this point together with the experimental details will be given shortly in a forthcoming publication.[18]

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Takashi Itou and Akio Teramoto*

Department of Macromolecular Science
Osaka University, Toyonaka, Osaka, 560 Japan

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