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Photoresponsive Polymers. Reversible Solution Viscosity Change of Poly(methyl methacrylate) Having Spirobenzopyran Side Groups

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ABSTRACT: Poly(methyl methacrylate) having spirobenzopyran side groups was synthesized in an attempt to construct a photoresponsive polymer, the conformation of which can be photoregulated. Solution viscosity of the polymer was reduced during irradiation and returned to the initial value after removing the light in benzene. The decrease/recovery cycles of the viscosity can be repeated many times without any noticeable fatigue. Solvent effects, as well as spectroscopic studies including laser photolysis, indicate that the photodecrease in viscosity is caused by intramolecular solvation by the methacrylate ester side groups of the polar merocyanines which are produced by irradiation of the spirobenzopyran side groups.

Photoreceptors for photoregulated biological processes seem to consist of photoisomerizable molecules embedded in protein matrices.[2,3] Upon photoexcitation, the molecules undergo geometrical isomerization, which causes changes of conformation of the proteins or the state of assembly in the membranes, leading to nerve excitation or to control of enzymatic activity. Vision, for example, is based on the cis-trans isomerization of retinal.[2]

Photoregulation of the conformation of synthetic polymers has been tried in several systems.[4-7] The basic condition for photoregulation of polymer conformation is to design polymer systems having chromophores capable of transforming light energy into a change in conformation. This condition can be achieved by incorporating the

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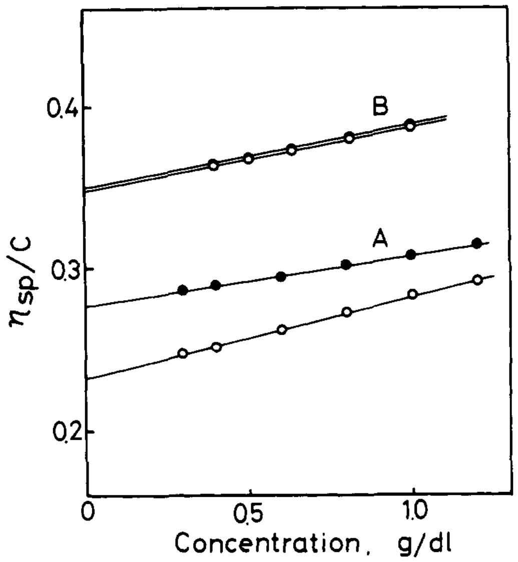
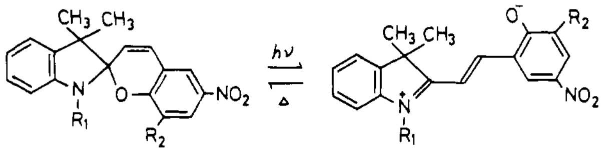


Figure 1. Viscosity of poly(methyl methacrylate) having spirobenzopyran units (13 mol % in base unit) at 30 °C: (A) in benzene (●) in the dark and (○) under irradiation (λ >310 nm); (B) in dichloroethane (●) in the dark and (○) under irradiation (λ >310 nm).

photoisomerizable chromophores into the side or main chains of the polymer by covalent bonds.

We wish to report here photoinduced conformational changes observed in poly(methyl methacrylate) having spirobenzopyran side groups.[8] This paper also aims to elucidate the physicochemical processes involved in the conformational change. Spirobenzopyrans are well known photochromic molecules, which undergo ring opening under ultraviolet irradiation with production of intensely colored merocyanines; the merocyanines can return thermally to the colorless spiropyrans, as follows,[9]



(1)

Important changes associated with the isomerization of spirobenzopyrans to merocyanines are (1) intense coloration and (2) an increase in dipole moment. This study is concerned with the second aspect. A change in dipole moment of the side groups upon photoexcitation is expected to alter the equilibrium conformation of the main chain.

Experimental Section

Polymers having spirobenzopyran as side groups were synthesized by copolymerization of 1,3,3-trimethylindolino-6′-nitro-8′-[(methacryloxy)methyl]spirobenzopyrans (1, R_1 = CH_3; R_2 = $CH_2OCOC(CH_3)=CH_2$)[10] with methyl methacrylate or styrene by radical initiation. The content of spirobenzopyran in the polymers was determined by elemental analysis. The molecular weights of the polymers were estimated by gel-permeation chromatography (GPC) with a Toyo-Soda H801 high-speed liquid chromatograph.

Irradiation was carried out with a 500 W high-pressure mercury lamp, and the wavelength was selected with Toshiba cutoff filters. Conformational change of the polymer was followed by viscosity measurements of the polymer solutions with an Ubbelohde viscometer specially designed for irradiation.

Absorption spectra were measured with a Cary 118 spectrophotometer. Laser photolysis was carried out at the second harmonic of a ruby laser, 347 nm, with a pulse width of 25 ns, as an exciting light source.

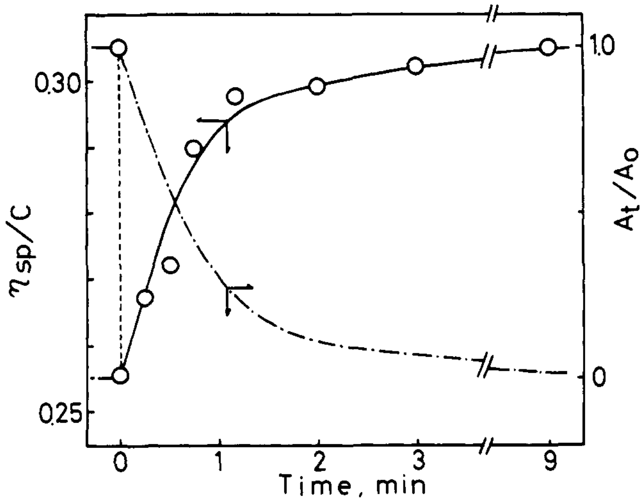


Figure 2. Recovery of the viscosity of poly(methyl methacrylate) having spirobenzopyran units (13 mol % in base unit) and fading of the absorption at 590 nm due to merocyanine formed in benzene at 20 °C in the dark. Concentration of the polymer is 1.0 g/dL.

Results and Discussion

A. Photoviscosity Effect. Figure 1 shows the viscosity of poly(methyl methacrylate) having spirobenzopyran as side groups (13 mol %) in benzene in the dark as well as during irradiation (λ >310 nm). The viscosity in dichloroethane is also shown as an example of the viscosity behavior in polar solvents. In benzene the intrinsic viscosity during irradiation is 17% lower than the viscosity in the dark. The decrease in viscosity implies that light energy is utilized in changing the conformation of the polymer chain. The constancy of viscosity in dichloroethane solution demonstrates that the photoviscosity effect is inherent to the polymer and not caused by thermal effects. It should also be noticed that solvent plays an important role in the process of conformational change.

The viscosity during photoirradiation in benzene returns to the initial value in less than 3 min at 20 °C after the light is removed. Figure 2 shows the recovery of the viscosity along with the fading behavior of the absorption at 590 nm attributed to the merocyanine form. These viscosity values for very short times after removing the light were estimated from the increase of the time of flow by changing the ratio of irradiation time and the dark period within the viscosity measurement time. The decrease/recovery cycles of the viscosity can be repeated many times without any noticeable fatigue. The degree of polymerization estimated by GPC measurement, ca. 100, remained constant even after the decrease/recovery cycle was repeated more than 20 times. Temperature of the solvent affected the amount of decrease of viscosity, as shown in Figure 3. The ratio of the viscosity during irradiation to that in the dark decreased when the temperature was decreased.

The decrease of viscosity depended on the polarity of the solvent as described above. The viscosity change in polar dichloroethane is only 1%, as shown in Figure 1. The effect of the polarity on the ratio of viscosity during irradiation to that in the dark was examined in several solvents and is shown in Table I along with macroscopic and microscopic polarity parameters of the solvents. Among several microscopic polarity parameters, the Dimroth scale E_{T30}[11] was adopted. The parameter is known to correlate well with other polarity parameters such as Z[12] or χ_B[13] values. The viscosity change decreased almost in parallel with increasing microscopic polarity rather than the macroscopic one. In chloroform, for example, the decrease

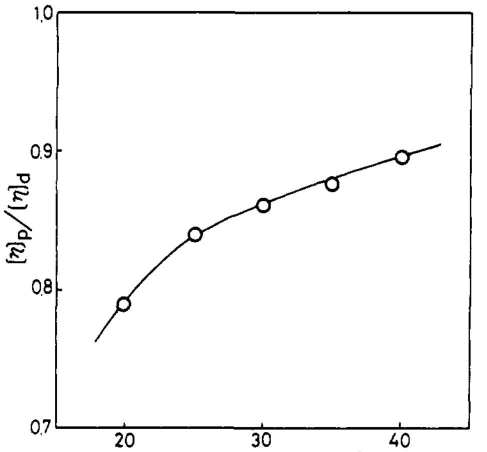


Figure 3. Temperature dependence of the photodecrease of the viscosity of the benzene solution of poly(methyl methacrylate) having spirobenzopyran units (8.1 mol % in the base unit). $[\eta]_p$ and $[\eta]_d$ are viscosities during irradiation (λ >310 nm) and in the dark, respectively.

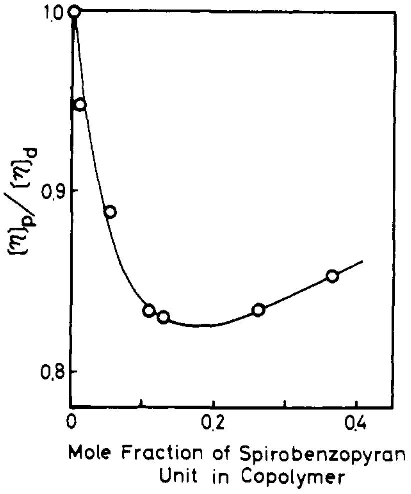


Figure 4. Dependence of the photodecrease of the viscosity of the benzene solution of poly(methyl methacrylate) having spirobenzopyran side groups on the content of the spirobenzopyran unit at 30 °C.

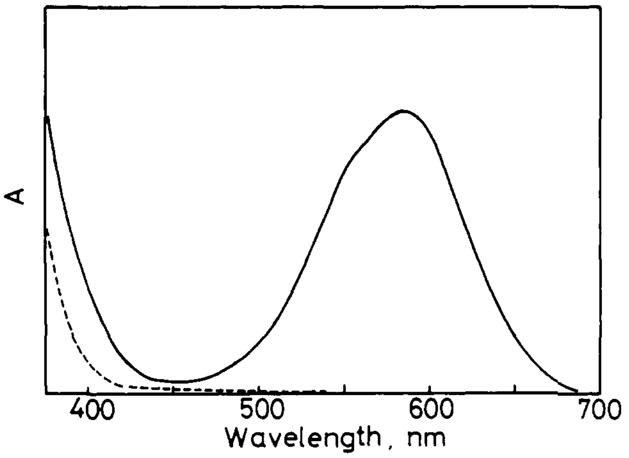


Figure 5. Absorption spectra of merocyanine bonded to poly(methyl methacrylate) in benzene (---) in the dark and (—) after irradiation by ultraviolet light (λ >310 nm).

Table I
Solvent Effect on the Ratio of the Viscosity during Irradiation, $[\eta]_p$, to the Viscosity in the Dark, $[\eta]_d$, at 30 °C

solvent	$[\eta]_p/[\eta]_d$	$\frac{D^a - 1}{2D + 1}$	$E_{T30}{}^b$
benzene	0.83	0.229	34.1
dioxane	0.87	0.223	36.0
THF	0.95	0.405	37.4
ethyl acetate	0.93	0.385	38.1
chloroform	0.97	0.356	39.1
dichloroethane	0.99	(0.420)^c	(41.1)^c

[a] Dielectric constant at 25 °C. [b] E_{T30} value of Dimroth at 25 °C. [c] Values of dichloromethane.

is lower than the decrease in ethyl acetate or in tetrahydrofuran, as expected from the microscopic polarity parameters, though the macroscopic polarity predicts a reverse order.

The solvent effect suggests that the shrinkage of the polymer chain is mainly caused by specific intramolecular solvation of the ester side groups of the poly(methyl methacrylate) chain of the photogenerated polar merocyanines, in competition with solvation by the solvent. The possibility of the decrease being caused by intramolecular dipole–dipole interactions between merocyanine side groups in a polymer chain can be rejected by the following experimental results: (i) the viscosity of benzene solutions of polystyrene having spirobenzopyran side groups does not show any response to the photoirradiation, and (ii) the photodecrease of the viscosity of benzene solutions of poly(methyl methacrylate) having spirobenzopyran side groups is highest at a spirobenzopyran content of 17 mol % in base unit as depicted in Figure 4. The occurrence of the maximum at a rather low content of spirobenzopyran implies that the viscosity change is due to intramolecular dipole–induced dipole interaction in between merocyanines and ester side groups. High content of spirobenzopyran side groups presumably suppresses flexibility of the polymer chain because of bulkiness, giving rise to a small change in viscosity.

B. Spectroscopic Study and Mechanism. In general, as the polarity of the solvent is increased, the visible absorption maximum of the merocyanine form shifts to a shorter wavelength, the extinction coefficient decreases, and the half-width of the band increases.[9] Figure 5 shows the absorption spectrum of the merocyanine bonded to poly(methyl methacrylate) in benzene. It has the absorption maximum at 583 nm. The maximum shifted to shorter wavelength by 17 nm when compared with the maximum of the absorption of a low molecular weight analogue, 1,3,3-trimethylindolino-6′-nitro-8′-(dimethyl carboxymethyl)spirobenzopyran (1, R_1 = CH_3; R_2 = $CH_2OCOCH(CH_3)_2$) in benzene. The blue shift indicates that the microenvironment around the merocyanines bonded to poly(methyl methacrylate) is more polar than that of the low molecular analogue in benzene. The higher polarity is considered to be caused by ester side groups of poly(methyl methacrylate). The intramolecular solvation by the ester side groups of the merocyanines causes the blue shift as well as the shrinkage of the polymer chain, resulting in a decrease of the viscosity.

The solvent effect on the absorption maximum of the merocyanine bonded to poly(methyl methacrylate) was examined to support further the concept of preferential intramolecular solvation.[14] The reciprocal of the maximum wavelength of the merocyanines bonded to the polymer and of the low molecular weight analogue is plotted against the Dimroth E_{T30} value of the solvent in Figure 6. Merocyanine bonded to the polymer does not exhibit noticeable solvatochromism, while a much stronger blue shift is observed in the spectrum of the low molecular weight analogue. The absence of strong solvatochromism in the

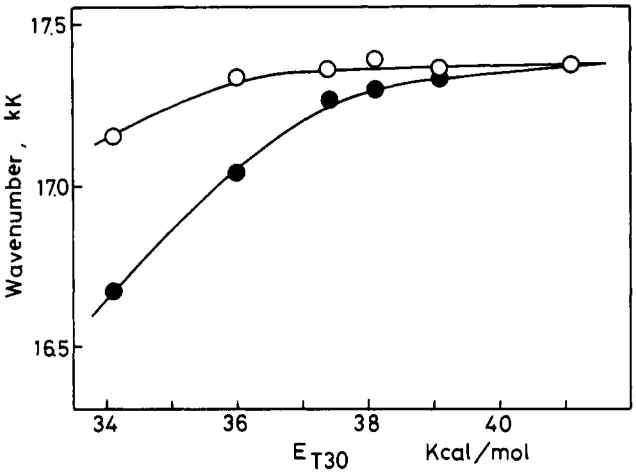


Figure 6. Correlation of absorption maxima (○) of merocyanine bonded to poly(methyl methacrylate) and (●) of 1,3,3-trimethylindolino-6′-nitro-8′-(dimethylcarboxymethyl)spirobenzopyran with the Dimroth polarity parameter E_{T30} (kcal/mol) for a series of solvents.

polymer spectrum implies that the photogenerated merocyanines are preferentially solvated by ester groups of the same polymer chain in a photostationary state and are shielded from the effect of bulk solvent. The free-energy change accompanying the intramolecular solvation of the merocyanines by the polar ester side groups of the polymer in less polar solvents is considered to be the origin of the shrinkage of the polymer chain. The stabilization energy arising from self-solvation can be estimated from the difference of absorption maxima of the polymer and the low molecular weight analogue shown in Figure 6 to be 1.4 kcal/mol in benzene. The decrease in the difference with an increase in the microscopic polarity of solvents correlates well with the photoviscosity effect shown in Table I.

The self-solvation process can be directly followed by measurement of the time-resolved absorption spectra of the merocyanines in the very short time region by laser photolysis. Figure 7 shows the time-resolved absorption spectra of the low molecular weight analogue in benzene and in methyl acetate. The dynamic behavior of the spectra is similar in both solvents except for the peak positions. The absorption around 450 nm appears immediately after the laser pulse and then converts to the absorption around 600 nm. The absorption peak in methyl acetate is 580 nm, while in benzene it is 600 nm. These absorptions increase without changing their shape and maximum positions and reach their highest intensity in 1 μs. The absorption around 600 nm is ascribable to the open merocyanines in the trans form about the double bond. The precursor of the trans merocyanine, with absorption around 450 nm, can be tentatively identified as the cis merocyanine which is produced immediately after bond breaking of the covalent bond between carbon and oxygen atoms. Thus, the absorption change corresponds to the ring opening followed by the configurational change from cis to trans forms.

Time-resolved absorption spectra of spirobenzopyran bonded to poly(methyl methacrylate) in benzene after the laser pulse are shown in Figure 8. The spectra exhibit dynamic behavior similar to that of the low molecular weight analogue, except the peak position of the trans merocyanine shifts to shorter wavelength with time from ca. 595 nm immediately after the pulse to ca. 580 nm in 1 μs. The peak position of the low molecular analogue is constant. The shift of the peak position indicates that the

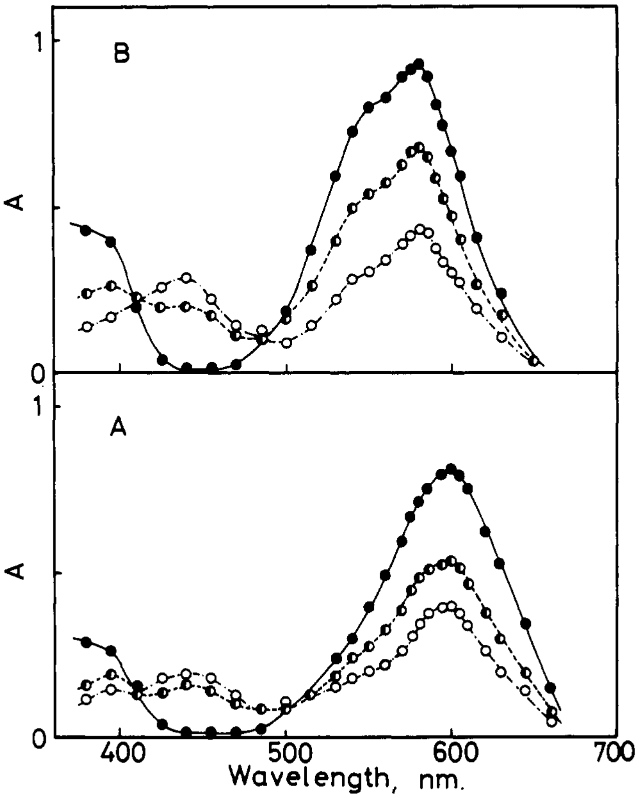


Figure 7. Transient absorption spectra of 1,3,3-trimethylindolino-6′-nitro-8′-(dimethylcarboxymethyl)spirobenzopyran (1, $R_1 = CH_3$; $R_2 = CH_2OCOCH(CH_3)_2$) (A) in benzene and (B) in methyl acetate (-·○-) immediately, (--◐-) 100 ns, and (—●-) 1 μs after the pulse at room temperature.

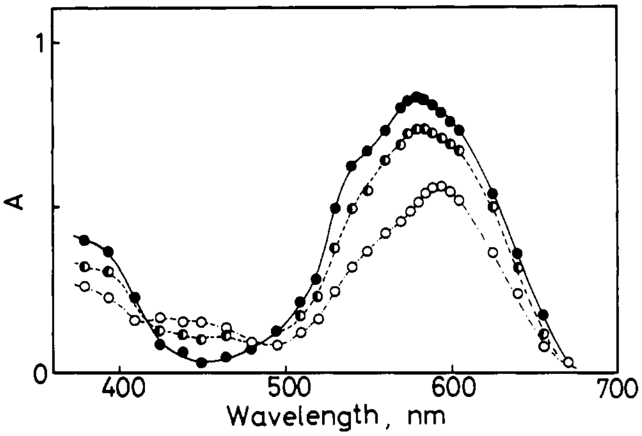


Figure 8. Transient absorption spectra of poly(methyl methacrylate) having spirobenzopyran units (13 mol % in base unit) in benzene (-·○-) immediately, (--◐-) 100 ns, and (—●-) 1 μs after the pulse.

microenvironment around the merocyanine changes from nonpolar to polar within 1 μs after the laser pulse. The polarity around the merocyanine immediately after the pulse is considered to be identical with the polarity around the precursor spirobenzopyran which is presumably surrounded mainly with benzene solvent molecules.

The large dipole moment of the merocyanine, however, is expected to cause changes in the microenvironment, because the dipole is stabilized when surrounded with polar molecules. The polarizable ester side groups of the polymer may come close to the merocyanine, replacing the benzene molecules located nearest to the merocyanine. Finally, the merocyanine is completely surrounded by ester groups, and the micropolarity becomes similar to that of the ester solvents even in benzene. The peak position reflects directly the dynamic process of the replacement of the molecules around the merocyanine and is also considered to correspond to the shrinkage of the polymer conformation. The time necessary for the shrinkage of the polymer chain is less than 1 μs in this system.

The dynamic process of the shift of the peak position followed by laser photolysis as well as a static absorption measurement demonstrates that the decrease of the viscosity during photoirradiation is consistent with the solvation by the ester side groups of the polymer of the strong dipole of the merocyanine molecules. Intermolecular solvation of the polymer chains and association of polymer chains make minor contributions to the effect because the effect was clearly observed even in very dilute solutions. The increase of polymer concentration suppressed the effect.

The time necessary for self-solvation corresponds to the relaxation time of the conformational change of the polymer chain. Although the direct measurement of the conformational change of poly(methyl methacrylate) has not yet been carried out, it is worthwhile to compare the self-solvation time with the relaxation times of helix–coil transitions of poly(α-amino acid)[15] as well as of the compact form–coil transition of the copolymer of maleic acid and styrene.[16] The relaxation time of the helix–coil transition of poly(α-L-glutamic acid) is reported to be less than 10 μs, while the value of the compact form–coil transition of the above vinyl copolymer increases to around 100 ms. The relaxation time reflects the cooperative nature of the transition as well as the flexibility of the polymer system. A factor in favor of the fast transformation of the polymer conformation of poly(methyl methacrylate) in our system is that the conformational change we observed can be reached by relatively small displacement of the polymer segments.

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Micellar Solutions Obtained with Amphiphilic Block Copolymers in the Presence of Water, Oil, and Alcohol. 1. Small Angle Neutron Scattering Structure Investigation in the Case of Poly(2-vinylpyridine-*b*-ethylene oxide) Block Copolymers

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ABSTRACT: Micellar solutions obtained with amphiphilic block copolymers in the presence of water, oil, and alcohol have been studied by the small angle neutron coherent scattering. The investigation of such systems in the Guinier range has shown that the scattering particles are micelles whose radius of gyration, molecular weight, and association number have been determined using the "contrast adjustment method". The examination of the variation of the scattered intensity in the submolecular range has given information on the chain's conformation within micelles. A model taking into account both SANS results and respective affinities of each copolymer block for the solvent medium has been proposed.

It is well known that transparent oil–water systems can be obtained in the presence of surface active materials. These systems have been called microemulsions, micellar emulsions, micellar solutions, or swollen micellar solutions by different authors.[1]

In several previous papers,[2,3] we have shown that amphiphilic block or graft copolymers can lead, in the presence of oil, water, and alcohol, to the formation of transparent phases. These stable four-component systems consist of a dispersed phase containing the copolymer molecules surrounded by a continuous phase. More precisely, the copolymer chains in the dispersed phase present a micellar structure such that the hydrophobic and hydrophilic parts are solvated preferentially by oil and water, respectively. As for the continuous phase, it is constituted of a mixture of the three solvents considered, whose composition corresponds to that of a solvent mixture located on the mutual solubility curve. In this work, the term "micellar solution" will be used for such transparent polymeric systems.

In a preceding paper,[3] we have studied the solubilization of poly(2-vinylpyridine-*b*-ethylene oxide) copolymer molecules by water–toluene–2-propanol mixtures. In particular, we have established the domain of existence of the micellar solutions obtained and determined the composition of the continuous and dispersed phases.