

## Segregation Processes in Segmented Polyurethaneurea Solutions Observed by Fluorescence Depolarization

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**ABSTRACT:** The onset of a segregation process in segmented polyurethaneurea (SPUU) solutions was studied by fluorescence spectroscopy using free fluorescein as a probe. For SPUUs with a given molecular weight and a constant ratio of the hard to soft segments, the time-resolved fluorescence measurements reveal the environmental inhomogeneity on the excited lifetime of fluorescein. It is shown in this work that the critical concentration for the segregation process detected by fluorescence spectroscopy through the transition of the anisotropy ratio of the fluorescein occurs at a concentration lower than that observed by small angle X-ray scattering (SAXS). These experimental results indicate that fluorescence depolarization can be used as an alternative method to investigate the structural transition in SPUU solutions.

**KEY WORDS** Polyurethaneurea / Lifetime / Depolarization / Microdomain /

Segmented polyurethaneurea (SPUU), are thermoplastic block copolymers which have mechanical properties similar to those of conventional elastomers. They belong to a class of (A-B)<sub>n</sub> type multi-block copolymers composed of two chemically dissimilar chain segments called hard and soft segments.<sup>1</sup> The hard segments act as multifunctional junctions, playing a role of both physical crosslinks and reinforcing fillers. These segments are formed by reacting an aromatic diisocyanate with a low molecular weight diol and/or diamine. On the other hand, the soft segments impart the elastomeric properties which are usually the aliphatic polyethers or polyester macroglycols. At low temperature, the low melting soft segments are incompatible with the hard segments of high melting point, leading to a microphase separation.

Similar to multiphase polymeric materials, it is expected that the physical properties of SPUUs critically depend on the phase separation between the hard and soft segment components. In the past decade, a large number of studies were carried out to establish the correlation between the morphology and the mechanical as well as the thermal properties of polyurethanes.<sup>2,3</sup> Therefore, understanding of microphase separation processes is important for the control of the physical properties of these materials. Microphase separation of SPUUs has been studied by a number of experimental techniques including small angle X-ray scattering (SAXS).<sup>4</sup> However, SAXS requires a certain threshold for the contrast in electron density difference to be observable and therefore, it would be interesting to observe these segregation processes by some other alternative methods which are sensitive to the structural transition in solutions of SPUU. Fluorescence depolarization is a promising candidate because transitions in the local structures can be detected through the changes in transport coefficients such as rotational relaxation time. This provides an alternative method to observe the microphase separation from the dynamic point of view. Furthermore, the rotational relaxation time is directly

related to the so-called local viscosity which is an indicator of the local structures of the polymers. Thus, a change in local structures at the segmental level can be detected by measuring the anisotropy ratios of the polymer segments or of a fluorescent probe dispersed in the solution.

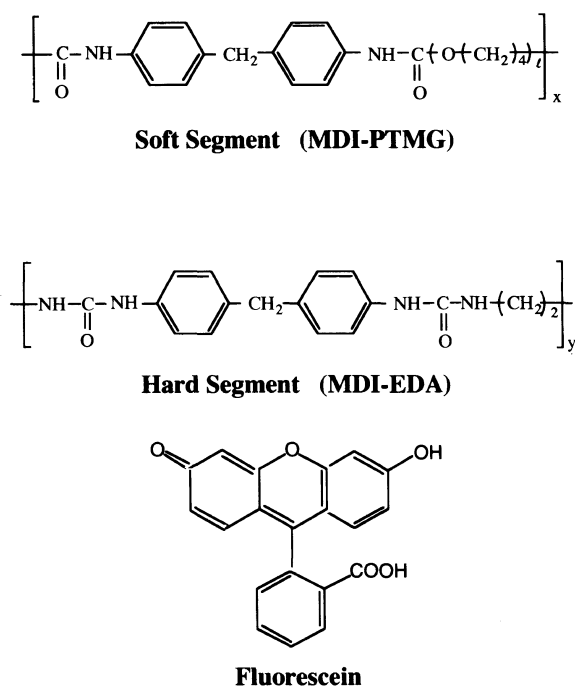
In this paper we experimentally show that fluorescence depolarization is a sensitive and useful technique to follow the segregation behavior of these multiphase polymer solutions. First, the experimental procedure is described in detail. Subsequently, the photophysical properties of the molecular probe fluorescein are investigated in SPUU solutions of various concentrations. The steady-state anisotropy and excited lifetimes of fluorescein in SPUU solutions are determined. From the dependence of the anisotropy ratio on the concentration of the polymers, information on the segregation process in SPUU solutions is extracted. This structural transition is finally discussed by comparing with the experimental data obtained from SAXS.

## EXPERIMENTAL

### *Samples*

Polyurethaneurea (SPUU) used in this work was provided by Asahi Kasei Co. ( $M_n = 55000$ ,  $\alpha = 1.8$ ), where  $\alpha$  is the molar ratio of the hard to the soft segments. The polymer was purified by reprecipitation using *N,N*-dimethylacetamide (DMAc) as good solvent and methanol as non-solvent. Subsequently, it was dried for 24 h *in vacuo* prior to the experiments. Solutions were prepared by using anhydrous DMAc of spectroscopic grade (Wako Chemicals, Japan). Free fluorescein (Fl, Wako) was used as the probe without further purification. The concentration of Fl in all the solutions was kept at  $3.4 \times 10^{-5}$  M to avoid the depolarization caused by concentration quenching which becomes significant at the concentration higher than  $10^{-4}$  M.<sup>5</sup> The pH for all the solutions was 7. In order to minimize the spatial inhomogeneity of samples, only solutions which can be prepared by mechanically stirring were used. All the experiments were performed at 26°C using non-degassed

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**Figure 1.** Chemical structures of the polyurethaneurea and the fluorescent probe used in this study.

**Table I.** Chemical composition of the SPUU

$\alpha$ Value	PTMG/MDI/EDA + DEA
1.8	1.0 / 1.8 / 0.80

solutions. The characteristics and the chemical structures of polyurethaneurea and Fl used in this work are shown in Figure 1 and Table I, respectively.

#### Absorption Measurements

Absorption spectra of Fl in DMAc solutions of SPUU were measured by using a UV-Vis spectrophotometer (Shimadzu, Model UV-160).

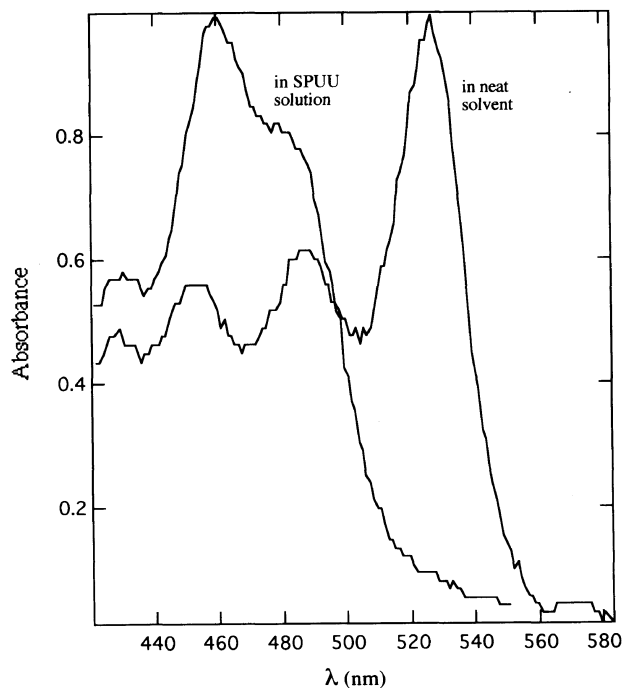
#### Refractive Index Measurements

The change in polarity of solutions with polymer concentration was obtained from the measurement of their refractive index ( $n$ ) using a refractometer (Atago, Model 2T, Japan). All the experiments were performed at 26°C using the D-line (589 nm) of a sodium lamp. The dielectric constant ( $\epsilon$ ) of solutions with different concentrations of SPUU was then calculated by using the relationship;

$$\epsilon = n^2 \quad (1)$$

#### Fluorescence Measurements

The stationary-state anisotropy were obtained from the two polarized components of fluorescence intensity measured on a fluorometer (Shimadzu, Model RF-5300PC) using quartz cuvettes with 1 cm path length. Fl was excited at 492 nm by using a Xe lamp and its fluorescence was detected at 544 nm. Details of the steady-state and time-resolved measurements conducted are as outlined in ref 5, 6, and 7.



**Figure 2.** Normalized absorption spectra of Fl in neat solvent (DMAc) and in a SPUU solution. The dimer peaks which are significant in neat solvent is weakened in the polymer solution.

#### SAXS Measurements

The onset of segregation in these solutions was observed by SAXS. The SAXS measurements were carried out at the Synchrotron Facilities of the National Laboratory for High Energy Physics (Tsukuba, BL-10C line). Briefly, the incident X-ray beam from synchrotron orbital radiation (SOR) with a wavelength of 1.488 Å selected from a 2.5 GeV storage ring was point focused on the sample using a double-flat monochromator combined with a cylindrical mirror. The sample thickness was about 1 mm and was sealed in a stainless steel cell with thin Mylar windows (poly(ethylene terephthalate) (PET), Teijin) each with a thickness of about 5 μm. Detection of the scattered X-ray was done by a one-dimensional position sensitive proportional counter (PSPC, 512 channels), placed at a distance of 1.9 m from the sample holder. Sampling time was maintained at 5 min. Data analysis was preceded by correcting the scattering intensity by subtracting the absorption of the sample and the two Mylar windows from the total intensity. The experimental temperature was controlled with a precision of ±0.5°C and all the curve fitting was carried out using a nonlinear least squares program with regression.

## RESULTS AND DISCUSSION

#### Photophysical Properties of Fluorescein in SPUU Solutions

Since the absorption spectra of the neat SPUU in the long wavelength side disappear above 460 nm, the intrinsic fluorescence of the polymer is negligible under excitation with 492 nm. Figure 2 shows the absorption spectra of Fl in neat DMAc and in DMAc solutions of SPUU. In both the neat solvent and in the polymer solutions, there exist two new peaks on both sides of the

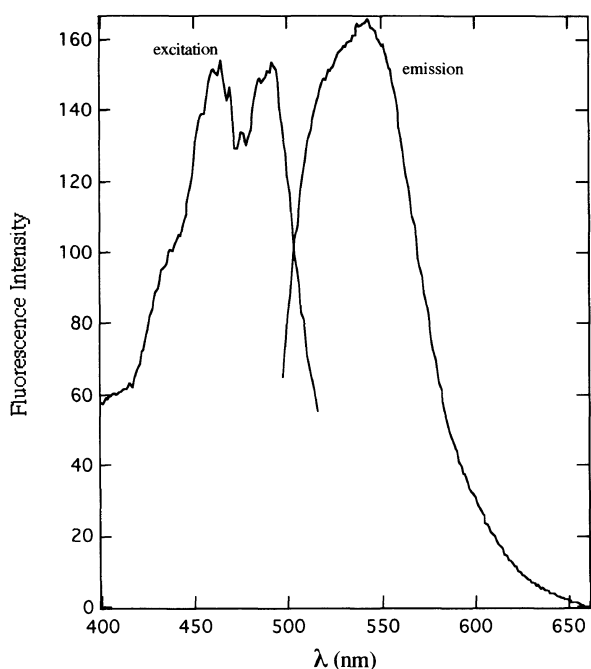


Figure 3. Excitation and emission spectra of FI in a 20 wt% DMAC solution of SPUU.

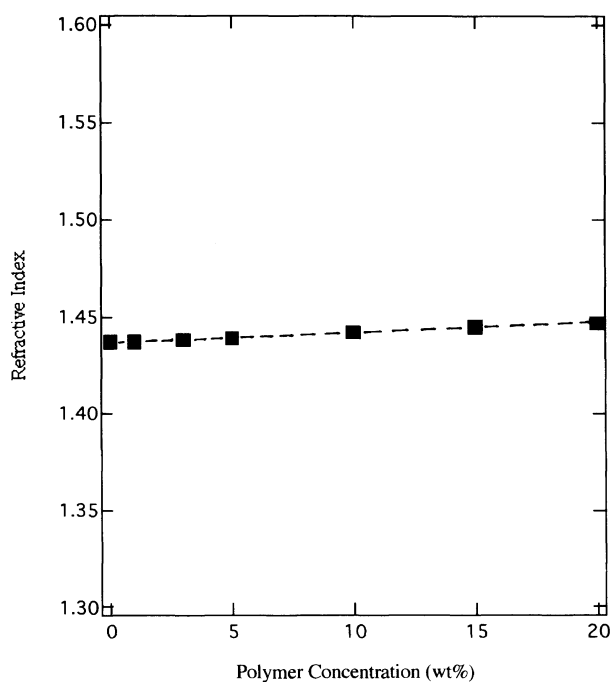


Figure 4. Dependence of the refractive indices of the SPUU polymer solutions on polymer concentration.

monomer peak of FI at 490 nm. These additional peaks have been identified as the absorption spectra of the dimers of types I (overlapping dimer) and II (side-by-side dimer).<sup>8</sup> On the other hand, the absorption peak of the dimer type II on the long wavelength side almost disappears in the presence of SPUU. Since it is well-known that urea weakens the hydrogen bondings,<sup>9,10</sup> the presence of the urea moieties on the SPUU molecules might be responsible for the change in the absorption spectra of FI in the solution. The fluorescence spectra of FI in a 20 wt% of SPUU solution are shown in Figure 3 where the typical emission band of FI

monomer can be seen at 544 nm which remains almost unchanged with the polymer concentration upto 25 wt%. Shown in the same figure are the corresponding excitation spectra monitored at 544 nm where the absorption spectrum of FI in Figure 2 is recovered. On the other hand, as illustrated in Figure 4, the change in the refractive-index of DMAC solutions of polyurethaneurea is less than 1% upto 20 wt% of the polymer. It is worth noting that the emission peak of FI only shifts *ca.* 1 nm toward the shorter wavelength side. Together with this insensitivity of the fluorescence spectra against the SPUU concentration, the result obtained in Figure 4 suggests that the increment of solution polarity with the polymer concentration does not seem to have a significant effect on the photophysical processes of FI.

In order to gain further information on the photophysical processes of FI in DMAC solutions of SPUU, lifetime measurements were carried out under various experimental conditions.

#### Fluorescence Lifetime of Fluorescein in SPUU Solutions

Figures 5(a)–(c) show respectively the fluorescence decay curves of FI in neat solvent, 20 wt% dimethylacetamide solution of SPUU and in a polytetramethylene glycol solution, the soft segment of SPUU. It was found that, in neat solvent, the decay curve is a single exponential function of time with an excited lifetime of *ca.* 3.8 ns. However, in the presence of SPUU, the fluorescence decay curve becomes non-exponential and is well fitted to a sum of two exponential functions of time as illustrated in Figure 5(b):

$$I(t) = F_1 \exp\left(-\frac{t}{\tau_1}\right) + F_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (2)$$

where  $\tau_1$  and  $\tau_2$  are the excited lifetimes of the short- and long-lived components, and  $F_1$  and  $F_2$  are their corresponding fractions. The best fit parameters for the decay curves are provided in Table II.

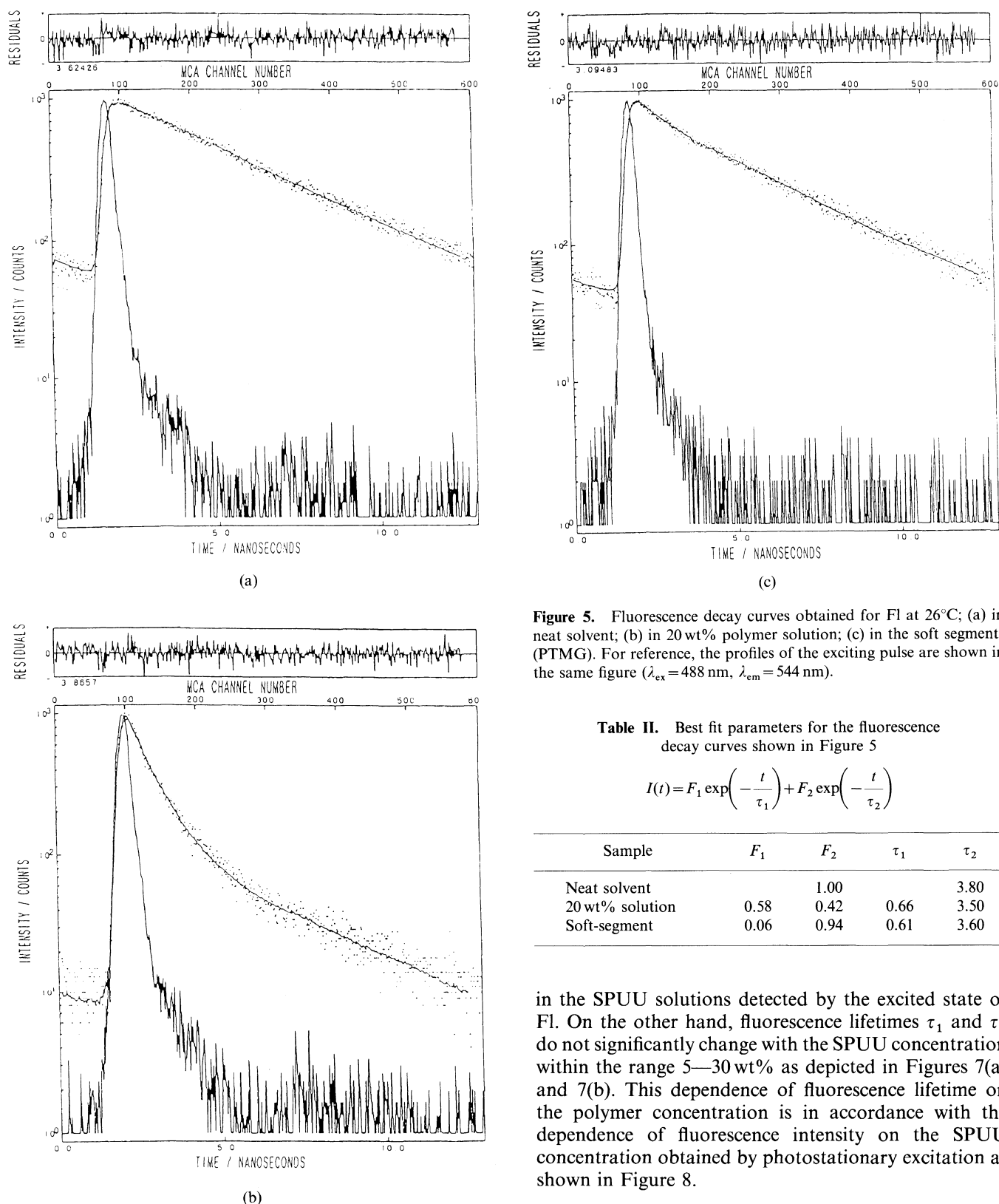
This multiplicity of FI lifetimes was also observed in the neat soft segment, *i.e.*, poly(tetramethylene glycol) (PTMG), measured at the same temperature. From the fact that:

- (1) The solubility of FI in solvent DMAC is better than in the polymer,
- (2) The absorption spectra of FI in the 3 environments: neat DMAC, SPUU solution and neat PTMG exhibit the characteristic absorption of dimers,
- (3) Dimer of FI does not fluoresce<sup>8,11</sup> and the fluorescence of monomer is strongly quenched by the dimer, we conclude that:

– The long-lived component with the lifetime *ca.* 3.7 ns which corresponds to that observed in the neat solvent, can therefore, be attributed to the lifetime of FI in the solvent-rich regions in the solution.

– The short-lived component with the lifetime *ca.* 0.6 ns can thus be attributed to the fluorescence lifetime of FI in the polymer-rich regions where the FI dimers might be formed due to the low solubility of the probe in the polymer-rich region.

As shown in Figure 6, this two-state model is also supported by the change in the two fractions of the long



**Figure 5.** Fluorescence decay curves obtained for FI at 26°C; (a) in neat solvent; (b) in 20 wt% polymer solution; (c) in the soft segments (PTMG). For reference, the profiles of the exciting pulse are shown in the same figure ( $\lambda_{ex} = 488$  nm,  $\lambda_{em} = 544$  nm).

**Table II.** Best fit parameters for the fluorescence decay curves shown in Figure 5

$$I(t) = F_1 \exp\left(-\frac{t}{\tau_1}\right) + F_2 \exp\left(-\frac{t}{\tau_2}\right)$$

Sample	$F_1$	$F_2$	$\tau_1$	$\tau_2$
Neat solvent		1.00		3.80
20 wt% solution	0.58	0.42	0.66	3.50
Soft-segment	0.06	0.94	0.61	3.60

in the SPUU solutions detected by the excited state of FI. On the other hand, fluorescence lifetimes  $\tau_1$  and  $\tau_2$  do not significantly change with the SPUU concentration within the range 5–30 wt% as depicted in Figures 7(a) and 7(b). This dependence of fluorescence lifetime on the polymer concentration is in accordance with the dependence of fluorescence intensity on the SPUU concentration obtained by photostationary excitation as shown in Figure 8.

#### *Rotational Relaxation of Fluorescein in SPUU Solutions and the Aggregation of Polyurethaneurea in DMAc*

FI can be considered as an isotropic rotor, *i.e.*, a pseudo-spherical molecule, with its absorption dipole parallel to the emission dipole. As a result, the rotational diffusion of FI is isotropic and can be expressed by a single relaxation time  $\rho$  which is related to the anisotropy ratio  $r$  by the Perrin equation<sup>12,13</sup>:

and short-lived components of the fluorescence decay upon increasing the polymer concentration. As the SPUU concentration increases, the fraction  $F_2$  of the long-lived component which corresponds to the solvent-rich regions, decreases whereas the fraction  $F_1$  of the short-lived component corresponding to the polymer-rich regions increases. These results provide further evidence for the existence of the two micro-environments

$$\frac{r_0}{r} = 1 + \frac{3\tau}{\rho} \quad (3)$$

where  $r$  is the anisotropy ratio which was experimentally obtained from steady-state measurements.  $r_0$  is the limiting anisotropy which is taken as 0.4 for the case of fluorescein.<sup>14</sup>  $\tau$  and  $\rho$  are respectively FI lifetime and the rotational relaxation time of FI. Equation 3 is obtained by numerical integration of the reorientational correlation function obtained from a three-dimensional rotational diffusion equation over time ranging from zero to infinity. Since the fluorescence lifetimes of the FI are almost unchanged within the range of SPUU concentrations used in this study, the dependence of the steady state anisotropy ratio ( $r$ ) can be used to discuss the structural changes accompanying an increase in polymer concentration.

Figure 9 shows the dependence of the steady-state anisotropy ratio of FI on the concentration of SPUU

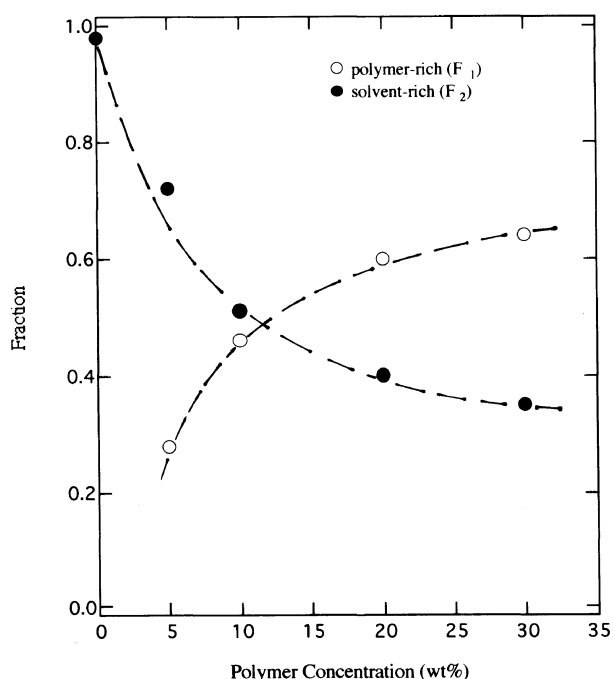


Figure 6. Dependence of the fractional contribution of the 2 components of the decay curve on SPUU concentration.

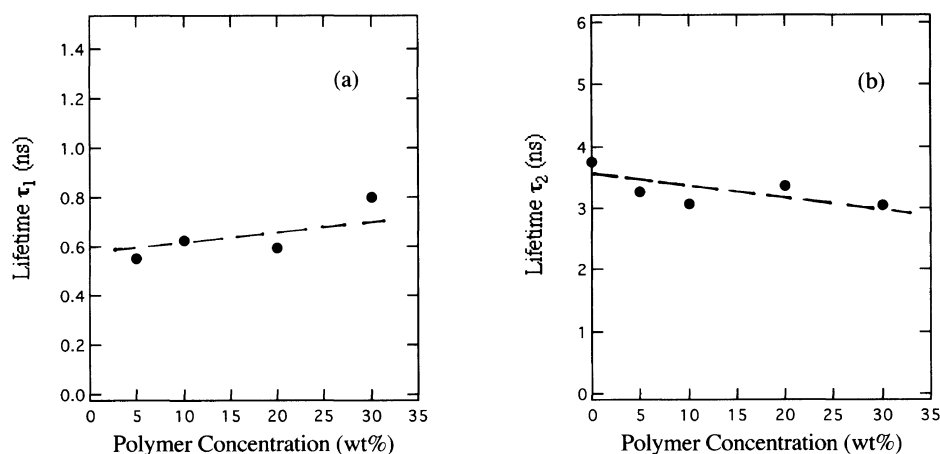
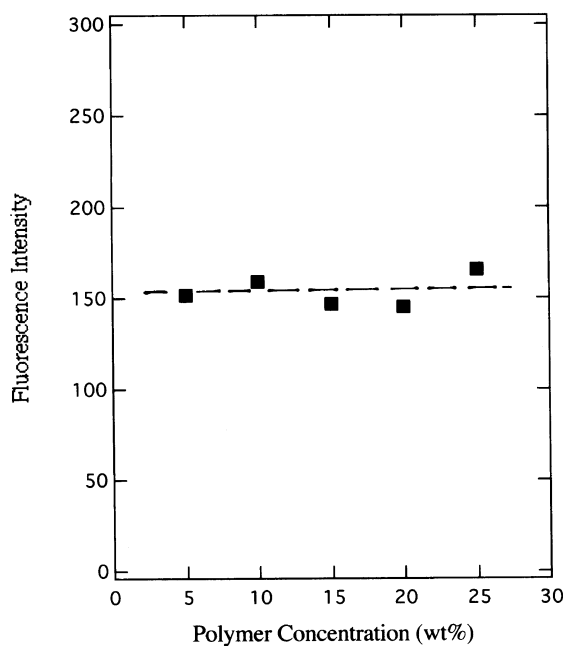


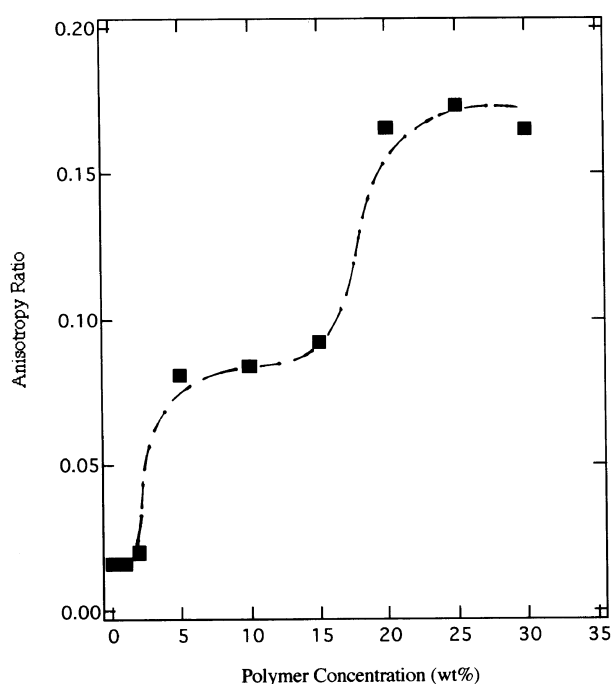
Figure 7. Dependence of the short-lived (a) and long-lived (b) components of FI on SPUU concentration observed at 26°C.

in the range 2–30 wt% obtained by photostationary excitation. Obviously, there exist transitions in the vicinity of 3 and 15 wt% of SPUU obtained at 26°C. The transition in the vicinity of 3 wt% can be attributed to the onset of the concentration at which the anisotropy of fluorescein becomes sensitive to polymer segments in its vicinity, (below this concentration, the anisotropy ratio of fluorescein in SPUU solutions is equivalent to that in neat solvent). The transition in the vicinity of 15 wt%, on the other hand, would reflect some structural changes in the solutions upon increasing the polymer concentration at the experimental temperature. In order to elucidate this transition in the anisotropy ratio of FI, SAXS of the SPUU solutions was undertaken under the same experimental conditions. The microphase separation of the solution can be confirmed from the emergence of a significant peak in the Kratky plots obtained for a 25 wt% SPUU solution as shown in Figure 10 where the product of the scattering intensity  $I(q)$  and the square of the magnitude of the scattering vector  $q^2$  was plotted versus  $q$ . Below this particular concentration, no any characteristic scattering was observed. Similar critical behavior of SAXS has been reported previously for a number of analog SPUUs in DMAc.<sup>4</sup> These SAXS results, indicate that the microphase separation in SPUU solutions takes place in the vicinity of 25 wt% for the SPUU used in this study. This critical concentration is slightly higher than the concentration 15 wt% observed by fluorescence depolarization of FI for the same solutions.

From these experimental results, it can be concluded that fluorescence depolarization of FI is sensitive to the onset of microphase separation in SPUU solutions. The transition in the anisotropy ratio shown in Figure 9 reflects the onset of the microphase separation of the SPUU solutions. This critical concentration is somewhat lower than that detected by SAXS. One of the reasons responsible for the difference in the critical concentrations observed by these two methods would be that fluorescence depolarization provides dynamical information within the excited lifetime of the probe whereas small-angle scattering measurements such as SAXS reveal the static information. For the fluorescence lifetime less than 10 ns, the rotational diffusion of FI is only sensitive with the structural changes at the order of



**Figure 8.** Dependence of the fluorescence intensity of FI on the SPUU concentration.

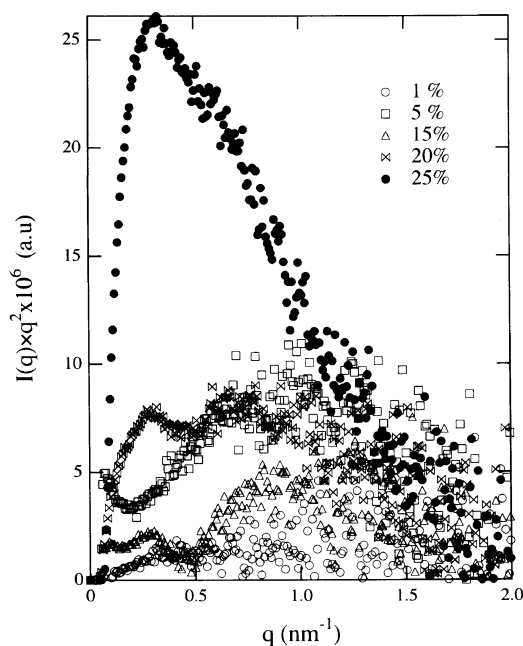


**Figure 9.** Variation of the fluorescence anisotropy ratio of FI with SPUU concentration. The data were taken at 26°C.

100 Å. This scale might be strongly reduced for shorter fluorescence lifetime. Therefore, the onset of microphase separation can be observed earlier by FI than by SAXS where the characteristic length scale corresponding to the maximum in the Kratky plot of Figure 10 is *ca.* 190 Å as estimated from the Bragg condition.

### SUMMARY

Microphase separation process of polyurethaneurea in dimethylacetamide was studied by fluorescence depolarization of FI. The following results were obtained:



**Figure 10.** Kratky plots for SPUU solutions with various concentrations observed at 26°C by small-angle X-ray scattering.

1) The onset of microphase separation in SPUUs can be detected by fluorescence depolarization using molecular probes such as FI.

2) The onset detected by fluorescence depolarization emerges at the polymer concentration lower than that observed by SAXS.

The experimental results described above indicate that fluorescence depolarization can be utilized as a useful technique to study the dynamics of structural transition in SPUU solutions. Experiments using fluorescent probes directly labeled to either hard and/or soft segments of SPUU are in progress and will be reported later.

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