Distinctly Different Conformations of an Amorphous Polymer with Azobenzene Side Chains in Solid and Solution

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A differential scanning calorimetry of a polymethacrylate with azobenzene side chains at the first heating exhibited a scan different from the subsequent ones. Comparison of absorption spectra in an aqueous dispersion, a cast film and dilute solutions of mixtures of dioxane and isopropyl alcohol revealed that the azobenzene forms J-aggregates in polymer solid resulting in the first heating scan whereas the subsequent heating scans corresponds to a polymer conformation with monomeric side chains.

Numerous studies have been made on azobenzene-containing polymers in relation to free volume problems[1] and functionalization including photoinduced optical anisotropy[2] and photoalignment of liquid crystals.[3] Azobenzene chromophores are also attractive as spectral probes for revealing molecular environments, because their absorption spectra are modified markedly by their formation of J- or H-aggregates in self-assembled monolayers[4] and liquid crystalline polymers.[5] In general, an ordinary procedure for studies on photochemical events of azobenzene-containing polymers consists of purifying a polymer dissolved in a good solvent, followed by precipitating in a poor solvent and dissolving the polymer again in a good solvent for film casting. Discussion on isomerization or orientation behavior of azobenzene mixed physically with or covalently attached to polymers is usually made on the basis of a glass transition temperature (Tg). During our revisit to photochemistry of an amorphous polymer with azobenzene side chains, we noticed that a differential scanning calorimetry (DSC) scan at the first heating is different from those of the subsequent ones. This observation motivated us to reinvestigate absorption spectra of the polymer, taking the azobenzene chromophore as a spectral probe into consideration, to reveal the origin of the difference in Tg. We show here that the azobenzene side chains exhibit two distinctly different $\lambda_{\max}$ ascribable to monomeric and J-aggregated states both in solid and dilute solution. The results suggest that a precipitated polymer solid incorporates predominantly J-aggregated azobenzene arranged in a head-to-tail manner whereas the chromophore is monomeric in a cast-film.

Poly{[2-(4-phenylazophenoxy)ethyl methacrylate]} (**1**: Mw $= 3.89 \times 10^5$, Mw/Mn $= 3.8$) is amorphous and was prepared by radical polymerization[6] and purified twice by pouring a dichloromethane solution into a 1:1 (v/v) mixed solvent of methanol and ethyl acetate, followed by drying in vacuo. As shown in Figure 1, DSC measurements demonstrated that a temperature (Tg-1) of an endothermal peak at the first heating shifts to lower one (Tg-2) at the second one, which is not altered by the repetition of heating. The results were reproducible, implying that the solid **1** possesses two conformational states while the state corresponding to Tg-2 is thermodynamically more stable. A film cast from a toluene solution exhibited a peak not at Tg-1, but rather closely at Tg-2 even at the first heating. Though differences in Tg between the first and second runs have been so far reported for some polymers,[7] no detailed discussion has been made on relationship between thermal properties and polymer conformations. Accordingly, in order to obtain a clue concerning the initial state of the precipitated polymer solid, it was milled in an aqueous solution of poly(vinyl alcohol) (PVA) as a dispersion stabilizer to give an aqueous dispersion of particles with an averaged size of 430 nm.[8] Figure 2A shows absorption spectral changes of the aqueous dispersion upon UV irradiation, whereas those in a film is presented in Figure 2B. The results are summarized as follows. First, although the spectral shape of the dispersion is transformed due to light scattering, it is evident that $\lambda_{\max}$ of *E*-azobenzene appears at 382 nm, displaying a considerably red shift when compared with that centered at 342 nm due to a monomeric state in film (Figure 2B). This situation suggests that azobenzene side chains are arranged in a head-to-tail manner to form J-aggregates[5a,5b,6b,6c] in the solid. The nature of the aggregated state is also confirmed by spectral changes during E-to-Z photoisomerization. Whereas isosbestic points appeared in a film

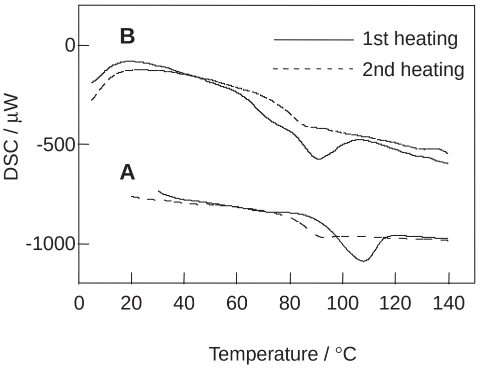

Figure 1. DSC scans of (**A**) precipitated powder and (**B**) a film of **1**.

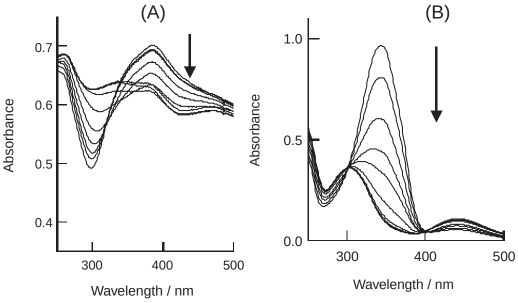

Figure 2. Spectral changes of (A) an aqueous dispersion and (B) a film of the polymer **1** upon exposure to 365 nm light.

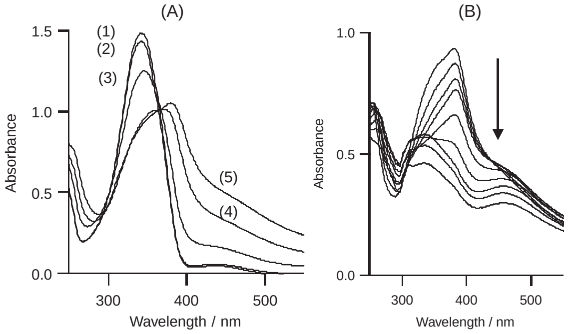

Figure 3. (**A**) Absorption spectra of the polymer **1** in mixed solvents of DOX and IPA in various mixing ratios. DOX/IPA in v/v; (1) 100/0, (2) 80/20, (3) 55/45, (4) 50/50, and 40/60. (**B**) Spectral changes of **1** in a 40/60 mixed solvent of DOX and IPA upon exposure to 365 nm light.

(Figure 2B), the dispersion sample displayed no isosbestic point during UV irradiation. And even after prolonged irradiation, the disappearance of the band at the $\lambda_{\max}$ was incomplete because of suppressing the photoisomerization by the molecular aggregation.

These results indicate that there is a distinct difference in conformations of polymer chains between the reprecipitated solid and a cast film even though the polymer is amorphous. The thermodynamically less stable state of the solid may stem from the drastic alteration from an extended chain conformation of **1** in a good solvent into the other triggered by pouring into a poor solvent. In this context, absorption spectra of **1** were taken in mixed solvents of dioxane (DOX) as a good solvent and isopropyl alcohol (IPA) as a poor solvent in versatile mixing ratios. Typical results are shown in Figure 3A. Whereas $\lambda_{\max}$ is centered at wavelengths not far from 342 nm for solvents of mixing v/v ratios ranging from 100/0 to 60/40, a red shift occurs when volume fractions of IPA exceed 50%. Note here that the red shift of the $\lambda_{\max}$ is accompanied by slight turbidity of solutions as a result of the aggregation of polymer coils. In fact, DLS analysis revealed that particle sizes in dilute solutions are a few hundred nm when fractions of DOX increased, whereas the polymer **1** in DOX exhibited an averaged particle size of 35.2 nm. Accordingly, two events occur when mixing ratios exceed ca. 50/50; the J-aggregation of *E*-azobenzene groups and the aggregation among polymer coils. Furthermore, it was confirmed that UV-induced spectral changes of **1** in a 40/60 (v/v) mixed solvent proceeded in a way quite similar to those of solid particles of **1** dispersed in water, as shown in Figure 3B. No isosbestic point was observed, because the J-aggregate with $\lambda_{\max}$ at 382 nm disappeared reluctantly in solution. Reverse isomerization traced similar spectral changes to regenerate the J-aggregation.

In order to shed more light on the behavior of polymer coils in dilute solutions, the effect of the photoisomerization of azobenzene on the aggregation polymer coils was elucidated, because the isomerization induces polarity changes of the side chains. Whereas no alteration of sizes of polymer coils as particles was detected by DLS before and after the photoisomerization in a dilute DOX solution, the reversible photoinduced transformation of particle sizes was observed when the polymer was dissolved in toluene as a less polar solvent. As shown in Figure 4, the polymer **1** possessed an averaged particle size of 34 nm before UV irradiation, supporting that the polymer is dissolved in the solvent homogeneously. UV irradiation induced a considerable increment of particle sizes, suggesting that the aggregation among polymer coils is accelerated by the formation of *Z*-azobenzene. The particle size of **1** with *Z*-azobenzene side chains was unstable after UV irradiation probably because of the growth of aggregated polymer coils, whereas a size of a polymer coil was essentially not changed at all for the polymer with *E*-azobenzene side chains.

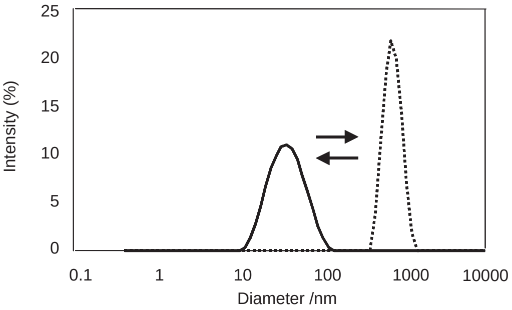

Figure 4. Particle size changes of the polymer **1** in a toluene solution before (full line) and after (dotted line) 365 nm light irradiation.

In conclusion, pouring a solution of **1** in a good solvent into poor solvent results in the formation of J-aggregates of azobenzene residues and the aggregation of polymer coils, whereas the azobenzene side chains are monomeric in a solution of a good solvent and in a film cast from a good solvent. An anomalous peak of a reprecipitated sample at the first heating in DSC is ascribable to Tg of thermodynamically less stable polymer coils with J-aggregated azobenzene side chains. Similar events exhibiting anomalous Tg at the first heating may occur for versatile polymer solids precipitated in a poor solvent when interplays among side chains work so that care should be taken when Tg is discussed.

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8 The polymer **1** (25.23 mg) suspended in 10.0 g of a 5 wt% of PVA (DP = 500) and zirconia beads (0.1 mm Φ) were placed in a zirconia vessel and milled with aid of a planetary mill (Fritsch, P7) at 750 rpm for 1 h to give an aqueous dispersion. Particle size distribution was analyzed by dynamic light scattering (DLS) (Sysmex; Nano-Z).

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