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Electronic Supplementary Information

Unusual Photoresponses in Upper Critical Solution Temperature of Polymer Solutions Mediated by Change in Intermolecular Interaction in an Azo-Doped Liquid Crystalline Solvent

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Appearance of phase separation structure below cloud point temperature

Fig. S1 shows the optical micrographs of the PMMA solution (polymer concentration = 5 wt%) at 90 and 75 °C during a cooling process at the rate of 1 °C/min without photoirradiation. The heterogeneous structure due to UCST-type phase separation could be observed only below the cloud point of ca. 80 °C (Fig. S1A). Above this temperature, no characteristic structures could be observed (Fig. S1B).

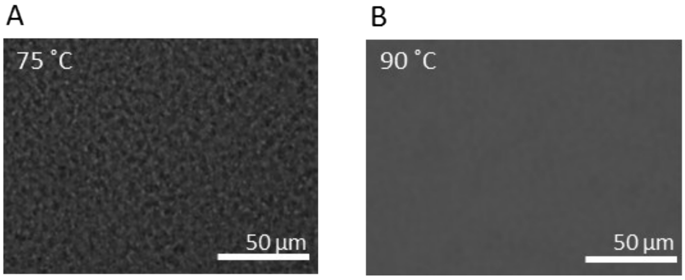

Fig. S1 Optical micrographs of the PMMA solution (polymer concentration = 5 wt%) at (A) 75 °C and (B) 90 °C during cooling.

Determination of χ parameters using Flory-Huggins theory

In the Flory-Huggins theory, the free energy of mixing a polymer and solvent in a unit cell (Δg_m) is expressed as [1, 2]

$$\frac{\Delta_{mix}g}{k_B T} = \frac{\varphi_s}{N_s} ln\varphi_s + \frac{\varphi_p}{N_p} ln\varphi_p + \chi\varphi_s\varphi_p \tag{S-1}$$

where φ_s and φ_p are the volume fractions of the solvent and polymer, and N_s and N_p are the numbers of repeating units in these molecules, respectively. The χ in eq. (S-1) is called the Flory-Huggins interaction parameter, and is given by

$$\chi = \frac{z\Delta w}{k_B T} \tag{S-2}$$

where z is the number of the nearest neighbor sites in the lattice assumed in the theory. Equation (S-1) successfully accounts for the phase separation driven by the thermodynamic instability in polymer solutions. In the case of UCST-type phase separation, the coexistence curve that is the phase boundary between 1-phase and 2-phase states is convex upward. At the critical point where the curve shows a maximum, $(d^2\Delta_{mix}g/d\varphi_p^2) = 0$ and $(d^3\Delta_{mix}g/d\varphi_p^3) = 0$. Thus, the volume fraction of polymer (φ_{pc}) and χ parameter at the critical point (χ_c) are expressed as follows.

$$\varphi_{pc} = \frac{\sqrt{N_s}}{\sqrt{N_s} + \sqrt{N_p}} \tag{S-3}$$

$$\chi_c = \frac{(\sqrt{N_s} + \sqrt{N_p})^2}{2N_s N_p} \tag{S-4}$$

The parameter χ is determined by fitting the experimental data with Equation (S-1), and it is often assumed to be a function of the temperature: $\chi = A + B/T$, where A and B are constants.[2-6] The constant term A is added in order to improve the agreement with experimental data. The weight fractions in the experimental data are converted to volume fractions before the fitting, assuming that the partial molar volumes in the solutions are identical to those of the polymer and solvent alone. The value of N_p is set to 485 on the basis of the number-averaged degree of polymerization of PMMA, and N_s is then determined as 4 according to Equation (S-3). The clouding points in Fig. 2B were fitted using Equation (S-1) while referring to Equation (S-4), yielding $\chi = -0.28 + (154.1\ \mathrm{K})/T$ in the initial state and $\chi = -0.25 + (136.4\ \mathrm{K})/T$ under the UV light irradiation. The coexistence curves in Fig. 2B were then calculated with the obtained χ parameters.

Estimation of change in interaction energies by photoirradiation

The intermolecular interaction in the isotropic azo-doped 7CB can be simply considered as an interaction between dipoles, since the dominant species (7CB) is a polar molecule with a permanent dipole moment along the long axis (4.14 D calculated with MOPAC AM1). We will assume that molecules in the azo-doped 7CB have the same dipole moment as 7CB molecules. In addition, the short-range order between liquid crystalline molecules remains even in an isotropic phase. Therefore, it is considered that the most probable arrangement of neighboring molecules in the isotropic azo-doped solvent would be roughly parallel along the long axis. When the dipoles are aligned antiparallel, their interaction is expressed as $-\mu^2/4\pi\varepsilon_0\varepsilon_r r^3$ using the dipole moment μ, permittivity of vacuum ε_0, relative permittivity of ε_r, and distance between the dipoles of r.[7] For example, at 45 °C where the azo-doped 7CB exhibits an isotropic phase both before and after the photoirradiation, the respective r values were calculated as 0.454 and 0.457 nm from the $q_{\max}$ values shown in Fig. 4B. The attractive interaction energy between two dipoles of $\mu = 4.14$ D could be then roughly estimated as -19.3×10^{-22} and -18.9×10^{-22} J before and after the irradiation, respectively, using the ε_r value of 7CB at 45 °C (9.5).[8] Thus, the difference in the intermolecular interaction energy of the azo-doped 7CB before and after the UV light irradiation is estimated to be approximately 0.4×10^{-22} J. This value indicates that the irradiation increases w_{ss} and reduces Δw at the order of 10^{-23} J in the solutions, according to Equation (2) in the main text. On the other hand, in PMMA solutions, the decrease of Δw can be also estimated from the photoinduced change in the χ parameter as 0.12×10^{-22} J at 45 °C. (The values of Δw calculated from the χ parameters before and after the irradiation were 1.1×10^{-22} and 0.98×10^{-22} J, respectively.) Consequently, the decrease in Δw expected from the photoinduced change in $q_{\max}$ roughly agrees with that estimated from the χ parameters. Therefore, the photoinduced increase in the overall intermolecular distance in theazo-doped 7CB would be large enough to improve the miscibility between PMMA and azo-doped 7CB and cause a significant reduction of UCST.

Isothermal phase transition between 2-phase and 1-phase states in PS solution by light irradiation

Fig. S2 shows optical micrographs of the PS solution (polymer concentration = 5 wt%) at 60 °C. The phase-separated structure denoting a 2-phase state disappeared upon the irradiation with UV light. However, further irradiation of visible light caused the reverse isomerization of the azo-dye, and the phase separation structure was reestablished.

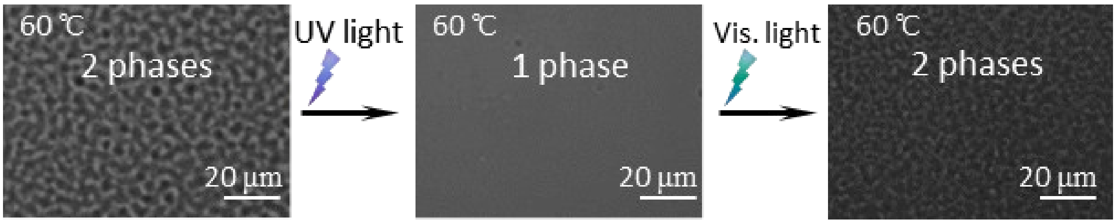

Fig. S2 Optical micrographs of PS solution (polymer concentration = 5 wt%) at 60 °C. The solution was irradiated with UV light (λ = 365 nm, intensity = 150 mW/cm^2), and then irradiated with visible light (λ = 435 nm, intensity = 200 mW/cm^2).

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