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Polymer Phase-Transition Behavior Driven by a Charge-Transfer Interaction**

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Charge-transfer (CT) interactions are intermolecular interactions between π-electron-rich (donor molecules) and π-electron-deficient species (acceptor molecules). The high specificity of CT interactions enables the arrangement between a donor and an acceptor to be controlled, and the resulting CT complex shows a characteristic absorption band in the visible region; this absorption band provides information on the association of supramolecular complexes.[1–4] Therefore, CT interactions are among the most powerful tools for the design of supramolecular complexes, such as organic crystalline materials with superconductivity or conductivity,[1] low-molecular-weight organic gelators,[2] preorganized building blocks for rotaxane,[3] and supramolecular polymers.[4] In many cases, the supramolecular CT complexes can be collapsed readily by heating, since a CT interaction provides a bond of modest strength unless a cavity, such as that of cucurbit[8]uril, is used to stabilize the CT complex.[4c]

Herein, we demonstrate the precise and facile control of the lower critical solution temperature (LCST) of a polymer solution, that is, its phase-transition behavior, by the use of a CT interaction. The well-known phase-transition behavior associated with the LCST of a polymer solution occurs as a result of primitive molecular recognition between the polymer chains and solvent molecules (e.g., H_2O). It has attracted broad interest with respect to the development of stimuli-sensitive materials because the solubility of the polymer chains changes drastically upon heating.[5] However, one of the major drawbacks of this phenomenon is the restriction imposed by the required conditions (temperature, solvent, or pressure); as result, stimuli-sensitive materials are limited to those based on intrinsic LCST polymers, such as poly(*N*-isopropylamide) (PNIPAM)[6] and poly(ethylene glycol) (PEG).[7]

Sophisticated supramolecular control of the LCST has been paid much attention, because such studies can uncover not only a fundamental perspective of the phenomenon but also potential applications in smart materials. As an outstanding example, Ritter and co-workers reported that a polymer bearing adamantyl moieties showed LCST behavior in the presence of methylated β-cyclodextrins (β-CD) in water owing to the dissociation of β-CD from the adamantyl group in the polymer chain upon heating and the subsequent association of adamantyl groups through a hydrophobic interaction.[8] We also demonstrated readily adjustable LCST behavior based on hydrogen bonding between a polymer bearing urea units and an alcohol as an "effector" for polymer solubility.[9] In both cases, the dissociation of supramolecular complexes at an increased temperature triggered a drastic change in solubility of the polymers. These findings inspired us to explore the applicability of other weak intermolecular interactions between polymers and effectors to clarify the molecular design of LCST polymer chains and external effectors. Herein, we demonstrate the first example of LCST behavior based on a CT interaction as the driving force (Figure 1). As the result of the appearance of a CT band in the UV/Vis absorption spectrum, a quantitative evaluation of the relationship between LCST behavior and the formation of supramolecular complexes was possible. Previously, the distinction between polymer–polymer interactions and polymer–effector (solvent) interactions was considered problematic in the common case of LCST behavior driven by hydrogen bonding.

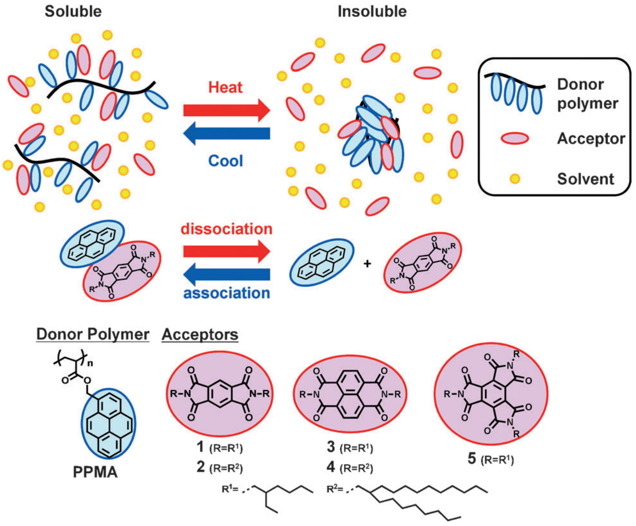

Figure 1. Concept of the LCST behavior of supramolecular complexes as caused by a CT interaction, and structure of the effectors studied and the polymer PPMA, which contains pyrene groups as donor moieties.

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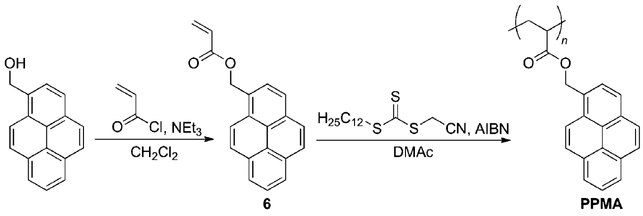
There are two requirements for LCST behavior: a high aggregation ability of the polymer and an interaction that can be cleaved readily upon heating, such as a charge-transfer interaction. Our approach to the design of such a system rested on poly((1-pyrene)methyl acrylate) (PPMA), in which the pyrene units on the polymer side chain induce aggregation through a π–π interaction that results in reduced solubility of the polymer, and the electron-accepting molecules **1**–**5** as effectors to form CT complexes with PPMA. The long alkyl chains in **1**–**5** were expected to change the solubility of PPMA in nonpolar media, and the relatively low binding constant between pyrene and the effectors were expected to give rise to the dissociation of CT complexes upon heating (Figure 1).

PPMA was obtained by the controlled radical polymerization of monomer **6**, which was synthesized by a condensation reaction of acryloyl chloride with 1-pyrenemethanol (Scheme 1). The number-average and weight-average molecular weights of PPMA were determined to be $M_n = 2.2\times10^4$ and $M_w = 4.4\times10^4$, respectively, by size-exclusion chromatography with polystyrene standards. The effectors **1**–**5** with long alkyl chains were synthesized by the corresponding dehydration–condensation reaction (see Scheme S1 in the Supporting Information).



Scheme 1. Synthetic route to PPMA. AIBN = azobisisobutyronitrile, DMAc = *N*,*N*-dimethylacetamide.

First, the solubility of PPMA (10 gL^{-1}) in various organic solvents at room temperature was investigated (see Table S1 in the Supporting Information). In some organic solvents, such as acetonitrile, acetone, ethyl acetate, 1,2-dichloroethane, toluene, and hexane, PPMA was practically insoluble, mainly because of the strong π–π interaction between the large aromatic rings on the polymer chain. Thus, a certain amount of an effector seemed to be necessary to solubilize PPMA by interruption of the π–π interaction between the pyrene moieties on the polymer chain.

As a poor solvent for PPMA, 1,2-dichloroethane was selected for the establishment of LCST behavior. When a solution of **1** (0.14 M) in 1,2-dichloroethane was added to a suspension of PPMA (10 gL^{-1}, [pyrene unit in PPMA] = 0.035 M) in 1,2-dichloroethane at room temperature, the suspension dissolved, and the white turbid mixture became a clear yellow solution. The change in turbidity indicated that PPMA became soluble in 1,2-dichloroethane upon the addition of **1**, and the yellow color was attributed to the charge-transfer absorption band observed at 430 nm in the UV/Vis spectra of PPMA in 1,2-dichloroethane in the presence of **1** (Figure 2a). These results provided evidence that the formation of CT complexes between the effector **1** and the pyrene unit in PPMA caused the dissociation of stacked pyrene groups and the consequent dissolution of PPMA in 1,2-dichloroethane.

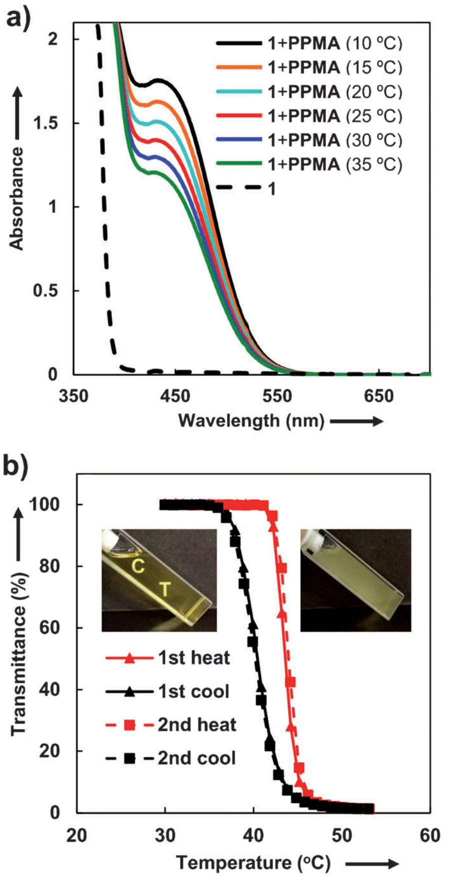


Figure 2. a) UV/Vis spectra of **1** in 1,2-dichloroethane with PPMA at various temperatures (solid lines) and without PPMA (dashed line). b) Transmittance (measured at 800 nm) as a function of temperature for PPMA with **1** in 1,2-dichloroethane (scan rate: 1 °C$\min^{-1}$). For (a) and (b), [**1**] = 0.14 M, [PPMA] = 10 gL^{-1} (0.035 M with respect to the pyrene units in the polymer).

Figure 2b shows the change in the transmittance of PPMA in the presence of **1** in 1,2-dichloroethane at various temperatures. A drastic change in transmittance was observed at 43 °C upon heating. The cloud point was determined as the temperature at which 90 % transmittance was observed. Upon subsequent cooling, transmittance was recovered to 100 %, and PPMA dissolved completely again. Repeated heating–cooling cycles resulted in a repeated change in transmittance; thus, reversible LCST behavior was observed. The absorption of the CT band in the UV/Vis spectrum decreased upon heating to 35 °C (Figure 2a). These results indicated that the dissociation of CT complexes between **1** and PPMA at increasing temperatures led to a decrease in the solubility of PPMA and promoted its aggregation, which resulted in precipitation. The addition of effectors **2**–**5** induced similar LCST behavior of PPMA in 1,2-dichloroethane (see Figures S1–S4 in the Supporting Information). Ethyl acetate and toluene also acted as poor solvents for PPMA and caused LCST behavior under similar conditions (see Figures S5 and S6). On the basis of these findings, we suggest that CT interactions can function as efficient intermolecular interactions to trigger LCST behavior.

We next investigated the dependence of the cloud point on the concentration of the effector. When the effector concentration was increased, the cloud point gradually increased (Figure 3). Higher temperatures were necessary to rupture the CT complexes at high effector concentrations. Furthermore, a decline in the cloud point was observed as the concentration of PPMA was increased (see Figure S7). These observations revealed that the equilibrium between the CT complex (between the pyrene groups of PPMA and the effector) and its dissociated state clearly dominated the thermoresponsivity and LCST behavior of the polymer.

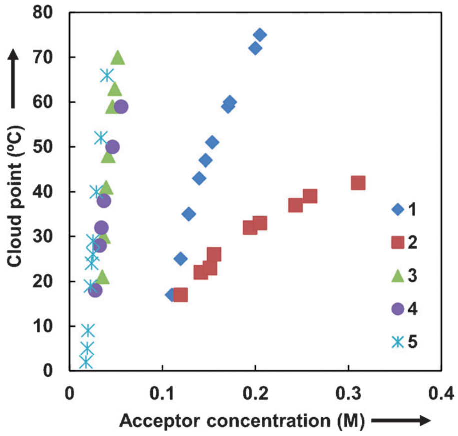


Figure 3. Dependence of the cloud point of PPMA in 1,2-dichloroethane on the concentration of the effector for effectors **1**–**5**. [PPMA] = 10 g L^{-1} (0.035 M with respect to the pyrene units in the polymer).

To elucidate the relationship between the CT interaction and the thermoresponsivity of PPMA in the presence of the effectors, we evaluated the association constants (K_a) between PPMA and effectors **1**–**5** and the thermodynamic parameters for the association (ΔH and ΔS) by the construction of Benesi–Hildebrand and van't Hoff plots, respectively (see Figures S8–S17). The linearity of the Benesi–Hildebrand plots implies the formation of a CT complex with a 1:1 donor–acceptor composition. All calculated association constants were relatively low ($< 10\,\text{M}^{-1}$), and they decreased with an increase in temperature (Table 1; see also Table S2). The low binding ability of the effectors to the pyrene moieties on the PPMA chain probably led to the dissociation of the CT complexes upon heating up to 80 °C. To gain deeper insight into the thermoresponsivity, we evaluated the degree of association (concentration of CT complexes/concentration of the pyrene unit in PPMA) required for the formation of CT complexes under our experimental conditions on the basis of the calculated thermodynamic parameters. For example, under the conditions of a concentration of 0.119 M in **1** and 0.035 M (for pyrene unit) in PPMA, for which a cloud point of 25 °C was found, 8.1 % of the pyrene units in the polymer chain were found to form a CT complex with **1**. In other words, PPMA in 1,2-dichloroethane became soluble through the formation of a CT complex involving **1** and 8.1 % of the pyrene groups in PPMA. Similarly, the other effectors **2**–**5** formed CT complexes around the cloud points with 6–12 % of the pyrene moieties in the polymer chain (Table 1; see also Table S2 and Figure S20).

Table 1: Association constant of complexes between PPMA and effectors **1**–**5** in 1,2-dichloroethane.

Effector	K_a [M^{-1}][a]	Effector concentration [M]	Cloud point [°C][b]	Degree of association [%][c]
1	0.74	0.119	25	8.1
2	0.50	0.155	26	9.1
3	4.23	0.036	30	10.3
4	3.99	0.032	28	9.1
5	4.68	0.024	24	9.1

[a] The association constant (K_a) was determined by the Benesi–Hildebrand method at 25 °C. [b] The cloud point was determined by a transmittance experiment versus temperature at the effector concentration given. [c] The degree of association was defined as the ratio [CT complex]/[PPMA] at the LCST.

The use of effectors **1** and **2**, for which low association constants were found, required a larger effector concentration; thus, a critical degree of association appears to exist for LCST behavior to occur (Table 1). These results showed that the solubility of PPMA and the cloud points depended on the degree of association between PPMA and the effector molecules. The reversible thermoresponsivity can be attributed to the relatively low association constant of pyrene groups and effector molecules in the CT interaction. This study provides the first quantitative description of the relationship between thermoresponsivity and the formation of a supramolecular complex; it had been assumed previously that the hydration number of poly(*N*-isopropylacrylamide) (PNIPAM) governed its thermoresponsivity.[10]

To further control the LCST behavior of the polymer, we added 1,2-dimethoxybenzene as a competitive donor and a good solvent molecule to the ternary mixture of PPMA and **5** in 1,2-dichloroethane. This additive indeed functioned as a competitive donor: the charge–transfer absorption band of monomer **6** and effector **5** in 1,2-dichloroethane decreased upon the addition of 1,2-dimethoxybenzene (see Figure S21). The addition of a small amount of 1,2-dimethoxybenzene induced a drastic decrease in the cloud point, although only 1,2-dimethoxybenzene is able to act as a good solvent for PPMA. This phenomenon can be interpreted as a cononsolvency effect (Figure 4 a); such an effect was also reported for a ternary system consisting of PNIPAM, H_2O, and other solvents.[11] This result indicated that the molar fraction of **5** accessible to PPMA was diminished owing to a competitive CT interaction between 1,2-dimethoxybenzene and **5** (Figure 4 c). For example, the lowest effective concentration of **5** decreased from 0.025 to 0.017 M upon the addition of 1,2-dimethoxybenzene (0.70 M), and the cloud point decreased from 26 to 1 °C. (The effective concentration was calculated on the basis of the association constant of the complex between **5** and 1,2-dimethoxybenzene; see Table S4 and Figures S18 and S19.) The calculated effective concentration agreed well with the observation that a mixture of **5** (0.017 M) and PPMA showed a cloud point of 2 °C (without 1,2-

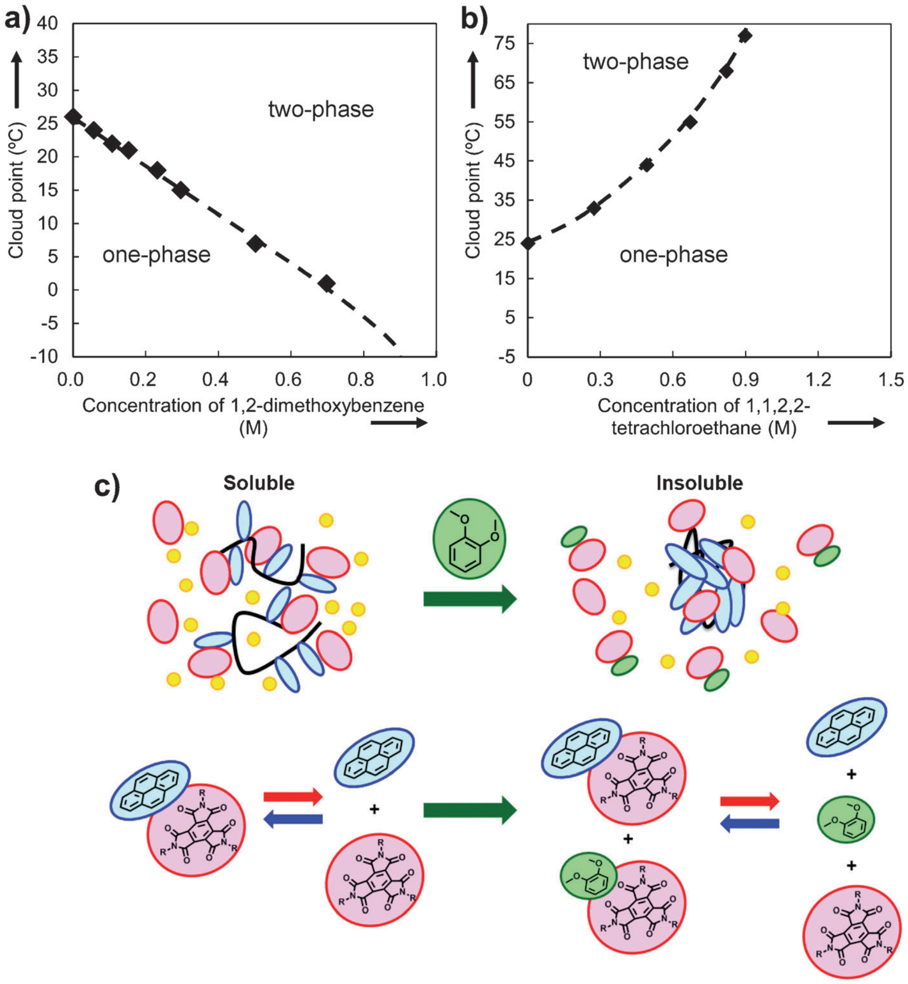


Figure 4. a,b) Cloud point (◆ = LCST) of PPMA in 1,2-dichloroethane in the presence of **5** versus the concentration of 1,2-dimethoxybenzene (a) or 1,1,2,2-tetrachloroethane (b). [PPMA] = 10 g L^{-1} (0.035 M with respect to the pyrene units in the polymer), [**5**] = 0.025 M^{-1}, scan rate = 1 °C min^{-1}. The dashed lines show the assumed boundaries between types of thermoresponsivity. c) Presumed mechanism of the competitive effect.

dimethoxybenzene; Figure S22). The variation in solubility was caused by the competitive association of **5** with pyrene groups in the PPMA or with 1,2-dimethoxybenzene. In other words, the addition of 1,2-dimethoxybenzene diminished the association between PPMA and **5**. Whereas an increase in the amount of 1,2-dimethoxybenzene resulted in a decrease in the cloud point, an elevation of the cloud point was observed upon the addition of 1,1,2,2-tetrachloroethane, which is known to act as a good solvent for PPMA but not to associate with **5** (Figure 4b). From these results, we conclude that the control of the degree of association between the pendant functional groups in the polymer chain and effectors enables the solubility of the polymer to be changed as desired.

In summary, we have demonstrated the controllable LCST behavior of pyrene-containing PPMA in organic solvents with effectors **1**–**5** and clearly showed a relationship between thermosensitivity and a CT interaction. Since the association between pyrene units and effectors plays a crucial role in determining the solubility of PPMA, the LCST behavior of PPMA can be controlled readily by changing the effector concentration or structure and by the further addition of a competitive donor. To our best knowledge, the design of polymers with LCST behavior on the basis of a π–π interaction and a charge-transfer interaction has not been described previously. We conclude that proper selection of the intermolecular interaction between the pendant group of the polymer chain and the effector by employing knowledge based on supramolecular chemistry can govern the solubility and thermosensitivity of the polymer solution. Many other intermolecular interactions should provide a wide range of LCST behavior in various media and at various temperatures. We are now exploring the use of different interactions for the design of smart thermosensitive systems.

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