

Stimuli-responsive polymers: chemical induced reversible phase separation of an aqueous solution of poly(*N*-isopropylacrylamide) with pendent crown ether groups

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(Received 19 October 1992; revised 11 January 1993)

Benzo[18]crown-6 was incorporated into pendent groups of poly(*N*-isopropylacrylamide) to obtain chemical-responsive polymer systems. The aqueous solution of the polymer containing 11.6 mol% pendent benzo[18]crown-6 groups underwent a phase transition from the phase-separated to the homogeneous state at 32°C by the addition of K⁺ and Na⁺. The threshold ion concentration to induce the phase transition depended on the kind of metal ion. A very small amount of K⁺ was sufficient to induce the transition, while 6.0 × 10⁻² M Na⁺ was required. At 37°C only K⁺ could induce the phase transition.

(Keywords: chemical-responsive polymers; phase transition; metal ions)

INTRODUCTION

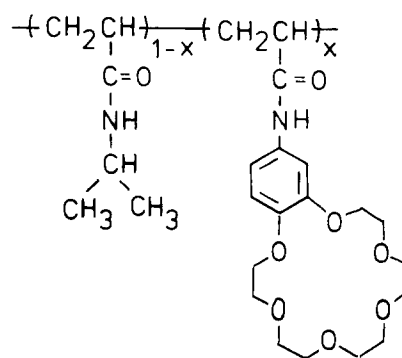
Various polymers which change their conformation reversibly by photoirradiation have been reported¹⁻⁶. The polymers contain pendent or backbone photochromic chromophores, and the molecular property changes of the chromophores, such as geometrical structure or dipole moment changes, control the conformation. The conformation changes are induced in proportion to the number of photons absorbed by the polymers. Thus, when the polymers contain more photochromic chromophores and absorb more photons, the conformation changes more.

Recently, a new concept was introduced to control the conformation efficiently by photoirradiation⁶⁻⁹. This concept utilizes the phase transition of polymer systems, such as a phase separation of polymer solutions or a volume phase transition. The phase transitions are accompanied by conformation changes of polymers¹⁰. Therefore, when the phase transitions are induced by external stimulation, such as photoisomerization of pendent photochromic chromophores, the photoirradiation causes efficient conformation changes. The concept can be applied to construct chemical-responsive polymers, which change conformation reversibly in response to certain chemicals. The polymers may be referred to as chemoresponsive polymers.

Figure 1 shows a general schematic illustration of the chemical-induced phase transition of a polymer system from the state X to the state Y. The polymer contains pendent host groups, such as crown ethers, and their molecular properties, such as hydrophilicity, change

when they bind special guest chemicals. In the absence of the guest chemicals the polymer system changes state at a temperature T_a . We assume that the phase transition temperature will rise to T_b when all host pendent groups contain the guest chemicals in their cavities, as shown in Figure 1a. Then, if the guest chemicals are added to the system at $T(T_a < T < T_b)$, the state will change from Y to X isothermally at the critical (or threshold) concentration of C_c , as shown in Figure 1b. The phase transition temperature progressively shifts to higher temperatures with increasing guest concentration, and reaches the measuring temperature T at C_c . At C_c the state changes sharply from Y to X.

In the present study, we have constructed chemoresponsive polymers, which change conformation in response to certain metal ions, by incorporating benzo[18]crown-6 into the pendent groups of poly(*N*-isopropylacrylamide) (PNIPAM).



PNIPAM is known to undergo a coil-globule transition in aqueous solution upon heating above 31°C¹⁰

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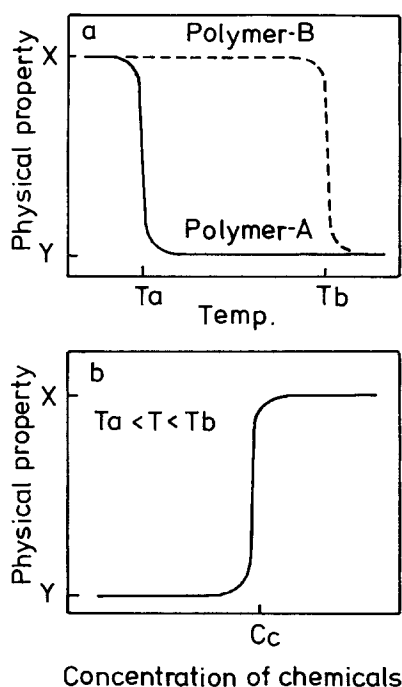


Figure 1 Schematic illustration of chemical-induced phase transition of a polymer system: (a) thermal phase transition from state X to Y in the presence and absence of chemicals; (b) isothermal phase transition by chemicals

and the solution shows phase separation at that temperature^{10–16}. Below 31°C the aqueous solution is transparent, while it becomes turbid above 31°C. The phase transition temperature, T_c , is determined by the balance of hydrophilic and hydrophobic properties of the polymer. When hydrophobic groups are introduced into the pendent groups, T_c decreases, while it increases when polar groups are introduced^{17,18}. The crown ether groups are anticipated to change the hydrophilicity when they capture metal ions. Therefore, the aqueous solution of the polymer with pendent crown ether groups is expected to undergo thermal as well as metal ion-induced, ion-selective discontinuous (or very sharp) phase transition.

EXPERIMENTAL

PNIPAM with pendent benzo[18]crown-6 groups was prepared by radical copolymerization of *N*-isopropylacrylamide with *N*-(benzo[18]crown-6)acrylamide^{19,20} in benzene using azobisisobutyronitrile (AIBN) as initiator at 60°C. The copolymers were purified by reprecipitation with diethylether from acetone solution. The content of the crown monomer units in the copolymers was determined by elemental analysis as well as absorption measurement. The relative molecular weight was estimated with a gel-permeation chromatograph (Shimadzu LC-6A) using polystyrene standard samples. Viscosity measurement was also carried out to evaluate the molecular weight¹⁴.

The phase separation temperature T_c was determined by measuring the transmittance at 500 nm of 1 wt% aqueous polymer solutions on heating at a rate of 0.3°C min⁻¹ in a spectrophotometer (Hitachi U-3410); the temperature at which the transmittance decreased to half the initial value was taken as T_c . The temperature of the solution was controlled with a thermocontroller

(Hitachi SPR-7) and a temperature programmer (Hitachi KPC-6). Thermal hysteresis in the phase separation was observed. The temperature difference between heating and cooling processes was 1–2°C in all systems examined. In the following, the phase transition temperature observed in the heating process was taken as T_c .

RESULTS AND DISCUSSION

Phase separation temperature changes on the addition of metal ions

The most convenient method to detect the phase separation of aqueous polymer solutions is by measuring the transmittance changes. *Figure 2* shows the transmittance changes of an aqueous solution of PNIPAM (1 wt%) containing pendent crown ether groups (11.6 mol%) in the presence and absence of potassium chloride. On heating at a rate of 0.3°C min⁻¹, the solution turned opalescent at 30°C in the absence of the metal ion and the transmittance at 500 nm decreased to half the initial value at 31.5°C. The T_c is similar to that of the aqueous solution of PNIPAM homopolymer. The pendent crown ether groups scarcely affected the phase separation behaviour.

In the presence of K⁺ (KCl, 1.05 × 10⁻¹ M), on the other hand, the aqueous solution remained transparent even when the solution temperature was raised to 31.5°C. The solution began to phase separate at 37°C. T_c was observed at 38.9°C. The T_c value increased by as much as 7.4°C. Such an increase in T_c was not observed for the aqueous solution of PNIPAM homopolymer. The T_c of the homopolymer solution decreased slightly to 30.8°C by the addition of 1.05 × 10⁻¹ M KCl. This decrease is possibly due to the hydrogen bond between the polymer and water being broken by the hydrated ions.

The increase in T_c depended on the metal ions, as shown in *Figure 3*. When potassium chloride was added to the aqueous solution of PNIPAM containing pendent crown ether groups, T_c increased by as much as 7.5°C and then decreased, while the increase was only 1.5°C when sodium chloride was added instead of potassium chloride. The temperature increase was not observed for

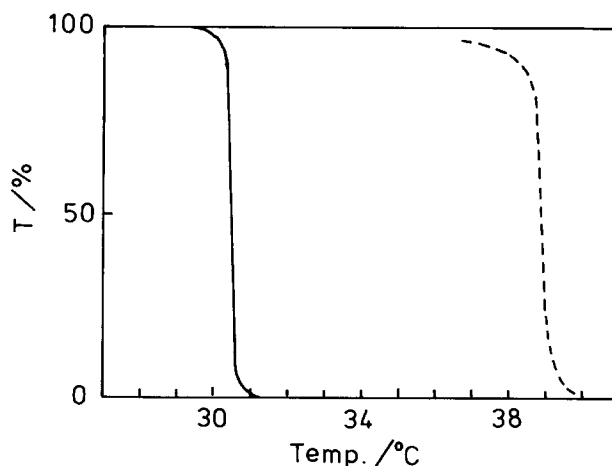


Figure 2 Phase separation of an aqueous solution of PNIPAM containing 11.6 mol% pendent crown ether groups in the absence (—) and presence (---) of 1.05 × 10⁻¹ M potassium chloride. The polymer concentration was 1 wt%. Molecular weight of the copolymer was calculated to be 55000 from g.p.c. measurement using polystyrene standards. Viscosity measurement gave a molecular weight of 3.6 × 10⁵

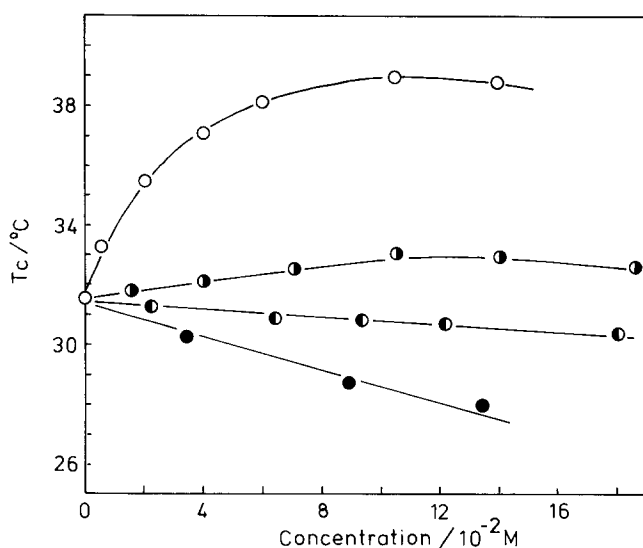


Figure 3 Phase separation temperature changes of the aqueous solution of PNIPAM containing 11.6 mol% pendent crown ether groups by the addition of potassium chloride (O), sodium chloride (●), lithium chloride (●) and caesium chloride (●). The polymer concentration was 1 wt%. The copolymer was the same as in Figure 2

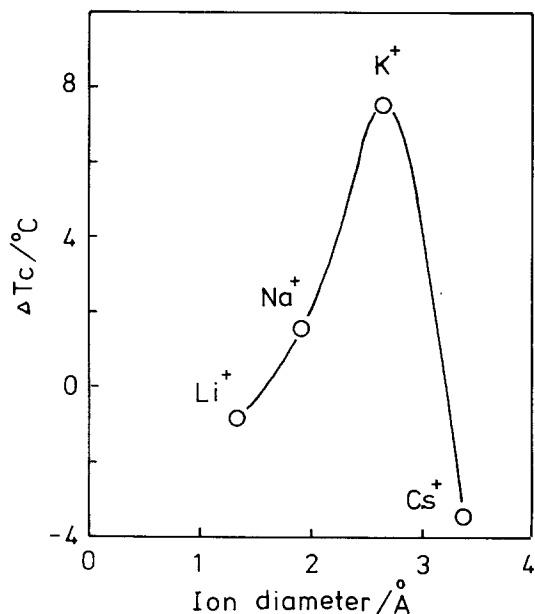


Figure 4 Relation between the diameter of metal ions and the increase or decrease in T_c by the addition of the metal ions (1.2×10^{-1} M)

the solutions containing lithium chloride or caesium chloride. The T_c decreased at high ion concentrations. The decrease is ascribable to breaking of the hydrogen bonds as observed for the homopolymer solution.

Figure 4 shows the relation between the metal ion diameter and the increase in T_c . The binding affinity of a crown ether with metal ions depends on the cavity size^{19,20}. When the cavity size fits the ion diameter, the ion is captured by the crown ether. The cavity size of benzo[18]crown-6 is known to fit the diameter of K^+ . The relative T_c increase shown in Figure 4 correlates well with the binding affinity of benzo[18]crown-6 to metal ions. K^+ , which binds efficiently to pendent benzo[18]crown-6, caused the greatest increase in T_c , while Li^+ , which is scarcely captured by the crown ether groups, could not increase T_c . When K^+ is captured by

the crown ether group, the hydrophilicity of the pendent group increases. This increase enhances the polymer solubility and shifts T_c to a higher temperature.

The value of T_c also depended on the amount of pendent benzo[18]crown-6 groups, as shown in Figure 5. With increasing pendent crown ether groups ΔT_c , which is the temperature difference in the absence and presence of potassium chloride, linearly increased at low ion concentration and then showed saturation at a content of around 12 mol%. When the content of the crown ether groups was low in the pendent groups, the T_c increase was low even at high ion concentration. These results support the mechanism whereby the increase in T_c is due to the property changes of the pendent crown ether groups by binding of metal ions.

The polymer concentration in the aqueous solution scarcely affected T_c . Even when the concentration was increased by as much as 30 times from 0.1 to 3 wt%, T_c remained almost constant. This behaviour agrees with the observation reported for PNIPAM homopolymer¹⁰.

Isothermal phase separation by the addition of metal ions

If T_c increases from T_a to T_b by ion binding of the pendent crown ether groups, the phase transition is induced isothermally at $T(T_a < T < T_b)$ by the addition of metal ions, as shown in Figure 1. When the measuring temperature T is higher than T_b or lower than T_a , the chemical-induced isothermal phase transition is not anticipated.

T_c was raised from 31.5°C to 38.9°C by the addition of potassium chloride, and from 31.5°C to 33.0°C by sodium chloride, as shown in Figure 3. Lithium chloride and caesium chloride did not raise T_c . These results imply that in the temperature range 31.5–33.0°C the phase transition is induced by the addition of both potassium and sodium chlorides, while in the temperature range 33.0–38.9°C only potassium chloride can induce the isothermal phase transition.

Figure 6 shows the phase transition at 32°C and 37°C by the addition of potassium and sodium chlorides. At 32°C both K^+ and Na^+ induce the phase transition from the phase-separated to the homogeneous state. A very small amount of K^+ was sufficient to induce the transition, while 5.0×10^{-2} M was required for Na^+ .

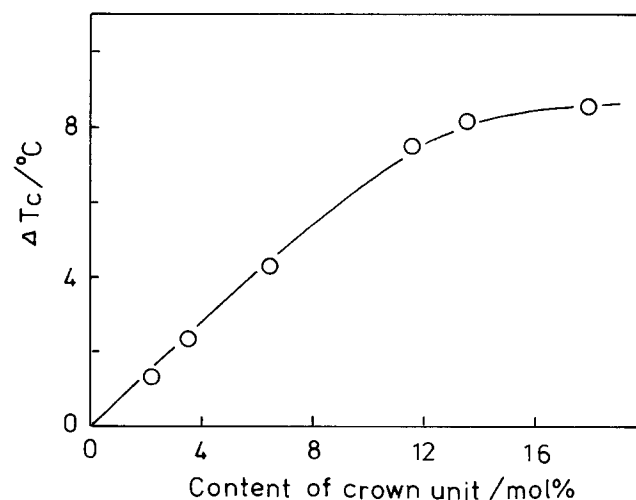


Figure 5 Dependence of ΔT_c , the temperature difference in the absence and presence of potassium chloride, on the content of pendent crown ether groups in the PNIPAM copolymers. The potassium concentration was adjusted to allow T_c to reach the maximum value

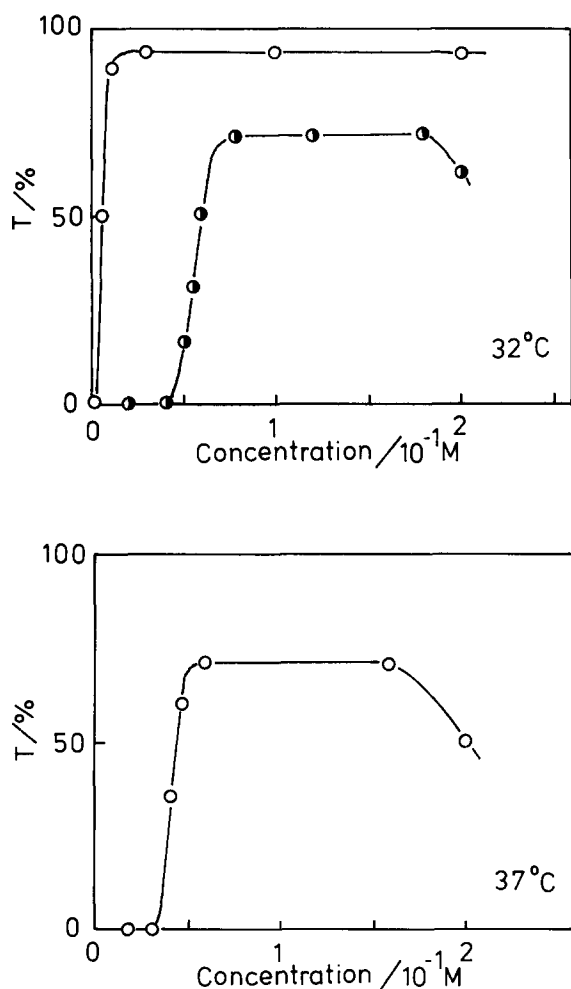


Figure 6 Isothermal phase transition from the phase-separated to the homogeneous state of the aqueous solution of the copolymer containing 11.6 mol% pendent crown ether groups by the addition of potassium and sodium chlorides at 32°C and 37°C. The polymer concentration was 1 wt%. The copolymer was the same as in Figure 2.

Below that concentration, the solution remained phase separated. There existed a critical ion concentration C_c , which can induce the transition, and the concentration depended on the type of ions.

The ion concentration dependence of T_c , shown in Figure 3, can predict the critical concentration C_c . The concentration at which T_c crosses the measuring temperature is C_c . As can be seen from Figure 3, T_c exceeds 32°C on the addition of a very small amount of K^+ , while $5.0 \times 10^{-2} M Na^+$ is required to increase T_c above 32°C. Therefore, the critical K^+ concentration was very low, while the Na^+ concentration was as large as $5.0 \times 10^{-2} M$ at 32°C. Neither Li^+ nor Cs^+ could induce the isothermal phase transition at 32°C. The transmittance decrease by the addition of sodium chloride above $1.8 \times 10^{-2} M$ is due to the decrease of T_c in the higher concentration range, as shown in Figure 3.

When the measuring temperature was raised to 37°C, the phase transition from the phase-separated to the homogeneous state was not observed on the addition of sodium chloride. Only K^+ could induce the transition. As observed at 32°C for Na^+ , a critical ion concentration existed for the transition. K^+ at a concentration $> 4.0 \times 10^{-2} M$ could induce the transition, while an ion concentration below $4.0 \times 10^{-2} M$ did not produce any effect. The isothermal phase transition was induced by specific ions depending on measuring temperature.

Figure 7 shows the reversible phase separation on alternate addition of potassium chloride and low-molecular-weight [18]crown-6 at 37°C. The addition of K^+ caused an increase of transmittance at 500 nm, while [18]crown-6 decreased the transmittance. As described above, K^+ with concentration $> 4.0 \times 10^{-2} M$ induced the phase transition to the homogeneous state and increased the transmittance. This is due to the increase of T_c by the ion binding of pendent groups. The transmittance decrease by subsequent addition of low-molecular-weight [18]crown-6 is considered to be due to the extraction of the metal ion from the pendent groups,

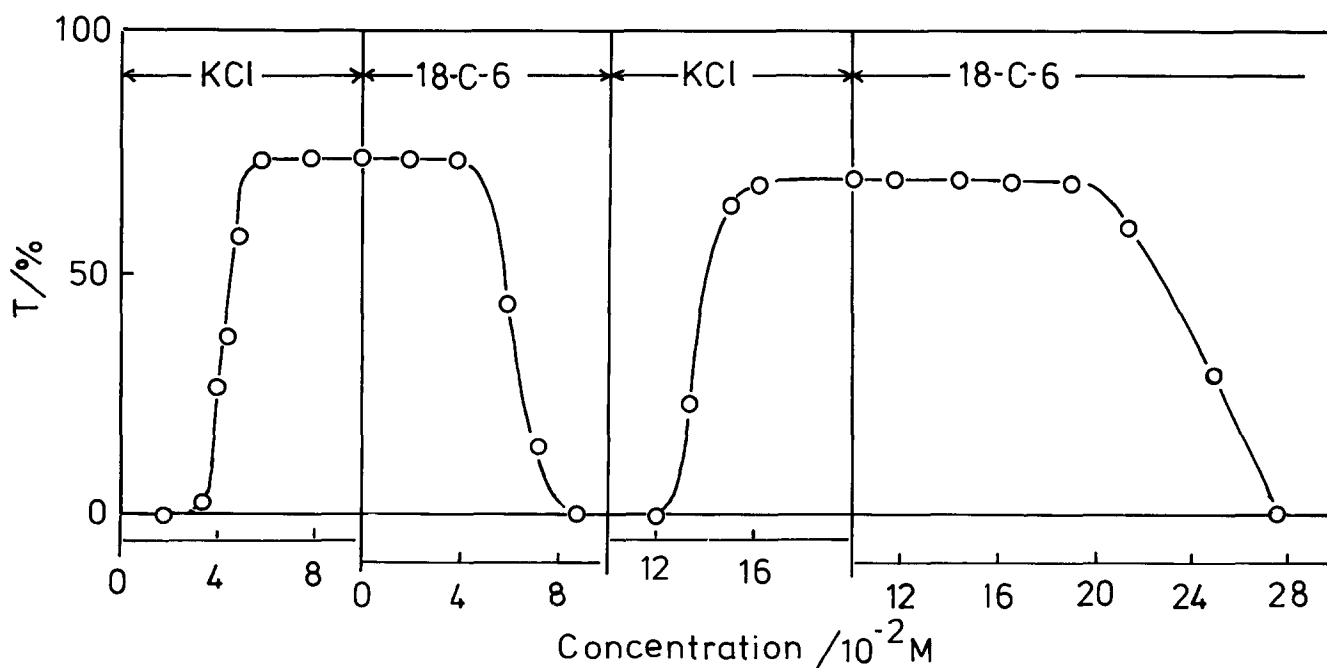


Figure 7 Transmittance changes on alternate addition of potassium chloride and [18]crown-6 to the aqueous solution of the copolymer containing 11.6 mol% pendent crown ether groups at 37°C. The polymer concentration was 1 wt%

because [18]crown-6 has higher binding affinity to K^+ than benzo[18]crown-6^{21,22} and does not influence the phase separation behaviour of PNIPAM homopolymer. The decrease of T_c below 37°C by losing K^+ resulted in phase separation and decrease in transmittance.

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in-Aid for Priority Area Research Program (03205098) from the Ministry of Education, Science, and Culture of Japan.

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