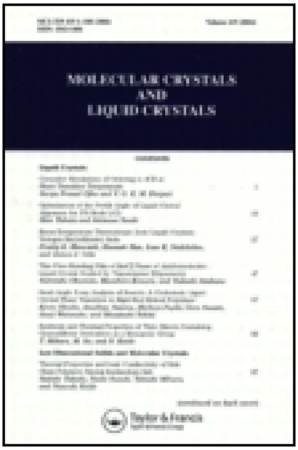

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Fluorescence Probe Studies of Thermosensitive N-Isopropylacrylamide Copolymers in Aqueous Solutions

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Fluorescence Probe Studies of Thermosensitive *N*-Isopropylacrylamide Copolymers in Aqueous Solutions

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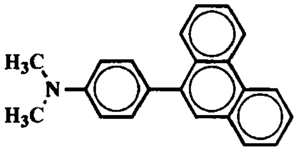
Temperature-induced phase transitions of some *N*-isopropylacrylamide (NIPAM) copolymers in aqueous solutions were studied with 9-(4-*N,N*-dimethylaminophenyl)phenanthrene (DP) as an intramolecular fluorescence probe. Lower critical solution temperature (LCST) of DP-labeled NIPAM copolymers depends on the properties and contents of comonomers incorporated in the NIPAM copolymers, i.e., a hydrophobic comonomer such as methyl methacrylate (MMA) lowers the LCST, and a hydrophilic comonomer such as methacrylic acid (MAA) raises it. The higher contents of comonomers, the bigger changes of the LCST. And the micro-environments of the NIPAM copolymers in aqueous solutions also depend on them. The temperature-induced phase transitions of NIPAM copolymers with *N*-*n*-propylacrylamide (NNPAM), and *N*-isopropylmethacrylamide (NIPMAM) appear to be very sharp as well as that of NIPAM homopolymer aqueous solution and their LCST values are good correlated with their copolymer compositions.

Keywords: an intramolecular fluorescence probe; temperature-induced phase transition; poly(*N*-isopropylacrylamide); *N*-isopropylacrylamide copolymer; lower critical solution temperature; microenvironment

INTRODUCTION

Fluorescence probe techniques have provided insight into micro-environments of organic assemblies such as micelles and polymers. We have studied the photophysical and photochemical properties of vinyl copolymers having pendant aromatic groups such as *N,N*-dimethylaniline (DMA) and phenanthrene (Phen) and their model bichromophoric compounds[1]. In the course of our studies, we have synthesized 9-(4-*N,N*-

dimethylaminophenyl)phenanthrene (DP : DMA-Phen). DP, in which an electron donor DMA and an electron acceptor Phen are linked directly by a Csp_2-Csp_2 single bond, shows an intense and structureless intramolecular charge-transfer (ICT) fluorescence[2]. We have been interested in this compound DP as a new fluorescence probe because of its strong solvatochromism.

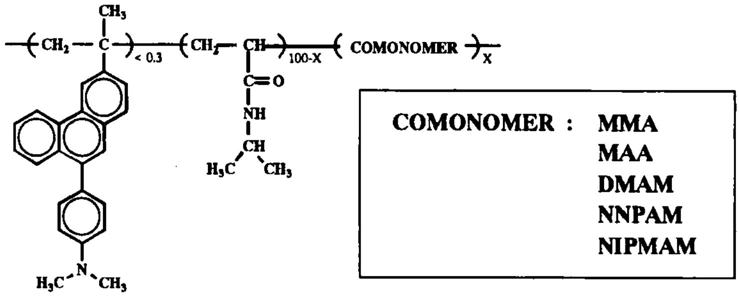


DP (DMA-Phen)

In this paper temperature-induced phase transitions of *N*-isopropylacrylamide (NIPAM) homopolymer and some NIPAM copolymers in aqueous solutions are studied with DP unit as an intramolecular fluorescence probe.

EXPERIMENTAL

DP-labeled thermosensitive NIPAM copolymers with a hydrophobic monomer methyl methacrylate (MMA) and with hydrophilic monomers such as methacrylic acid (MAA), *N,N*-dimethylacrylamide (DMAM), *N-n*-propylacrylamide (NNPAM), and *N*-isopropylmethacrylamide (NIPMAM) were prepared by free radical copolymerization with AIBN as a radical initiator. The NIPAM copolymers have small contents (< 0.3 mol%) of



P(VDP-co-NIPAM-co-COMONOMER)

FIGURE 1 Structure of DP-labeled NIPAM copolymer.

pendant DP units as an intramolecular fluorescence probe. Structure of a DP-labeled NIPAM copolymer is shown in Fig. 1. Fluorescence measurements were performed using 0.01 w/v% aqueous polymer solutions. The temperature of the solution was monitored with a thermocouple immersed in the solution.

RESULTS AND DISCUSSION

NIPAM homopolymer

It is known that PNIPAM exhibits a lower critical solution temperature (LCST) at ca. 32°C in water above which it precipitates upon heating[3,4]. The maximum wavelength (λmax) of ICT emission from DP unit linked to PNIPAM dramatically blue-shifted from 481 nm at 20°C to 434 nm at 37°C. This suggests that DP unit locates in more hydrophilic environments at 20°C and in more hydrophobic environments at 37°C which is above LCST. λmax of the DP fluorescence underwent noticeable change as the solution temperature reached at ca. 32°C and the LCST estimated by fluorescence probe and cloud point methods are in good agreement with each other as shown in Fig. 2. But even below the LCST λmax gradually blue-shifted with increasing solution temperature although there was no change observed

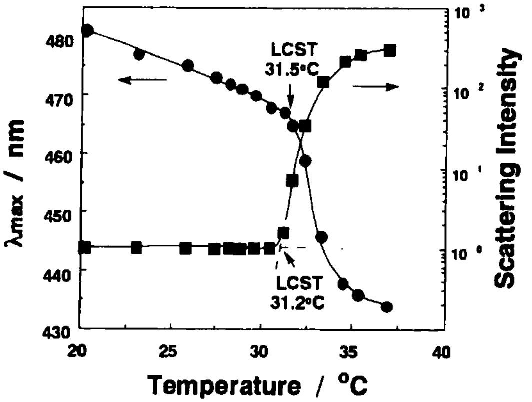


FIGURE 2 Plots of λmax (●) for P(VDP-co-NIPAM) in water as a function of solution temperature and its cloud point curve (■).

in the turbidity of the polymer solution. We interpret these observations in the following manner. In this system the DP probe can follow that the thermally-induced separation of PNIPAM occurs in two steps, i.e., the collapse of individual polymer chains from an expanded coil to a more compact coil and the aggregation of the contracted polymer chains which triggers macroscopic phase transition.

NIPAM copolymers with MMA, MAA, and DMAM

The changes of λmax upon heating aqueous solutions of DP-labeled NIPAM copolymers with MMA, MAA, and DMAM are different from that of NIPAM homopolymer as shown in Fig. 3. LCST of DP-labeled NIPAM copolymers estimated by the fluorescence probe method depends on the properties and contents of comonomers incorporated in the NIPAM copolymers, i.e., a hydrophobic comonomer such as MMA lowers the LCST, and a hydrophilic comonomer such as MAA and DMAM raises it. The higher contents of comonomers, the bigger changes of the LCST.

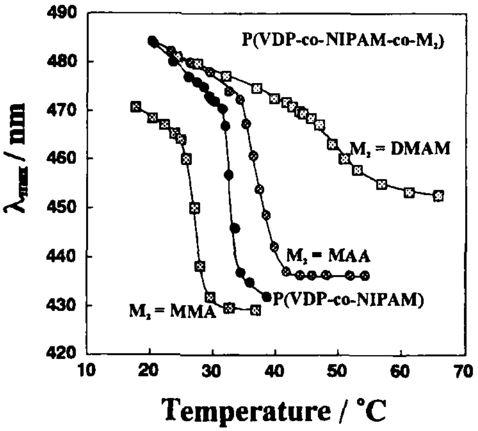


FIGURE 3 The changes of λmax upon heating aqueous solutions of DP-labeled NIPAM copolymers. Contents of comonomer M_2 are 31 mol% (MMA), 15 mol% (MAA), and 32 mol% (DMAM).

The microenvironments of the NIPAM copolymers in aqueous solutions also depend on the properties and contents of comonomers incorporated in the NIPAM copolymers. With a hydrophobic monomer MMA as a comonomer ca. 15 nm of blue-shift of λmax was observed as compared with P(VDP-co-NIPAM) even below its LCST. On the other hand with a hydrophilic monomer MAA or DMAM as a comonomer some red-shift of λmax was observed above its LCST. These results suggest that the incorporation of above mentioned monomers into PNIPAM affects not only its LCST but also its microenvironment.

NIPAM copolymers with NNPAM and NIPMAM

PNNPAM and PNIPMAM are soluble in cold water but separate from aqueous solution upon heating like PNIPAM[5]. Similarly we estimate LCST values of the DP-labeled PNNPAM and PNIPMAM in water to be ca. 19 and 46°C, respectively. NIPAM-NNPAM copolymers exhibit their LCST between 19 - 32°C and NIPAM-NIPMAM copolymers show them between 32 - 46°C. And their temperature-induced phase transitions appear to be very sharp as well as that of NIPAM homopolymer and almost no effects to the microenvironment was observed in these copolymers as shown in Fig.4.

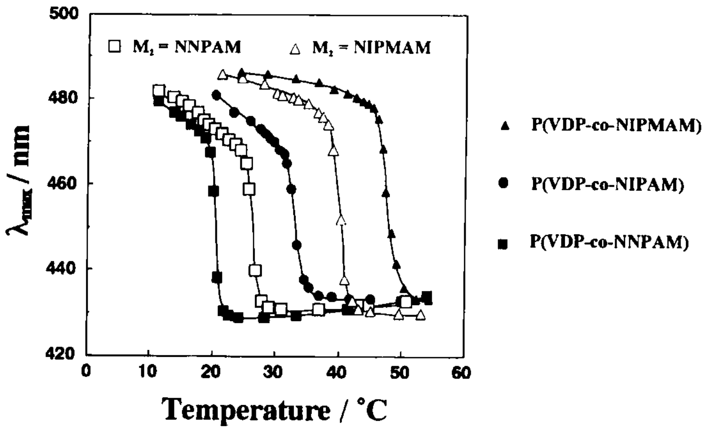
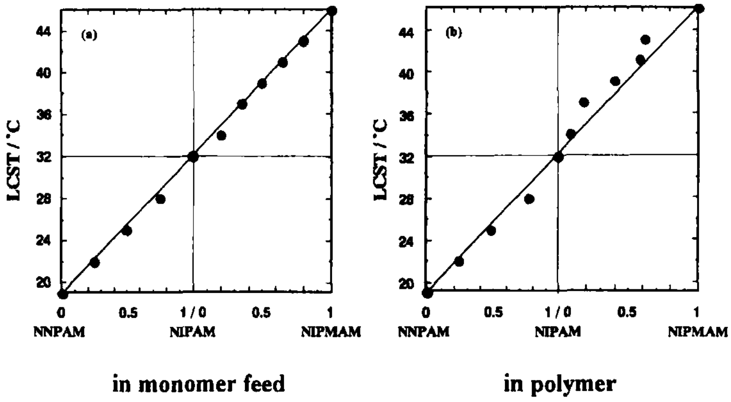


FIGURE 4 The changes of λmax upon heating aqueous solutions of DP-labeled NIPAM copolymers with NNPAM and NIPMAM together with DP-labeled three kinds of homopolymers. Contents of comonomer M_2 are 51 mol% (NNPMA) and 60 mol% (NIPMAM).

And their LCST values estimated by the fluorescence probe method are good correlated with their copolymer compositions as shown in Fig. 5.



in monomer feed

in polymer

FIGURE 5 Plots of LCST of NIPAM copolymers with NNPAM and NIPMAM vs (a) compositions in monomer feed and vs (b) copolymer compositions.

Our results show that the thermoresponsive NIPAN copolymers with similar thermosensitive properties and microenvironments to NIPAM homopolymer in aqueous solution can be obtained by copolymerizing NIPAM with NNPAM and NIPMAM.

Acknowledgments

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