

The synthesis and thermal phase transition behavior of poly(N-isopropylacrylamide)-b-poly(ethylene oxide)

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Received: 12 November 1997/Revised version: 24 December 1997/Accepted: 27 December 1997

Summary

By using the redox reaction between Ce(IV) and terminal $-CH_2OH$ groups of polyethylene oxide(PEO), block copolymers composed of poly(N-isopropylacrylamide)(PNiPAAm) and poly(ethylene oxide) was prepared. The aqueous solution of the block copolymers exhibited thermal phase transition and the phase transition temperature of these block copolymers became higher than the PNiPAAm homopolymer.

Introduction

Poly(N-isopropylacrylamide)(PNiPAAm) has attracted much interest owing to the thermal properties in aqueous solution. PNiPAAm has a lower critical solution temperature (LCST) of about 32 °C in aqueous solution (1,2) and this LCST phenomenon has been extensively investigated due to its practical and theoretical importance (1-10). This LCST phenomenon is associated with the temperature dependence of hydrogen bonding and hydrophobic interaction of this polymer in aqueous solution (11, 12).

Introducing other monomers or polymers changes LCST of PNiPAAm copolymers (13-16). When NiPAAm is copolymerized with a more hydrophilic monomer such as acrylamide(AAm) or acrylic acid(AAc), the LCST increases with contents of hydrophilic units and (3,4,15).

Ce(IV) salts in aqueous acidic solution, either by themselves or in combination with reducing agents, are well known initiator for vinyl polymerization. By using this method radical block copolymerization of vinyl monomers were prepared (17,18). In the present study, the PNiPAAm-PEO block copolymers were synthesized by using this redox initiation and the block copolymers were characterized with nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy. The thermal phase transition of synthesized block copolymer was studied by spectrophotometer.

Experimental

Materials

Polyethylene oxide(PEO); Aldrich($M_w=3400$), was used without further purification. N-isopropylacrylamide(NiPAAm), Kodak, was recrystallized from benzene/hexane mixture and dried in vacuum oven for one day. Ammonium

cerium(IV) nitrate, Aldrich(99+%), was used without further purification. Reagent grade nitric acid was used for preparing 0.1M $\text{Ce}(\text{NO}_3)_6(\text{NH}_4)_2$ stock solution in 200mL 1M nitric acid. The deionized water was used as a solvent for the synthesis.

Measurements

Fourier transform infrared (FT-IR) spectra were obtained using a Bruker EQUINOX 55. The solution of block copolymer in methanol was cast onto the KBr pellet. NMR spectra were obtained at 25°C using a Bruker AM-300 FT-NMR spectrometer in D_2O . The phase transition temperatures of block copolymer in aqueous solution (0.001g/mL) were monitored by measuring the transmittance of a 500-nm light beam through 1-cm sample cells at various temperatures. The transmittance was measured by using Miltonroy company spectronic 20D.

Polymerization

Nitrogen was bubbled for 15 min through each NiPAAm and PEO solution prior to polymerization. In 100mL round bottom flask equipped with magnetic stirring bar, 1g PEO was dissolved in water (10mL). In this solution, 3.3mL 0.1M $\text{Ce}(\text{NO}_3)_6(\text{NH}_4)_2$ stock solution was added and stirred for 5 minutes. And then, NiPAAm monomer dissolved in 12.7mL water was added to above solution. The ratios of added PEO and NiPAAm are described in Table 1. The polymerizations were carried out at 30 °C for 24 hours under the slightly positive pressure of nitrogen. After the reactions were completed, the solutions were diluted by cold water and neutralized with 1M aqueous NaOH solution. To this neutralized solution, same volume of acetone was added and NiPAAm homopolymer was filtered off. The resulting solution was evaporated.

Results and Discussion

The block copolymers, designated as B2, B3, and B4, were not soluble in acetone, so they were washed several times with acetone to eliminate PNiPAAm and PEO homopolymers, monomer, and water. The copolymers were dissolved in methanol and the salts were filtered off. Precipitation was carried out by dropwise copolymer B1 was soluble in acetone, thus another method was used for addition

Table 1: Polymerization condition of block copolymers

sample	NiPAAm ($\times 10^{-3}$ g/mL)	PEO ($\times 10^{-3}$ g/mL)	Yield (g)	the weight % of NiPAAm ^a
PNiPAAm	4	0	0.7	100
B1	2	4	0.2	66
B2	3	4	0.18	80
B3	5	4	0.2	78
B4	8	4	0.22	79

^a Determined by NMR

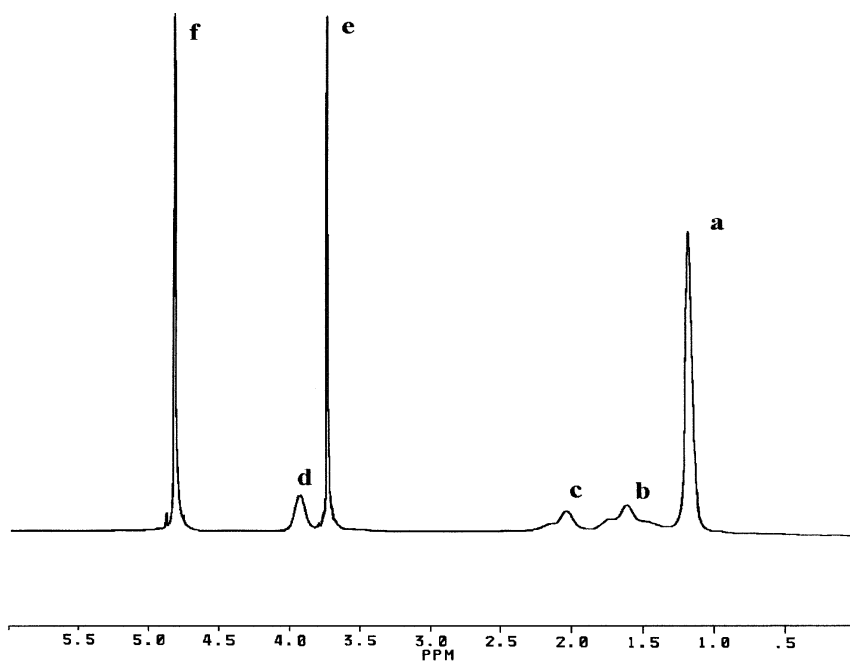


Figure 1. Proton NMR spectrum of block copolymer B4 dissolved in D_2O at room temperature: (a) methyl protons of isopropyl group, (b) methylene protons, (d) methyne proton of N-isopropyl group, (e) methylene protons of the PEO, and (f) HOD in D_2O

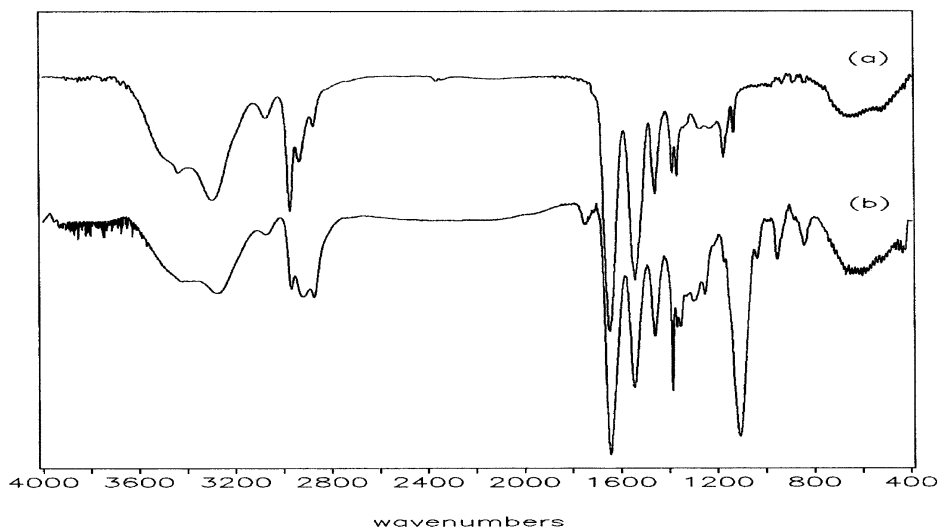


Figure 2. IR spectra of PNiPAAm (a) and block copolymer, B1, (b)

of polymer solution to diethyl ether and vacuum dried. However, the block separation from acetone soluble polymer mixtures. The polymer mixtures were dissolved in acetone and salt was filtered off. Then the filtered solution was refrigerated at -77°C , PEO and block copolymer were precipitated. These precipitated polymer mixtures were isolated by centrifugation and vacuum dried. These polymer mixtures were dissolved in cold water and temperature was raised to 60°C . The block copolymer was then precipitated. The block copolymer was obtained by decantation of this solution. The block copolymer was dissolved in methanol and precipitation was carried out by dropwise addition of polymer solution to diethyl ether. The precipitated block copolymer was filtered and vacuum dried for one day.

Figure 1 shows the NMR spectrum of synthesized block copolymer B4. The signal of methylene proton of PEO appeared at 3.71PPM and that of methyne proton of isopropyl group in PNiPAAm appeared at 3.90PPM. From the integral area ratio of these two peaks, the weight fraction of PNiPAAm in synthesized block copolymer could be calculated. Table 1 represents these PNiPAAm weight percent.

Figure 2 shows FT-IR spectra of PNiPAAm homopolymer and PEO-PNiPAAm block copolymer B1. Figure 2 (a) and (b) show the characteristic absorption peaks of PNiPAAm at 3300, 1649, 1541, 1458, 1385, 1365, 1170, and 1130 cm^{-1} and Figure 2 (b) shows the characteristic peak of PEO appeared at 1107 cm^{-1} .

The thermal phase transition behaviors of the polymers were observed by spectrophotometer. Figure 3 (a) shows the thermal phase transition behaviors of PNiPAAm homopolymer and simple physical mixtures of the PNiPAAm and the PEO (1:1 wt./wt.) in aqueous solution. The phase transitions of two systems occur at 32°C . It is shown that the thermal phase transition of PNiPAAm solution is not affected by PEO homopolymer. Figure 3 (b) shows the thermal transition temperature of the PNiPAAm, B1, B2, B3 and B4. The phase transition temperatures of these block copolymers are higher than that of PNiPAAm

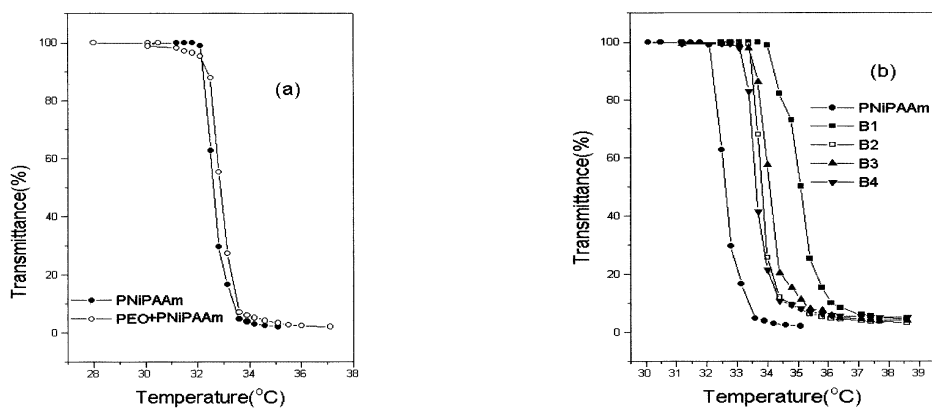


Figure 3. Light transmittance of PNiPAAm, polymer mixtures of PNiPAAm and PEO (a), and block copolymers (b) in aqueous solution

homopolymer and the phase transition temperature increases with PEO content. The block copolymers exhibited LCST at high content of PEO, and thermal phase transition temperatures were 34 ~ 36 °C

LCST of PNiPAAm copolymers incorporated with hydrophilic units has been studied (13-16). The hydrophilic units affect the LCST of these copolymers in aqueous solution. Although these copolymers have an equal amount of same hydrophilic units on the weight basis, thermal phase transition behaviors of another type copolymers are quite different. The LCST of aqueous solution of random copolymers composed of NiPAAm and PAAc dramatically increased with AAC content. The thermal phase transition of random copolymers was occurred in narrow temperature range. The aqueous solution of the random copolymer with more than 7-weight % of AAC no longer shows a phase transition. But the aqueous solution of graft copolymers with backbone PAAc and graft chain PNiPAAm appeared the thermal phase transition at high content of PAAc. The phase transition of graft copolymer solutions started at almost the same temperature as PNiPAAm. and the LCST of a graft copolymer was shown wide temperature range (15).

The aqueous solution of block copolymer composed of PNiPAAm and PEO exhibited steep thermal phase transition curves, as shown in Figure 2. These curves are similar to the shape of thermal phase transition curves of PNiPAAm homopolymers or random copolymers stated above. But the block copolymers show the LCST at high content of PEO. The LCST change of the block copolymers is smaller than the LCST change of random copolymers. The intra- and/or intermolecular hydrophobic interaction of random copolymer is more influenced by small hydrophilic units in PNiPAAm chains. But the block copolymer has a long NiPAAm and PEO sequences so that the hydrophilic units do not influence the hydrophobic interaction between NiPAAm units significantly. Therefore the thermal phase transition temperature of linear block copolymers composed of PNiPAAm and PEO in aqueous solution is slightly increased with PEO content, and thermal phase transition is occurred in narrow temperature range.

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