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Preparation of Poly(N-Msopropylacrylamide)-B-Poly(Ethylene Glycol) and Calorimetric Analysis of Its Aqueous Solution

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PREPARATION OF POLY(*N*-ISOPROPYLACRYLAMIDE)-*b*-POLY(ETHYLENE GLYCOL) AND CALORIMETRIC ANALYSIS OF ITS AQUEOUS SOLUTION

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ABSTRACT

A block copolymer composed of poly(*N*-isopropylacrylamide) [poly(NIPAAm)] and a hydrophilic polymer such as poly(ethylene glycol) was prepared. The aqueous solution of the block copolymer exhibited a calorimetric endothermic peak on heating, similar to a poly(NIPAAm) homopolymer, although in a random copolymer composed of NIPAAm and a hydrophilic monomer such as acrylamide, no endothermic peak was observed. This result suggests that it is the NIPAAm sequence length which dominantly affects the LCST phenomenon of the copolymer rather than the content of hydrophilic comonomers.

INTRODUCTION

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] has a lower critical solution temperature (LCST) of about 32°C in aqueous solution [1]. The LCST phenomenon has attracted much attention and been extensively investigated [1–7] because of its

practical and theoretical importance. When NIPAAm is copolymerized with a more hydrophilic comonomer such as acrylamide (AAM), the LCST increases with AAM content and disappears when the AAM content is higher than the NIPAAm content on a molar basis [4, 5]. The LCST phenomenon is induced by the aggregation caused by hydrophobic interaction between the intramolecular NIPAAm groups [3].

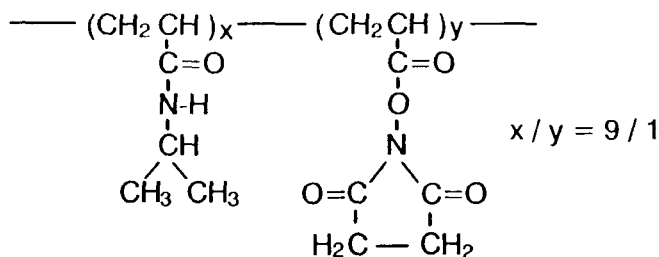
In this paper, in order to study the effect of NIPAAm sequence length on the LCST phenomenon, we synthesized a block copolymer composed of poly-(NIPAAm) and a hydrophilic polymer, poly(ethylene glycol) (PEG).

EXPERIMENTAL

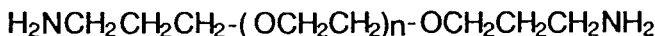
NIPAAm was purchased from Eastman Kodak Co. and recrystallized from acetone. Diamino-PEG6000 was provided by Kawaken Fine Chemicals Co., and the number-average molecular weight was estimated as about 1×10^4 ($n = 230$) from primary amine determination using 2,4,6-trinitrobenzenesulfonic acid (TNBS) [8].

NIPAAm was copolymerized with 10 mol% *N*-acryloxysuccinimide (NASI, Kokusan Chemical Works Co.) to give an activated polymer poly(NIPAAm-co-NASI) [7] (Fig. 1). The copolymerization was carried out in CHCl_3 at 60°C for 8 hours using azobisisobutyronitrile (AIBN) as the initiator. The activated polymer was precipitated with diethylether and recovered at about an 85% yield. NASI content in the activated polymer was found to be the same as the feed ratio by $^1\text{H-NMR}$ measurement.

A block copolymer was prepared by using an amido condensation reaction between the activated polymer and diamino-PEG at a ratio of 2:1 on a weight basis. This ratio is equivalent to a molar ratio condition of $[\text{NH}_2]/[\text{NASI}] = 1/10$. The reaction was carried out at room temperature overnight in CHCl_3 at a total polymer concentration of less than 2 wt%. After the reaction, an excess amount of isopropylamine (IPA) was added to the solution to convert unreacted NASI residue to



Activated Polymer : Poly(NIPAAm-co-NASI)



Diamino-PEG

FIG. 1. Chemical structures of the activated polymer and diamino-PEG.

NIPAAm. After being dried, a crude residue was dissolved in distilled water and filtered through a membrane filter (0.8 μm) in a refrigerator. A by-product, *N*-hydroxysuccinimide, was removed by diafiltration by using an ultrafiltration membrane (Amicon, YM-100, nominal molecular weight limit = 100,000), and a retentate solution was lyophilized to give the block copolymer at about an 80% yield.

For control, the homopolymer of NIPAAm was synthesized by converting all the NASI of the activated polymer to NIPAAm by using IPA. The average molecular weight of the homopolymer was estimated as about 3×10^4 from viscometric measurement [9].

A random copolymer composed of NIPAAm and AAm was synthesized according to the literature [4]. The AAm content in the poly(NIPAAm-*co*-AAm) was calculated as 37 mol%, i.e., 27 wt% from elemental analysis.

The IR spectrum was measured using an FT-IR spectrometer (Nicolet, 510) in KBr pellets. The NMR spectrum was measured using an NMR spectrometer (Varian, EM390) in CDCl_3 solution.

Calorimetric analysis was carried out on a DSC apparatus (Seiko, DSC-220) and a data processor (Seiko, SSC/5200). The thermogram was recorded at a heating rate of $1^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Under the conditions described in the Experimental Section, the condensation reaction of the activated polymer and the diamino-PEG gave a water-soluble block copolymer. The content of PEG in the block copolymer poly(NIPAAm)-*b*-PEG was calculated as 38 wt% from elemental analysis. Since almost no primary amine was detected in the block copolymer by the TNBS method, the diamino-PEG was fully reacted with NASI residues in the activated polymer. IR spectra of the block copolymer showed no NASI residue remaining in the block copolymer, which shows a complete conversion of NASI to NIPAAm by IPA.

We observed the LCST phenomenon of the polymers by using calorimetry. The LCST phenomenon is usually observed by measurement of the cloud point. However, such measurements are inaccurate due to variations in precipitated aggregate size and settling precipitation. We therefore used a more powerful technique that may be applicable to the study of LCST phenomenon [2].

As shown in Fig. 2, the poly(NIPAAm) homopolymer showed a very sharp endothermic peak at 34°C , and the block copolymer poly(NIPAAm)-*b*-PEG showed a broader peak at 38°C . On the other hand, the random copolymer poly(NIPAAm-*co*-AAm) showed no endothermic peak.

Although both the block copolymer and the random copolymer have an equivalent hydrophilic portion on a weight basis, their endothermic features are quite different. This remarkable difference between the block copolymer and the random copolymer is attributable to the difference in the NIPAAm sequence length. In the block copolymer a long NIPAAm sequence and a PEG chain are independently present, while in the random copolymer the sequence of NIPAAm and AAm is considered to tend toward alternation [4]. That is, in the case of the block copolymer, hydrophilic moiety does not influence the hydrophobic interaction between intramolecular NIPAAm groups significantly, while in the random copolymer the

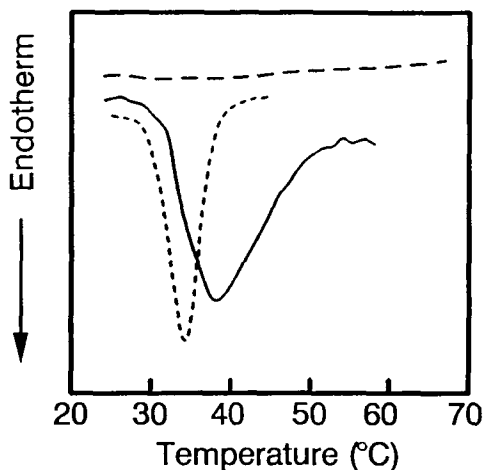


FIG. 2. DSC thermogram of the block copolymer poly(NIPAAm)-block-PEG (—) compared with those of the poly(NIPAAm) (---) and the random copolymer poly(NIPAAm-co-AAm) (-·-·).

alternatively copolymerized hydrophilic monomer interferes with the hydrophobic interaction between intramolecular NIPAAm groups.

The result obtained here suggests that the NIPAAm sequence length is the dominant effect on the LCST phenomenon rather than the content of the hydrophilic portion.

REFERENCES

- [1] M. Heskins and J. E. Guillet, *J. Macromol. Sci. - Chem.*, **A2**(8), 1441 (1968).
- [2] H. G. Schild and D. A. Tirrell, *J. Phys. Chem.*, **94**, 4352 (1990).
- [3] K. Kubota, S. Fujishige, and I. Ando, *Ibid.*, **94**, 5154 (1990).
- [4] C. K. Chiklis and J. M. Grasshoff, *J. Polym. Sci., Part A-2*(8), 1617 (1970).
- [5] L. D. Taylor and L. D. Cerankowski, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2551 (1975).
- [6] H. Iwata, M. Oodate, Y. Uyama, H. Amemiya, and Y. Ikada, *J. Membr. Sci.*, **55**, 119 (1991).
- [7] C. A. Cole, S. M. Schreiner, J. H. Priest, N. Monji, and A. S. Hoffman, *ACS Symp. Ser.*, **350**, 245 (1987).
- [8] A. F. Habeeb, *Anal. Biochem.*, **14**, 328 (1966).
- [9] S. Fujishige, *Polym. J.*, **19**, 297 (1987).