ELSEVIER

European Polymer Journal 37 (2001) 1985–1989

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Temperature-induced phase transition at the polymer–water interface

Soon Hong Yuk [a,*], Sun Hang Cho [b]

[a] *Department of Polymer Science and Engineering, Hannam University, 133 Ojeong Dong, Daedeog Ku, Taejeon 306-791, Republic of Korea*

[b] *Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Taejeon 305-600, Republic of Korea*

Received 9 October 2000; received in revised form 7 March 2001; accepted 20 March 2001

Abstract

Temperature-induced phase transition of polymer shows the bulk swelling change in the polymer network, which may induce the change of polymer surface properties. The contact angle measurements at the polymer–water interface were performed to observe the temperature-induced phase transition at the polymer–water interface using two-liquid technique. The dispersive and nondispersive components of surface free energy of polymer were measured above or below the phase transition temperature (lower critical solution temperature). A semi-interpenetrating polymer networks composed of sodium alginate and poly(*N*,*N*-dimethylaminoethyl methacrylate-co-ethyl acrylamide) were used as a model polymer system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature-induced phase transition; Polymer–water interface; Contact angle

1. Introduction

Since Heskins and Guillet had reported the solution properties of poly(*N*-isopropylacrylamide (NIPAAm)) [1], many researchers have investigated the thermosensitive property of polymer. Especially, Hoffman et al. and Kim et al. have extensively investigated temperature-sensitive swelling behavior of poly(NIPAAm) gels and explained the temperature-induced phase transition of poly(NIPAAm) gels from the point of bulk property of polymer network [2–5].

In this study, the temperature-induced phase transition of polymer network was investigated at the polymer–water interface. For this purpose, semi-interpenetrating polymer network (semi-IPN) composed of sodium alginate (SA) and poly(*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA)-co-ethyl acrylamide (EAAm)) were prepared. The role of SA is to provide the crosslinked network at a later stage and that of poly(DMAEMA-co-EAAm) is to provide the thermosensitivity of the polymer network. In our previous studies [6–8], the temperature-induced phase transitions of aqueous poly(DMAEMA-co-EAAm) solution, poly(DMAEMA-co-EAAm) gel, and semi-IPN gel of SA and poly(DMAEMA-co-EAAm) were reported. The temperature dependence of equilibrium swelling of poly(DMAEMA-co-EAAm) gel was not in accordance with the change of the phase transition temperature (lower critical solution temperature, LCST) of aqueous poly(DMAEMA-co-EAAm) solution as a function of chemical composition. However, semi-IPN gel of SA and poly(DMAEMA-co-EAAm) showed the similar trend to the change of LCST of aqueous poly(DMAEMA-co-EAAm) solution. To understand the relation between poly(DMAEMA-co-EAAm) in solution and that in the gel state in the temperature-induced phase transition, semi-IPN gel was selected as a model polymer system. To uphold the condition that the polymer gel

---

[*] Corresponding author. Fax: +82-42-626-8841.
E-mail address: shyuk@mail.hannam.ac.kr (S.H. Yuk).

PII: S0014-3057(01)00101-X

remains swollen, we choose a water (W)-alkane liquid (L)-polymer surface (S) system and the contact angle measurement using two-liquid technique [9] were used to observe the change of surface property in the temperature-induced phase transition.

2. Materials and methods

2.1. Materials

DMAEMA monomer, *N*,*N*-azobis(isobutyronitrile) (AIBN), and calcium chloride were purchased from Aldrich. SA and sodium acetate were purchased from Sigma Chemical Co. The alkanes used for contact angle measurements were *n*-hexane, isooctane, *n*-heptane, *n*-octane and cyclohexane which were purchased from Junsei Chemical Co. and were purified by conventional distillation. The γ_L for the alkanes and γ_{WL} for the interfacial tension were summarized in the literature [9]. DMAEMA monomer was distilled before use. Other reagents were used as received.

2.2. Synthesis

EAAm was synthesized in our laboratory as described previously [10]. Copolymers of DMAEMA and EAAm were prepared by free radical polymerization as follows: 6.68 g of DMAEMA, 1.12 g of EAAm and 0.02 g of AIBN as an initiator were dissolved in 100 ml of water/ethanol binary solvent mixture (5/5 by volume). The ampoule containing the solution was sealed by a conventional method and immersed in a water bath held at 75°C for 15 h. After polymerization, all polymers were dialyzed against distilled–deionized water at 4°C and freeze-dried.

2.3. Preparation of semi-IPN gel film

Semi-IPN gel films composed of SA and poly(DMAEMA-co-EAAm) were prepared as follows: The known amounts of 2 wt.% SA aqueous solution and 10 wt.% poly(DMAEMA-co-EAAm) aqueous solution were mixed thoroughly using a homogenizer (Janke & Kunkel Gmbh). The prepared solution was cast on a known area of a glass plate and dried in a vacuum oven. After drying, the noncrosslinked polymer film was removed from the glass plate and immersed in 5 wt.% calcium chloride solution. Because SA formed a gel in the presence of divalent ion, the gel network was formed from the surface with the penetration of calcium chloride into the noncrosslinked polymer film. The noncrosslinked polymer was completely converted to the crosslinked one (semi-IPN gel film) within 30 min. The semi-IPN gel film was immersed in distilled–deionized water to remove nonbonded calcium chloride. There is an equilibrium of calcium ions corresponding to dissociation equilibrium if the immersion in distilled–deionized water is applied long enough and many times. The immersion in distilled–deionized water was applied for 3 h to avoid the dissociation equilibrium.

2.4. Swelling measurements

After immersion in water at a desired temperature, the semi-IPN gel film was removed from the water and tapped with a filter paper to remove excess water on gel film surface. The gel film was repeatedly weighed and reimmersed in water at a fixed temperature until the hydrated weight reached a constant value. After equilibration at one temperature, the gel film was reequilibrated at a higher temperature. The swelling, defined as the weight of water uptake per unit weight of dried gel, was calculated by measuring the weight of swollen gel until weight changes were within 1% of the previous measurement. The swelling equilibrium was obtained from both sides, e.g. on heating and cooling in order to detect possible nonequilibrium states.

2.5. Contact angle measurements

The contact angle measurement was performed using contact angle goniometer with environmental chamber based on two-liquid technique. The liquid droplet was introduced by a microsyringe onto a gel film immersed in a doubly distilled water. The contact angles on both sides of each droplet were measured to assure symmetry. The measurements were performed for several parts of the same film and averaged, and this procedure was repeated at various temperatures. In every case, the advancing contact angle was measured.

2.6. Surface analysis

To uphold the condition that the semi-IPN gel film remains swollen, a water (W)-liquid (L)-solid (S) system was selected. Assuming that Young's equation holds for such a system, the following expression is obtained.

$$\gamma_W - \gamma_L - \gamma_{WL}\cos\theta_{SL} = 2[(\gamma_W^d)^{1/2} - (\gamma_L^p)^{1/2}](\gamma_S^d)^{1/2} + 4\gamma_S^p\gamma_W^p/(\gamma_S^p + \gamma_W^p) + \pi_e$$

where symbols p and d represent the nondispersive and dispersive components of surface tension (γ), θ_{SL} is the contact angle of a liquid droplet (L) on solid (S) under water (W) and π_e is the surface spreading pressure. Neglecting π_e and measuring the contact angle against several alkanes under water, γ_S^p and γ_S^d are obtained from the plot of $(\gamma_W - \gamma_L - \gamma_{WL}\cos\theta_{SL})$ vs. $2[(\gamma_W^d)^{1/2} - (\gamma_L^p)^{1/2}]$.

3. Results and discussion

Prior to observing the temperature-induced phase transition at the polymer–water interface, temperature-induced phase transitions of poly(DMAEMA-co-EAAm), which is the major part of polymer network, is summarized as presented previously [6,7]. When the temperature of a poly(DMAEMA) aqueous solution was raised above 50°C, the polymer precipitated from the solution. This is due to hydrophobic interaction between *N*,*N*-dimethylamino groups above LCST. Because not the pure polymer is precipitating in the polydispersive polymer system, the LCST cannot be measured exactly from the turbidity curve as functions of temperature and concentration. Therefore, we could roughly expect the LCST of polymer from the turbidity curve. With the incorporation of EAAm in the copolymer, LCST was shifted to a lower temperature. In general, the LCST of copolymer should be increased with the incorporation of hydrophilic comonomer [11]. However, in the case of poly(DMAEMA-co-EAAm), the LCST was shifted to the lower temperature with the incorporation of hydrophilic EAAm. This is due to the hydrogen bond formation between ethylamide group in EAAm and *N*,*N*-dimethylamino group in DMAEMA which decreases the exposure of *N*,*N*-dimethylamino groups to water resulting in a significant hydrophobic contribution to the LCST [6,7].

Firstly, the temperature-induced swelling transition of the gel films composed of SA and poly(DMAEMA-co-EAAm) with a semi-IPN structure was observed as shown as Fig. 1. For this purpose, a novel semi-IPN has been prepared. The system consisted of two chemically independent polymers in which the proportions and properties of both polymers can be independently varied. The first network consists of SA which provides the crosslinked network. The other is poly(DMAEMA-co-EAAm) which imparts temperature sensitivity into the polymer network. SA forms gel in the presence of divalent ions at concentrations of >0.1% w/w. Based on this property of SA, the solution mixture of SA and poly(DMAEMA-co-EAAm) was treated with calcium chloride to form a gel matrix. It could be expected that SA formed a gel matrix (calcium alginate) and poly(DMAEMA-co-EAAm) chains entangled through the calcium alginate matrix, resulting in semi-IPN.

Poly(DMAEMA-co-EAAm) used in this study has a LCST at 25°C according to the previous study on the LCST change of poly(DMAEMA-co-EAAm) as a function of EAAm content [6]. The transition temperature of gel film between the shrunken and swollen state was 25°C. (The transition temperature was defined as the temperature at the inflection point in the swelling versus temperature curve.) This is in accordance with the LCST change of poly(DMAEMA-co-EAAm) aqueous solution. It is well known that the inflection point of a swelling curve corresponds to a critical point in an uncrosslinked polymer system [12]. With the increase of the content of poly(DMAEMA-co-EAAm) in the gel film, the swelling change caused by temperature-induced phase transition increases.

Fig. 2 shows the change of octane contact angle as a function of poly(DMAEMA-co-EAAm) content at two temperatures. Above LCST, the contact angle of all gel

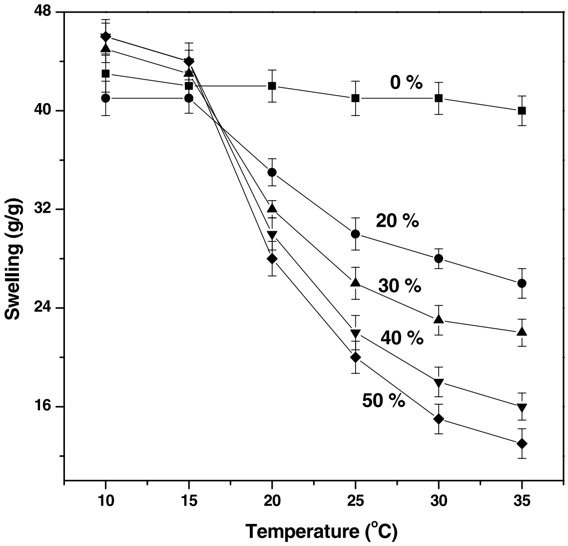

Fig. 1. Temperature-dependence of equilibrium swelling of semi-IPN gel film as a function of the content of poly(DMAEMA-co-EAAm).

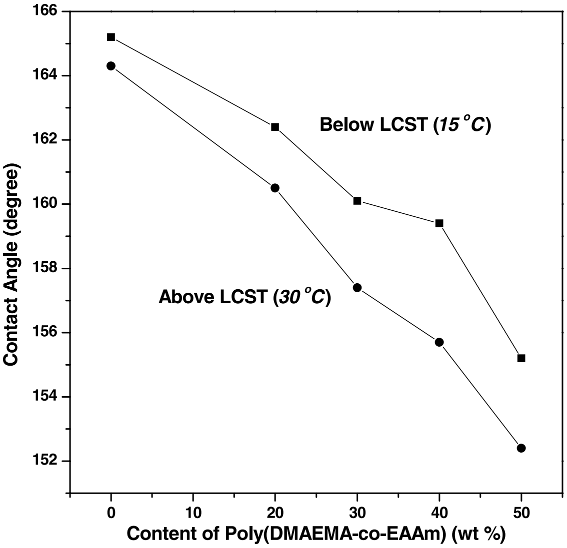

Fig. 2. The change of octane contact angle as a function of the content of poly(DMAEMA-co-EAAm) at two temperatures.

films was decreased compared that below LCST. This indicates that the significant change at the polymer surface with the temperature-induced phase transition occurs and this leads the polymer surface more hydrophobic.

To understand the temperature-induced phase transition at the polymer–water interface more in detail, γ_S^d and γ_S^p were measured as a function of the content of poly(DMAEMA-co-EAAm) at two temperatures (15°C and 30°C), which are shown in Figs. 3 and 4. Below LCST (15°C), minimal change was observed in γ_S^d as a function of the content of poly(DMAEMA-co-EAAm). However, above LCST (30°C), the significant increase in γ_S^d was observed with the increase of the content of poly(DMAEMA-co-EAAm). And the significant change in γ_S^p was not observed with the temperature-induced phase transition. The hydrophobization of polymer surface is closely related to the swelling change caused by the temperature-induced phase transition (see Figs. 1 and 3). With high swelling change in the case of semi-IPN gel film of high content of poly(DMAEMA-co-EAAm), more significant change in γ_S^d was observed. This indicates that the change at polymer surface is strongly dominated by the change in the polymer network with the temperature-induced phase transition.

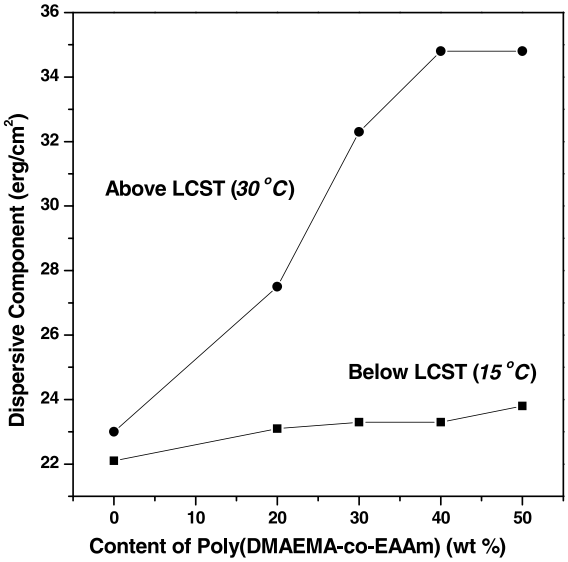

Fig. 3. The change of γ_S^d as a function of the content of poly(DMAEMA-co-EAAm) at two temperatures.

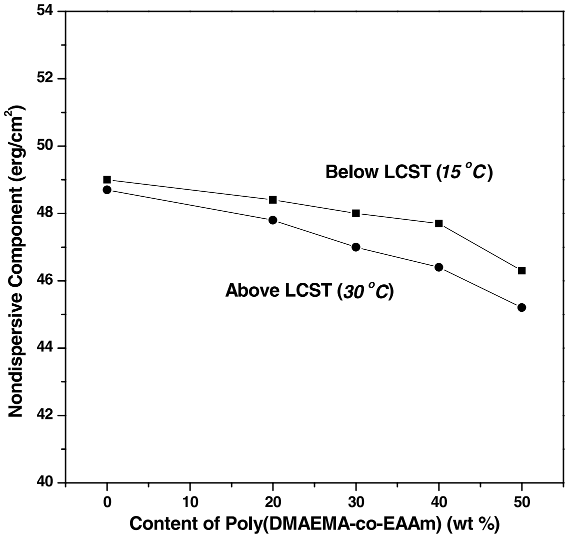

Fig. 4. The change of γ_S^p as a function of the content of poly(DMAEMA-co-EAAm) at two temperatures.

With the temperature-induced phase transition in the polymer network, the hydrophobic character of polymer surface was significantly increased and this is due to the formation of hydrophobic domain at the polymer surface caused by the hydrophobic interaction between *N*,*N*-dimethylaminoethyl groups of DMAEMA above LCST. Our previous studies showed that the hydrogen formed between ethylamide group in EAAm and *N*,*N*-dimethylamino group in DMAEMA which decreased the exposure of *N*,*N*-dimethylamino group to water resulted in hydrophobic contribution to the LCST. This led to more hydrophobic surface with the increase of the content of poly(DMAEMA-co-EAAm) in the semi-IPN gel film.

4. Conclusions

To understand the temperature-induced phase transition at the polymer–water interface, the surface properties and their temperature dependence were observed. With the temperature-induced phase transition, dispersive component of polymer surface tension (γ_S^d) was significantly increased. The hydrophobization of polymer surface is closely related to the swelling change caused by the temperature-induced phase transition and this indicates that the change at polymer surface is strongly dominated by the change in the polymer network with the temperature-induced phase transition.

Acknowledgements

This work was supported by grant no. 2000-1-30800-003-3 from the basic research program of the Korea Science and Engineering Foundation.

References

[1] Heskins M, Guillet JE. J Macromol Sci Chem 1968; A2(8):1441.

[2] Hoffman AS, Afrassiabi A, Dong LC. J Controlled Release 1986;4:213.

[3] Hoffman AS. J Controlled Release 1987;6:297.

[4] Bae YH, Okano T, Kim SW. Makromol Chem, Rapid Commun 1987;8:481.

[5] Bae YH, Okano T, Kim SW. Makromol Chem, Rapid Commun 1988;9:1985.

[6] Yuk SH, Cho SH, Lee SH. Macromolecules 1997;30:6856.

[7] Cho SH, Jhon MS, Yuk SH. Eur Polym J 1999;35:1841.

[8] Yuk SH, Cho SH. Kor Polym J 2000;8:89.

[9] Yuk SH, Jhon MS. J Colloid Interface 1987;116:25.

[10] McCormick CL, Blackmon KP, Elliott DL. Polymer 1986;27:1976.

[11] Feil H, Bae YH, Feijen J, Kim SW. Macromolecules 1993;26:2496.

[12] Borchard W. Eur Polym J 1978;14:661.