

Preparation, Characterization, and Properties of EVA Preirradiation Grafted NIPAAm

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SYNOPSIS

An ethyl-vinyl acetate copolymer (EVA) preirradiation-grafted with *N*-isopropylacrylamide (NIPAAm) was prepared. Various methods which can be used to control the grafting reaction are described. DSC and TMA were employed to characterize the surface thermosensitivity of the graft copolymer. It is indicated that the surface of EVA grafted with NIPAAm shows thermosensitivity similar to a partially crosslinked poly-NIPAAm (PNIPAAm) gel. The response to the change of temperature through the lower critical solution temperature (LCST) of the graft was swifter than that of the PNIPAAm gel. SEM revealed a micropore structure in the surface layer of the sample. DSC was also used to analyze the water state in the surface layer of the sample. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A hydrogel is a kind of polymer which can be swollen but cannot be dissolved in the water. There are some hydrogels which can modulate the swelling ratio in response to environmental stimuli such as temperature,^{1,2} pH,^{3,4} chemicals,⁵ photoirradiation,⁶ and electric field.⁷ The collapse in a gel in response to environmental changes was predicted by Dusek and Patterson⁸ and was intensively investigated by Tanaka and co-workers.⁹⁻¹³ Thermosensitive hydrogels, one kind of these environmental stimuli response hydrogels, collapse at elevating temperature through the lower critical solution temperature (LCST). The volume change occurs within a quite narrow temperature range and could be as large as 1000-fold.^{14,15} Permeability of water through the gel can be changed by an on-off switch according to the environmental temperature. Therefore, such materials can be used in many fields such as drug delivery systems,^{16,17} extraction,¹⁸ and enzyme activity control.¹⁹

Partially crosslinked poly(*N*-isopropylacrylamide) (PNIPAAm) with an LCST about 32°C has at-

tracted much attention for its representative thermosensitivity and easy preparation. However, because of the high water content, PNIPAAm has a weak mechanical strength which may limit its practical applications. To improve the mechanical properties, copolymerizing with other monomers or forming interpenetrating polymer networks (IPN) had been tried.^{16,17,20} The swelling transition temperature as well as the swelling ratio of the copolymers were altered when the copolymerization was employed. In the IPN system, the LCST may be kept at the same temperature as that of the PNIPAAm networks, while the swelling ratio decreases with the formation of IPN. The surface-grafting copolymerization is, perhaps, another way to solve these problems. By grafting NIPAAm onto a trunk polymer, we can get both high mechanical strength and a thermosensitive surface. The thermosensitivity is expected to be the same as that of PNIPAAm. The grafted polymers are suitable for applications of immobilization and extraction.

Radiation grafting is widely used in the preparation of biomedical materials for its well-known advantages. In the present work, electron beam (EB) preirradiation grafting was employed to produce a thermosensitive surface of the ethyl-vinyl acetate copolymer (EVA). Various factors which control the

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reaction are discussed. The thermosensitivity of the grafted surface of EVA was characterized by differential scanning calorimetry (DSC) and a thermal mechanical analyzer (TMA). Scanning electron microscopy (SEM) and DSC were used to determine the physical structure of the surface layer of the sample.

EXPERIMENTAL

Radiation Grafting of NIPAAm onto EVA

Preirradiation of the washed, dried, and weighed EVA slices were carried out at a dose rate of 100 Gy/s and a dose of 100 KGy with EB of 0.9 MeV energy from a Van de Graff accelerator at room temperature in the presence of air. The irradiated slice was immersed in an aqueous solution of recrystallized NIPAAm (Eastman Kodak) in a test tube. After being degassed by purging with nitrogen, the test tube was sealed. The grafting reaction was achieved by keeping the test tube in a water bath at a desired temperature, say 90°C, for hours. After being washed with deionized water completely, the slice was kept in deionized water and put into a water bath at a desired temperature for 20 h. Before recording the weight, the excess water of the surface was removed by wet filter paper. The swelling ratio was measured in the temperature range of 20–40°C. After the swelling measurement, the grafted slices were dried and weighed. The degree of grafting was defined as

$$DG = (W_d - W_0)/W_0 \times 100\%$$

and the swelling ratio was defined as

$$R = (W_w - W_d)/W_d \times 100\%$$

where W_d is the weight of the slice after grafting; W_0 , the weight of the slice before grafting; and W_w , the weight of the swollen graft sample.

Characterization of Thermosensitivity of EVA-g-NIPAAm by DSC and TMA

The surface layer of the swollen graft sample was carefully cut with a knife and sealed with some deionized water in aluminum pans with a DSC sample sealer to prevent water evaporation during the measurement, and a sealed empty aluminum pan was used as a reference. The temperature of the pan was kept at 20°C for 10 min, and then the sample

was heated to 60°C at a rate of 1°C/min (DSC-4, Perkin-Elmer).

The swollen graft sample was cut into the size of 8 × 8 mm² and placed on the test platform of the TMA (Perkin-Elmer) with a test load of 5 mN. The temperature of the sample was kept at 20°C for 10 min, and then the sample was heated from 20 to 60°C at a rate of 1°C/min.

Analysis of the Physical Structure of the Surface Layer by SEM and DSC

Specimens for SEM studies were swollen in deionized water with different temperatures (above or below LCST) for about 24 h. The morphology of the surface layers of the specimens was frozen rapidly by liquid nitrogen and then freeze-dried. The gold-coated surface morphology of the specimens was observed by SEM (AMRAY 1000B).

The surface layers of the swollen samples were carefully cut with a knife and blotted with wet filter paper to remove extra surface water. The samples were sealed in the aluminum pans and a sealed empty aluminum pan was used as a reference. The temperature of the pan was kept at -20°C for 10 min, ensuring that any supercooled water was frozen, and then the sample was heated to 20°C at a rate of 1°C/min. The amount of freezing water was estimated from a calibration graph obtained by measuring deionized water at identical conditions, based on the assumption that the heat of water fusion in the samples is the same as that of deionized water. The amount of bound water was taken as the difference between the total water and free water in the samples.

RESULTS AND DISCUSSION

Control of the Grafting Reaction

Various methods, such as radiation dose, dose rate, inhibitor, reaction temperature, monomer concentration, and reaction time, can be used to control the preirradiation grafting reaction. Reaction temperature, monomer concentration, and reaction time may be the most convenient methods which can be employed.

Plotted in Figure 1 is the effect of the grafting reaction temperature on the degree of grafting (DG). As the EVA slice was irradiated at room temperature with the presence of air and heated to 90°C for grafting, the grafting reaction was initiated by peroxides produced in the preirradiation.²¹ The higher

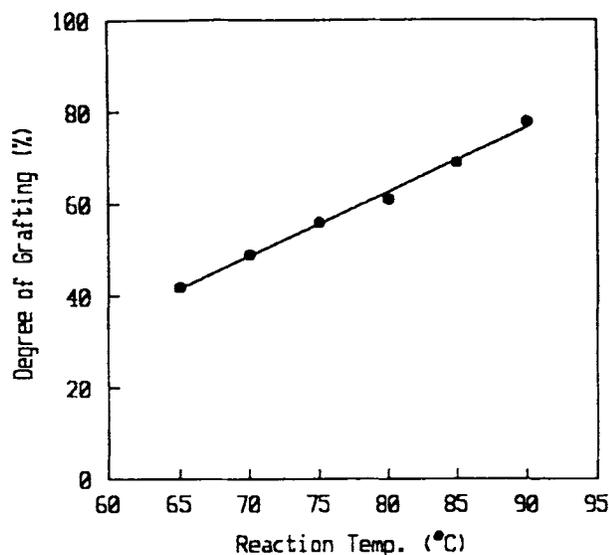


Figure 1 Effect of grafting reaction temperature on DG of EVA-*g*-NIPAAm. Preirradiation dose: 100 KGy; dose rate: 100 Gy/s; grafting reaction time: 5 h; monomer concentration: 20 wt %.

the temperature is, the more the peroxides are decomposable or the higher is the effective concentration of the initiators. These factors cause the increase of the grafting reaction rate. The DG, hence, increases with elevating grafting reaction temperature.

Figure 2 shows the grafting reaction kinetics. The DG is linear with time up to fairly high DG and then levels off. In low monomer conversion, the viscosity of the reaction solution does not change obviously; therefore, the monomer diffusion rate is steady. As DG increases, the monomer diffusion is more and more difficult because of the high viscosity of the system. But the retarding action due to the diffusion of the monomer might be compensated by an acceleration resulting from the Trommsdorf effect.²¹ The grafting conversion curve remains linear even at higher DG. As to the leveling off, it may be due to that the diffusion of the monomer becomes too slow to secure chain propagation.

Figure 3 shows the dependence of the DG on the monomer concentration. The DG increases with increase of the NIPAAm concentration and levels off above 15 wt % of NIPAAm.

Characterization of Thermosensitivity of the Graft Copolymer

Plotted in Figure 4 is the effect of the swelling temperature on the swelling ratio of the samples with different DG. The LCST of the EVA surface-grafted

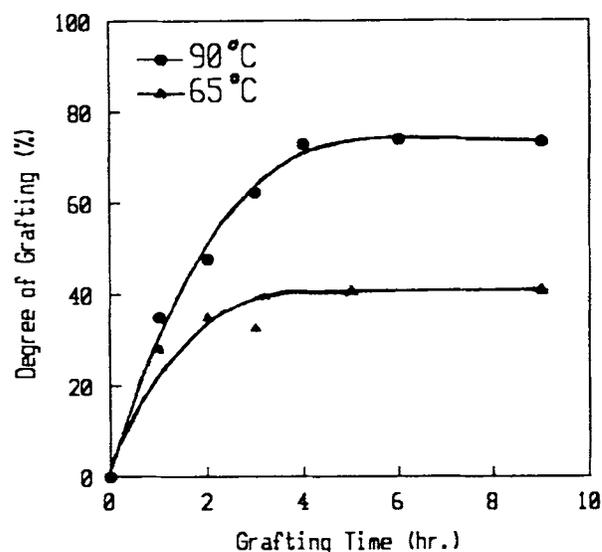


Figure 2 Effect of grafting time on DG of EVA-*g*-NIPAAm. Preirradiation dose: 100 KGy; dose rate: 100 Gy/s; grafting reaction temperature: (●) 90°C, (▲) 65°C; monomer concentration: 20 wt %.

NIPAAm does not change with the variation of DG. The swelling ratio increases with increase of the DG when the DG is less than 50%. The curve shape is very similar to that of the PNIPAAm gel.^{19,22} As the DG increases, the surface of the sample becomes more and more hydrophilic below the LCST. Therefore, the swelling ratio increases. Above the LCST, the shranked graft copolymer contains water, al-

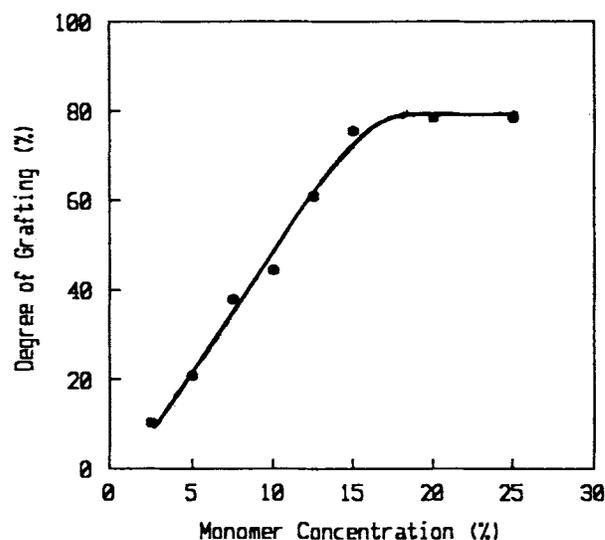


Figure 3 DG changes as a function of NIPAAm concentration. Grafting reaction temperature: 90°C. The other conditions are the same as those in Figure 1.

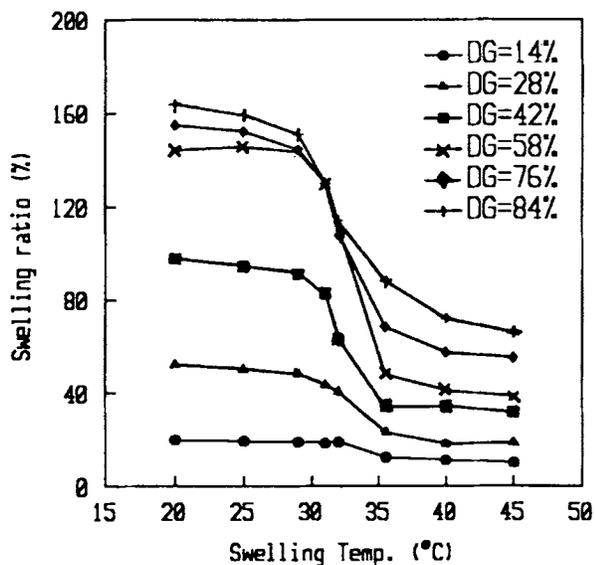


Figure 4 Swelling ratio curves change as a function of DG. DG (%) of the samples: (●) 14; (▲) 28; (■) 42; (×) 58; (◆) 76; (+) 84.

though much less than it does below the LCST. The higher the DG is, the higher the water content is.

A thermosensitive transition is a kind of phase transition which has a characteristic DSC peak. The typical DSC peak for the phase separation of EVA-*g*-NIPAAm is shown as curve A in Figure 5. The phase-separation temperature of EVA-*g*-NIPAAm is 30.63°C, while the EVA-*g*-AAm has no peak (curve B in Fig. 5).

An abrupt change of volume near the LCST is another property of a thermosensitive hydrogel. So, we can use the TMA to detect the relationship be-

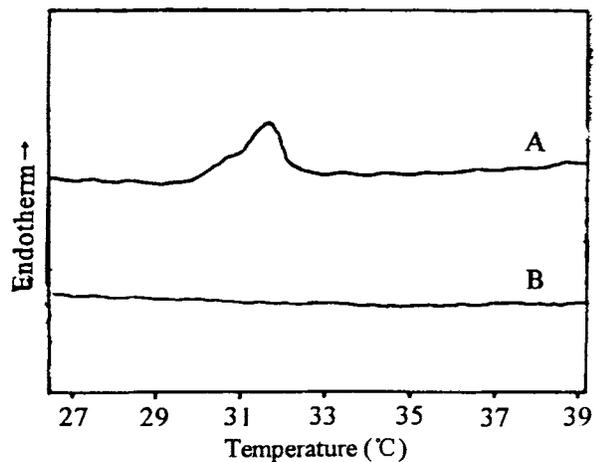


Figure 5 DSC thermograms of the swelling surface layer of EVA-*g*-NIPAAm and EVA-*g*-AAm: (A) EVA-*g*-NIPAAm; (B) EVA-*g*-AAm.

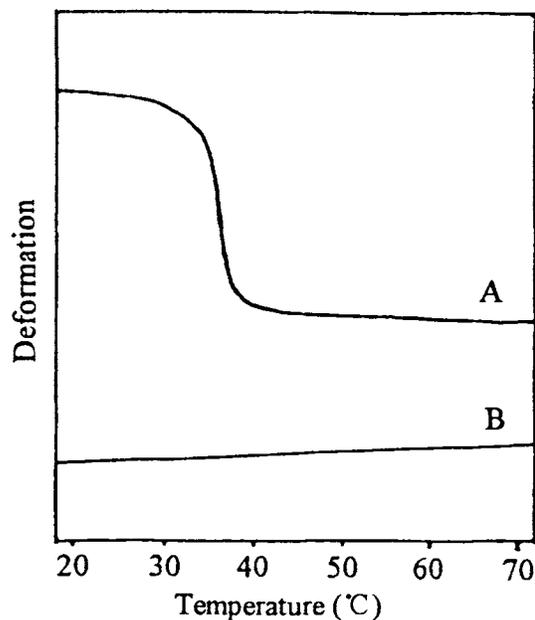


Figure 6 TMA curves of the swelling surface layer of EVA-*g*-NIPAAm and EVA-*g*-AAm: (A): EVA-*g*-NIPAAm; (B) EVA-*g*-AAm.

tween deformation and temperature near the LCST of the EVA-*g*-NIPAAm. Curve A in Figure 6 is the typical TMA curve of EVA-*g*-NIPAAm. We can also see the abrupt change of deformation near 31°C, while the EVA-*g*-AAm only has a small increase of deformation due to thermal expansion and no abrupt change of deformation, i.e., the swollen EVA-*g*-AAm has no thermosensitivity. This result agrees well with the results of Figures 4 and 5.

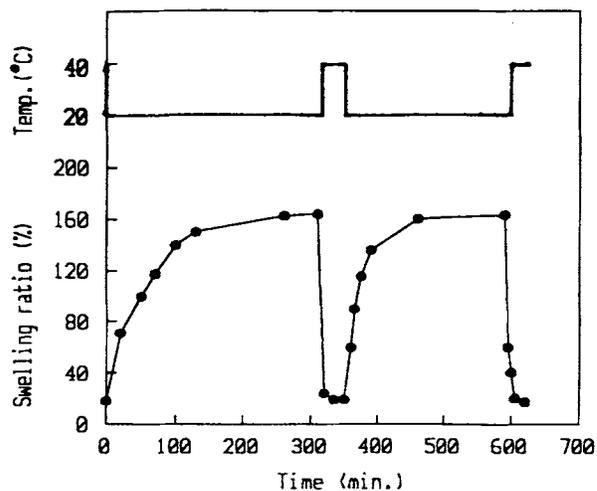


Figure 7 Swelling-deswelling kinetics of EVA surface grafted with NIPAAm.

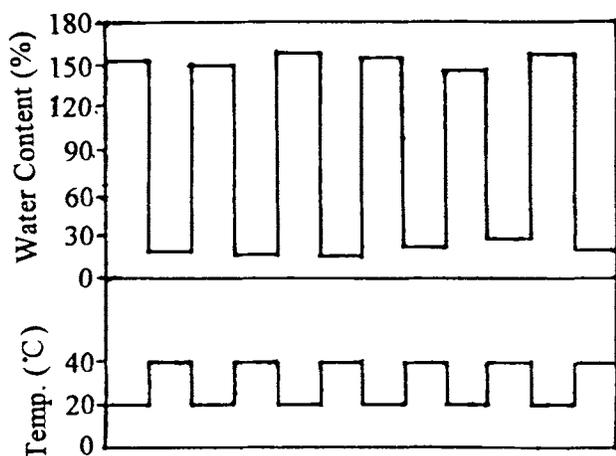


Figure 8 The reversibility of EVA-*g*-NIPAAm between swelling and deswelling.

Swelling and Deswelling Kinetics of the Graft Copolymer and Its Reversibility

The swelling–deswelling kinetics of EVA grafted with NIPAAm is shown in Figure 7. The temperature was modulated stepwise between 20 and 40°C. The response to the temperature change is very quick. An abrupt decrease of the swelling ratio is observed when the temperature is modulated from 20 to 40°C. It takes only 15 min to squeeze out 80% of the water. The reswelling is relatively slow. Twenty-five minutes is needed to reach 80% of full swelling. Mukae and colleagues²⁰ reported that a PNIPAAm gel took about 1 h to extrude the 70% water that it contained in response to a temperature change from 25 to 40°C. In reswelling, 2 h was needed to absorb 80% of the water. Concerning the rate of the swelling rate change, it is supposed that the EVA surface grafted with NIPAAm is more sensitive to temperature than is the PNIPAAm gel.

The gel used by Mukae et al. for their swelling and deswelling kinetic study was a disk. When the temperature was increased to the gel shrinking temperature, the outlayer of the disk was the first area to be affected. Skin was formed, which retarded the flux of water out of the disk. So, the deswelling rate is slow. In contrast, the NIPAAm grafting layer on the EVA surface is quite thin and loose. No skin is formed as the temperature increases through the LCST. The water in the grafting layer passes through very easily when it shrinks. A fast response to the temperature is presented. Compared with the PNIPAAm disk, this is an advantage of the EVA-*g*-NIPAAm.

The sample of EVA-*g*-NIPAAm was swollen in deionized water of 20 and 40°C for 4 h and weighted, respectively (from Fig. 7, we know that 4 h is enough for full swelling). This procedure was carried out several times. In this way, we can know the reversibility of the sample, as shown in Figure 8. Compared with the first swelling ratio at 20°C, the last swelling ratio at 20°C has no significant decrease or increase except for the errors of the experiments. This indicated that the thermosensitivity of EVA-*g*-NIPAAm has a very good reversibility. Thus, EVA grafted with NIPAAm is more suitable to serve as the substrate for an immobilizing enzyme which can self-regulate its activity according to the environmental temperature.

Analysis of Physical Structure of the Surface Layer

SEM results are shown in Figure 9. Figure 9(A) is the surface morphology of the sample swollen at 5°C, which is below the LCST (about 32°C). It has a distinguishable netlike pore structure which can

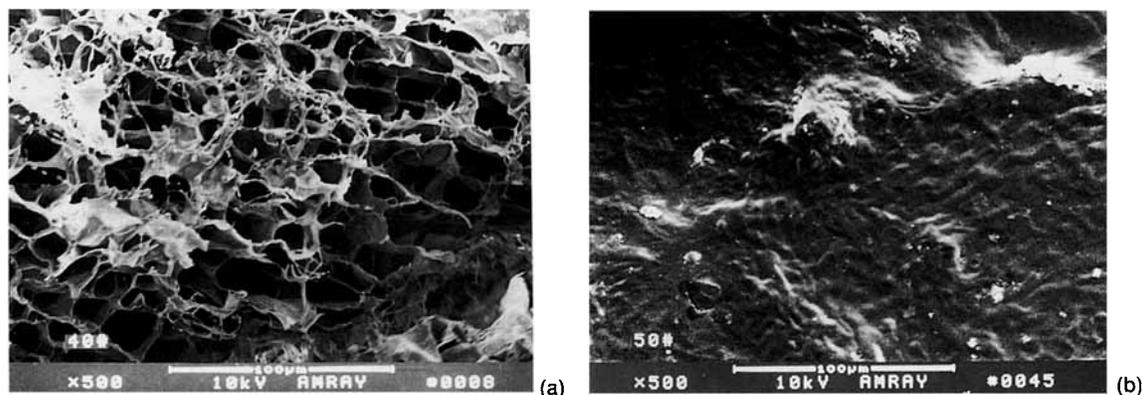


Figure 9 SEM of the surface of EVA-*g*-NIPAAm [samples were swollen in 5°C (picture A) and 40°C (picture B), respectively, before being frozen].

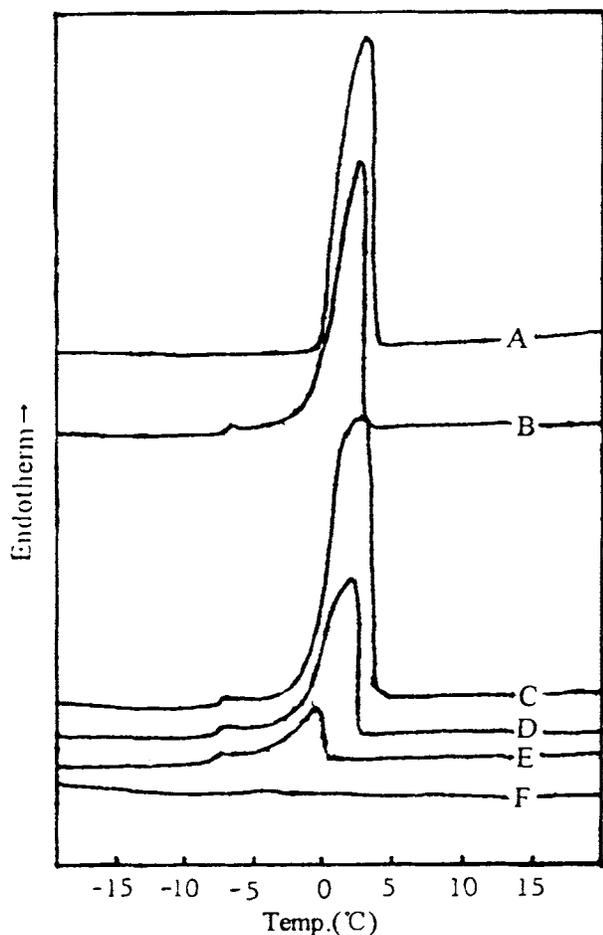


Figure 10 DSC thermograms for the surface layer of EVA-*g*-NIPAAm equilibrated in deionized water at various temperatures: (A) Deionized water, $\Delta H = 331$ J/g; (B–F) swelling temperature, respectively, 15, 25, 29, 32, and 40°C and, correspondingly, $\Delta H = 264, 260, 234,$ and 123.0 J/g.

contain much free water. But the sample at 40°C (above LCST) as shown in Figure 9(B) has no pore structure: Its water content is very low.

The DSC heating thermograms of the samples are shown in Figure 10. There apparently exist two phase-transition peaks: one first-order transition peak and one second-order phase-transition peak. The large first-order transition peak occurring at about 0°C corresponds to the melting of the free water in the hydrogel. As seen from Figure 10, the area under the water melting peak decreases with increase in the equilibration temperature. The peak area for the hydrogel equilibrated above its LCST becomes negligible. From the calibration graph curve A, we found that the latent heat of water fusion is 331 J/g. Comparing A with other values in curves B–F, we can estimate the free water content in the

surface of the samples at different swelling temperatures.

Figure 11 shows both the total water and bound water contents of EVA-*g*-NIPAAm gel as a function of the equilibration temperature. The total water content decreases with increase of the equilibration temperature, while an abrupt drop occurs at the LCST. Simultaneously, the percentage of bound water increases with the temperature, sharply rising at the LCST. The results shown in Figure 11 also indicate that above its LCST (around 32°C) nearly all the water in the hydrogel is bound water. This property is very important for the design of the controlled-release systems of drug or enzyme activity.

CONCLUSION

Various methods, mainly reaction temperature, reaction time, and monomer concentration, can be used to control the grafting reaction. The higher the temperature and monomer concentration are, the higher the DG is. The longer the reaction time is, the higher the DG is. But when the monomer concentration and reaction time was increased for a certain period, the DG levels off.

EVA surface grafted with NIPAAm presents the typical thermosensitivity similar to that of PNIPAAm gel, with a 90% change of swelling ratio within 2–3°C around its LCST of 32°C. The response of EVA surface-grafted NIPAAm to temperature is swifter than that of the PNIPAAm gel disk. The graft is porous below the LCST and dense over the LCST. Therefore, EVA-*g*-NIPAAm would

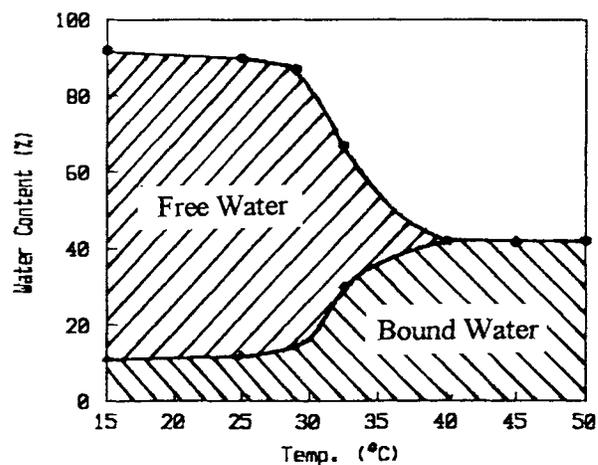


Figure 11 The states of water in the surface layer of the EVA-*g*-NIPAAm samples as a function of equilibration temperature.

be useful for the immobilization of enzymes which can "on-off" release its activity.

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