

SHORT COMMUNICATIONS

Relaxation Phenomena of Thermo-Shrinkage of Methacryloyl Polymer Gels with Pendant α -Amino Acid Groups

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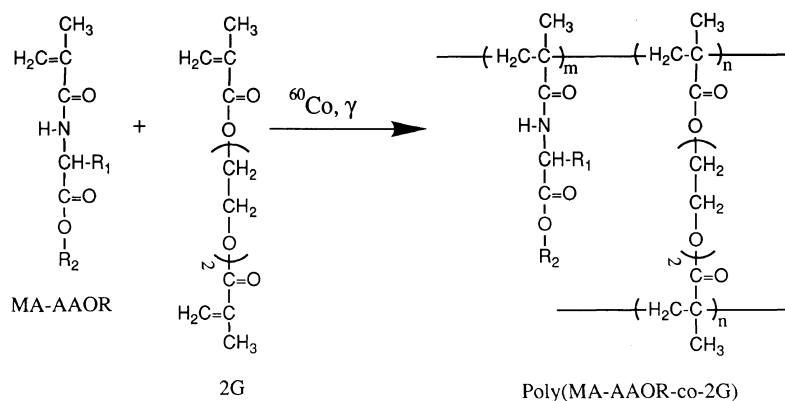
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Much attention has been paid to the phase transition of poly(*N*-isopropylacrylamide) gels responding to environmental change.¹⁻⁷ Although the homopolymer was soluble in water at a relatively low temperature, it precipitated above "lower critical solution temperature" (LCST) around 32°C.⁸ Inamoto *et al.* reported that a balance between hydrophobic isopropyl group and hydrophilic C=O or NH group plays an important role in the appearance of phase transition of poly(*N*-isopropylacrylamide) gel.⁹ Ito synthesized a series of poly(*N*-alkylacrylamide) to examine LCST in water and proved that LCST depended strongly upon the side-chain length of hydrophobic alkyl group.¹⁰ We studied the phase transition of methacryloyl polymer gels with pendant α -amino acid residues containing various terminal ester groups, in which intelligent function should be expected from a mutual interaction among the pendant C=O, NH, amino acid, and terminal ester groups. This communication shows a new finding that pendant α -amino acid-containing gels are accompanied by an irreversible reswelling due to thermal break of shrinking of the gel.

EXPERIMENTAL

Eight kinds of methacryloyl-L-amino acids with various terminal ester groups (MA-AAOR) were synthesized according to the procedure previously described,¹¹ *e.g.*, methacryloylglycine methyl ester (MA-GlyOMe), methacryloyl-L-alanine methyl ester (MA-AlaOMe), methacryloyl-L-valine methyl ester (MA-ValOMe), methacryloyl-L-isoleucine methyl ester (MA-ILeOMe), methacryloyl-L-alanine (MA-AlaOH), methacryloyl-L-alanine ethyl ester (MA-AlaOEt), methacryloyl-L-alanine tertiary butyl ester (MA-AlaOBu^t), and methacryloyl-L-alanine benzyl ester (MA-AlaOBzL). A mixture of MA-AAOR monomer (10 mmol), diethyleneglycol dimethacrylate (0.01 mmol), and ethanol (1 ml) was charged into a 5 mm inner diameter glass ampoule. The irradiation for polymerization was carried out up to 30 kGy with γ -rays from a ⁶⁰Co source at 40°C under nitrogen atmosphere, as shown in Scheme 1.

The rod-like gels obtained were cut into round slices (5 mm in diameter, 10 mm length), washed with an excess ethanol to remove unreacted chemicals, washed with excess water, lyophilized, and finally immersed in pure water



Scheme 1.

at 0°C (ice-water system) for approximately 3 weeks. The degree of gel swelling in water at selected temperatures, $100(W - W_0)/W_0$, where W is the weight of swollen sample and W_0 is the weight of dried sample, was estimated by measuring the weight change of gels.

RESULTS AND DISCUSSION

Figure 1 shows the changes in percent swelling of loosely cross-linked poly(MA-AAOR) gels treated for 24 hours at temperatures of 0, 10, 20, 30, 40, 50, 60, 70, and 80°C after pre-swelling with water at 0°C for 3 weeks. In the case of polymer gels of MA-GlyOMe ($R_1 = \text{H}$, $R_2 = \text{CH}_3$), MA-AlaOH ($R_1 = \text{CH}_3$, $R_2 = \text{H}$), and MA-AlaOMe ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$), the high percent swelling at 0°C decreases with increasing temperature and increases again after reaching a minimum at 50–60°C. Other polymer gels such as MA-ValOMe ($R_1 = \text{CH}(\text{CH}_3)_2$, $R_2 = \text{CH}_3$), MA-ILeOMe ($R_1 = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, $R_2 = \text{CH}_3$), MA-AlaOEt ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_2\text{CH}_3$), and MA-AlaOBu^t ($R_1 = \text{CH}_3$, $R_2 = \text{C}(\text{CH}_3)_3$), which swell in water at low temperature, exhibit a shrinkage with a rise in temperature. When the alkyl group contains bulky phenyl groups as MA-AlaOBzL ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_2\text{C}_6\text{H}_5$), gel swelling does not depend on temperature.

Changes in swelling of gels were further

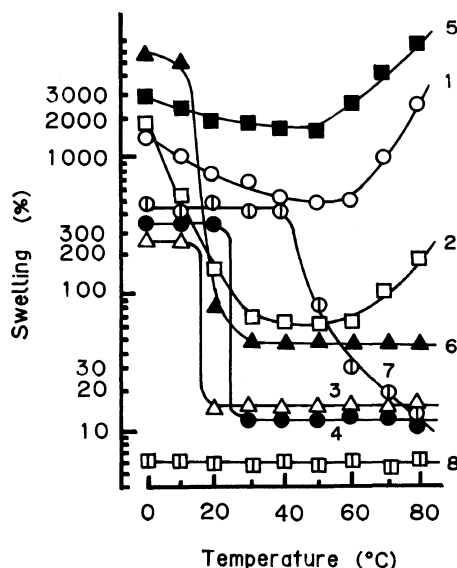


Figure 1. Changes in percent swelling of loosely cross-linked poly(MA-AAOR) gels treated for 24 hours at each temperature after pre-swelling with water at 0°C for 3 weeks. Numbers in figure refer to kinds of MA-AAOR given in Table I.

investigated as a function of time at 60°C. For hydrogels of MA-GlyOMe, MA-AlaOH, and MA-AlaOMe, irreversible reswelling occurred after 2, 16, and 48 hours from the start of treatment, respectively, owing to the thermal break of shrinking process of the gel. These changes were not observed with the MA-ValOMe, MA-ILeOMe, MA-AlaOEt, MA-

Table I. Kinds of MA-AAOR monomers and critical relaxation temperature (T_{CR}) of their poly(MA-AAOR) hydrogels

No.	MA-AAOR			T_{CR}
	Kind	R_1	R_2	°C
1	MA-GlyOMe	-H	-CH ₃	10
2	MA-AlaOMe	-CH ₃	-CH ₃	15
3	MA-ValOMe	-CH(CH ₃) ₂	-CH ₃	95
4	MA-ILeOMe	-CH(CH ₃)CH ₂ CH ₃	-CH ₃	95
5	MA-AlaOH	-CH ₂	-H	5
2	MA-AlaOMe	-CH ₃	-CH ₃	15
6	MA-AlaOEt	-CH ₃	-CH ₂ CH ₃	75
7	MA-AlaOBu ^t	-CH ₃	-C(CH ₃) ₃	90
8	MA-AlaOBzL	-CH ₃	-CH ₂ C ₆ H ₅	95

AlaOBu^t, and MA-AlaOBzL gels throughout an experimental period of 10 days. The increase in temperature from 60°C, however, brought about similar change in swelling with the gels when kept in water at prescribed temperatures up to 95°C for 10 days. The temperature which showed an irreversible increase in reswelling within 10 days was defined as the "critical relaxation temperature" (T_{CR}) and the values are listed in Table I. T_{CR} markedly increased with the size of the alkyl R_1 and R_2 groups. It was therefore concluded that the difference in degree of percent swelling of poly(MA-AAOR) gels is strongly dependent on the kind of α -amino acid and size of terminal ester groups, in which irreversible gel-reswelling is determined by two factors, temperature and time. Further details on this mechanism will be reported in the near future.

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