

Induced Thermoresponsive Volume Changes of Poly(methacryloyl L-alanine ethyl ester) Hydrogel

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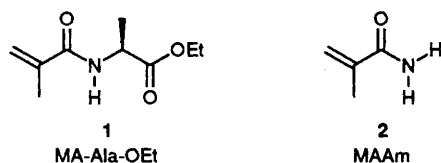
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Hydrogels containing L-alanine ethyl esters as side chains show an intrinsic temperature-responsive water absorption characteristic, which has been suppressed in the homopolymer by association of the terminal hydrophobic alkyl groups in the side chain, by introduction of comonomer methacrylamide which serves as a spacer for disruption of the association of the side chains.

Hydrogels are of current interest because they have a high potential as functional materials¹ owing to their ability to undergo volume changes by either absorption or exclusion of water in response to external stimuli such as temperature, pH, etc.²⁻⁴ We have shown that vinylpolymers having L-alanine methyl ester (Ala-OMe)⁵ as a side chain form a hydrogel which shows this volume change: expansion at low temperatures and shrinkage at elevated temperatures. Recently, we found that the terminal alkyl group of the amino acid esters controls the volume change. A hydrogel with L-alanine ethyl ester (Ala-OEt) **1** does not show this volume change, unlike the corresponding hydrogel with a methyl ester. As shown in Fig. 1, the hydrogel containing Ala-OMe has a water absorption of 1800% at 0 °C but 250% at 30 °C while that containing Ala-OEt has a water absorption of 450% at 0 °C and 300% at 30 °C.[†]

We supposed that the lack of volume change in the hydrogel containing Ala-OEt may be attributed to the association of the terminal ethyl ester groups caused by enhanced hydrophobic bonding in aqueous medium. The formation of such a hydrophobic tight structure in the side chains by this association could suppress this volume change characteristic in response to variation of the external temperature, of hydrogels with Ala residues. If this is true, then disruption of the association of the terminal hydrophobic ethyl esters on Ala residues could allow the hydrogel to exhibit thermoresponsive volume changes. One of the simplest methods for disrupting the association of the terminal hydrophobic groups is to isolate individual hydrophobic groups. Thus, we considered preparing a hydrogel containing isolated Ala-OEt groups by introducing another component, a so-called 'spacer', which does not contribute to the thermoresponsive volume change of the hydrogel. We prepared copolymer hydrogels consisting of two types of monomer residue methacryloyl (MA) Ala-OEt and methacrylamide (MAAm) **2** and investigated their water absorption behaviour.[‡]

Fig. 2 shows the change in water absorption of the copolymer hydrogels consisting of MA-Ala-OEt and MAAm



[†] Water absorption (%) refers to a hundred times the mass of water (g) absorbed by 1 g of the hydrogel.

[‡] The monomer MA-Ala-OEt was prepared by the acylation of L-alanine ethyl ester with methacryloyl chloride. The monomer, MAAm as a comonomer and 0.2 mol% of tricosaglycol dimethacrylate as a crosslinking agent were polymerized in ethanol by irradiation of 30 kGy of γ -rays from a ⁶⁰Co source at 25 °C. The unconverted monomer was extracted with ethanol from the gel, which was allowed to stand in fresh water (300 ml) several times to give a hydrogel.

as well as the homopolymer of MAAm with variation in temperature. Poly-MAAm hydrogel showed a consistent water absorption over the temperature range examined. This fact shows that the acrylamide residue does not possess a temperature-responsive function for water absorption. The copolymer of MA-Ala-OEt with 10 mol% of MAAm absorbed 900% water at 0 °C and 150% at 10 °C. Water absorption was a constant value (100%) at higher temperatures. The abrupt decrease in water absorption with the elevation of temperature was also observed for the copolymer

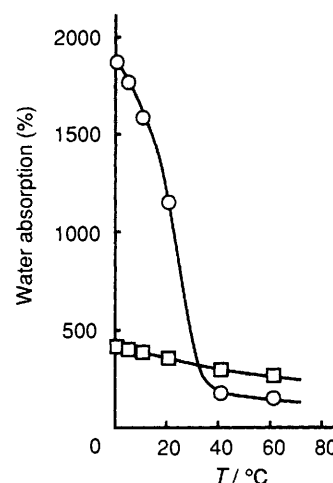


Fig. 1 Change in water absorption of polymer hydrogels containing methacryloyl L-alanine alkyl esters, ○: methyl, □: ethyl

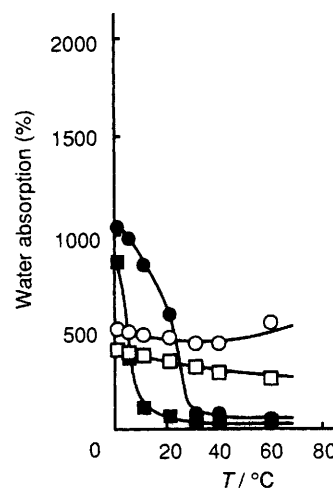


Fig. 2 Change in water absorption of copolymer hydrogels containing methacryloyl L-alanine ethyl ester (MA-Ala-OEt) and methacrylamide (MAAm), □: MA-Ala-OEt, ■: MA-Ala-OEt-MAAm (9:1), ●: MA-Ala-OEt-MAAm (5:5), ○: MAAm

MA-Ala-OEt with 50 mol% of MAAM: 1050% at 0 °C, 600% at 20 °C and 100% at 30 and 40 °C. These results indicate that the copolymers show a thermoresponsive volume characteristic. It is surprising that the introduction of only 10 mol% of MAAM recovered the thermoresponsive water absorption of the poly-MA-Ala-OEt hydrogel. The copolymer hydrogel containing 50 mol% of MAAM showed a similar change in water absorption (but at half scale) to that of MA-Ala-OMe as the temperature increased.

These results demonstrate that the Ala-OEt residues in copolymer hydrogels show the same function of water absorption as Ala-OMe ester group as their terminal ethyl esters are isolated by MAAM residues. It is also interesting that the water absorption of the copolymer hydrogels at higher temperatures was lower than that of poly-MA-Ala-OEt hydrogel. This fact suggests that the poly-MA-Ala-OEt hydrogel is prevented not only from absorbing but also from

excluding water by the formation of the tight structure in the side chains owing to the association of the terminal hydrophobic alkyl groups.

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