Preparation and Characterization of Two HEMA/PVA Copolymers: Poly[HEMA-co-(PVA-AA)] and Poly[HEMA-co-(PVA-MA)]

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SYNOPSIS

The copolymers of poly[HEMA-co-(PVA-AA)] and poly[HEMA-co-(PVA-MA)] were synthesized and characterized. The presence of PVA-AA in the copolymer increased the mechanical strength but decreased the water content of the material. The presence of PVA-MA, on the other hand, caused a decrease of mechanical strength and an increase of water content. The ionization of acidic group in poly[HEMA-co-(PVA-MA)] resulted in the swelling of the copolymer, and the swelling extent was controlled by the change of pH. Both copolymers have great potential in biomedical application. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are known for their excellent biocompatibility in the physiological environment. Of the hydrogels studied, poly(vinyl alcohol) (PVA) and poly(2-hydroxyethyl methacrylate) (poly-HEMA) have received considerable attention in biochemical and biomedical applications.[1-6] It is believed that poly-HEMA contained significant amount of water, therefore, exhibiting surface energy similar to that of the body tissues.[7,8] On the other hand, PVA was claimed to have good mechanical strength.[9,10] To fully utilize these properties, we were interested in making the copolymers based on HEMA and PVA. The PVA polymer was esterified with acrylic (PVA-AA) or maleic acids (PVA-MA) and then copolymerized with HEMA monomers to form hydrogels. Because PVA-MA contained extra ionizable carboxylic acids as compared to that of PVA-AA, the properties of the two copolymers are significantly different. We now report the preparation of these two copolymeric materials. The characteristics and possible applications of these two polymers are also discussed.

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EXPERIMENTAL

Materials

All chemicals used in this experiment are of reagent grade. Poly(vinyl alcohol), 2-hydroxyethyl methacrylate, maleic anhydride, acryloyl chloride, and *N*-methyl-2-pyrroldone were purchased from Merck-Schuchardt (Germany). Poly(vinyl alcohol) used in this experiment has molecular weight of 72,000. 1,1,1-Trimethyloyl propane trimethacrylate (TMPTMA) and 2,2-diethoxyacetophenone (DEAP) were obtained from TCI (Kasei, Tokyo, Japan).

Methods

PVA Esterified with Maleic Anhydride (PVA-MA)

Five grams of PVA was mixed with 11.2 g of maleic anhydride in 50 mL dimethyl sulfoxide, and the esterification reaction was carried out at 60°C for 5 h with continuous stirring. The PVA-MA polymer was then isolated according to the method described by Chiang et al.[11] The isolated product was characterized by IR spectum, and the extent of esterification was determined by the amounts of NaOH required to titrate the PVA-MA to its end point. The PVA-MA was stored in solid form at 4°C until used.

PVA Esterified with Acrylic Acid (PVA-AA)

Fifteen grams of PVA was dissolved in 500 mL of hot *N*-methyl-2-pyrroldone (85°C). The solution was cooled to room temperature, and about 18 mL of acryloyl chloride was added. The reaction was stopped after 3–5 min by slowly pouring the mixture into 40× volume of cold water. The PVA-AA product formed a fiberlike structure, and it could be dissolved in HEMA. The isolated PVA-AA was further purified by repeated precipitation (in water) and dissolution (in HEMA). The PVA-AA was then characterized by IR spectrum and the extent of esterification was determined from the results of element analysis. The PVA-AA was dissolved in HEMA and stored at 4°C until used.

Thin Films of Hydrogels

Thin films of three different hydrogels, poly-HEMA, poly[HEMA-co-(PVA-AA)] and poly[HEMA-co-(PVA-MA)] were made according to the procedure described previously.[12] The reaction mixture contained HEMA (monomer), TMPTMA (crosslinking agent), DEAP (initiator), and PVA-AA or PVA-MA. These components were mixed as specified in Table I and then injected into the square cavity between two glass plates with a spacer of 0.3 mm thick. Photopolymerization was performed by irradiation of UV light (365 nm, model B-100, Black-ray, USA) onto the glass plates at a distance of 30 cm. The total irradiation time was 30 min with 15 min on each side of the reaction system. After the reaction the polymeric film was removed from the glass plates, washed, and immersed in water.

RESULTS AND DISCUSSION

Indentification of PVA-AA and PVA-MA

The IR spectra of the PVA, PVA-AA, and PVA-MA are shown in Figure 1. Two adsorption bands (1720 and 1640 cm^{-1}) for both PVA-AA and PVA-MA were due to the stretching of $-O-C=O$ and $-C=C-C=O$, respectively. The broader absorption band (around 3000 cm^{-1}) observed for PVA-MA are due to the strong hydrogen bonding between carboxylic acids and other hydroxyl groups. By using the methods of acid titration (Fig. 2) and elemental analysis (C: 52.0%, H: 5.93% for PVA-AA), the extents of esterification of PVA-MA and PVA-AA were estimated to be about 42 and 36%, respectively. The titration end point of PVA-MA was found to be about pH 6.5 with pKa of 3.2, which is between the first pKa (1.9) and second pKa (6.3) of the maleic acid.

Table I Various Compositions of the Two Copolymers: Poly[HEMA-co-(PVAL-AA)] and Poly[HEMA-co-(PVAL-MA)][a,b]

Item	HEMA	PVA-AA	PVA-MA	TMPTMA	DEAP	Weight Ratio, PVA-X/HEMA
1	100	0	0	0.6	0.4	0
2	100	0	0	6.0	0.4	0
3	99	1	0	0.6	0.4	0.010
4	95	5	0	0.6	0.4	0.053
5	90	10	0	0.6	0.4	0.111
6	90	10	0	6.0	0.4	0.111
7	99.5	0	0.5	0.6	0.4	0.005
8	97	0	3	0.6	0.4	0.031
9	95	0	5	0.6	0.4	0.053
10	90	0	10	0.6	0.4	0.111
11	90	0	10	2.4	0.4	0.111
12	97	0	3	6.0	0.4	0.031
13	95	0	5	6.0	0.4	0.053
14	90	0	10	6.0	0.4	0.111
15	90	0	10	7.2	0.4	0.111
16	90	0	10	9.6	0.4	0.111

[a] Number represents part (in weight) for each component.
[b] Abbreviations: HEMA, 2-hydroxyethyl methacrylate; TMPTA, 1,1,1-trimethylol propane trimthacrylate; DEAP, 2,2-diethoxyacetophenone.

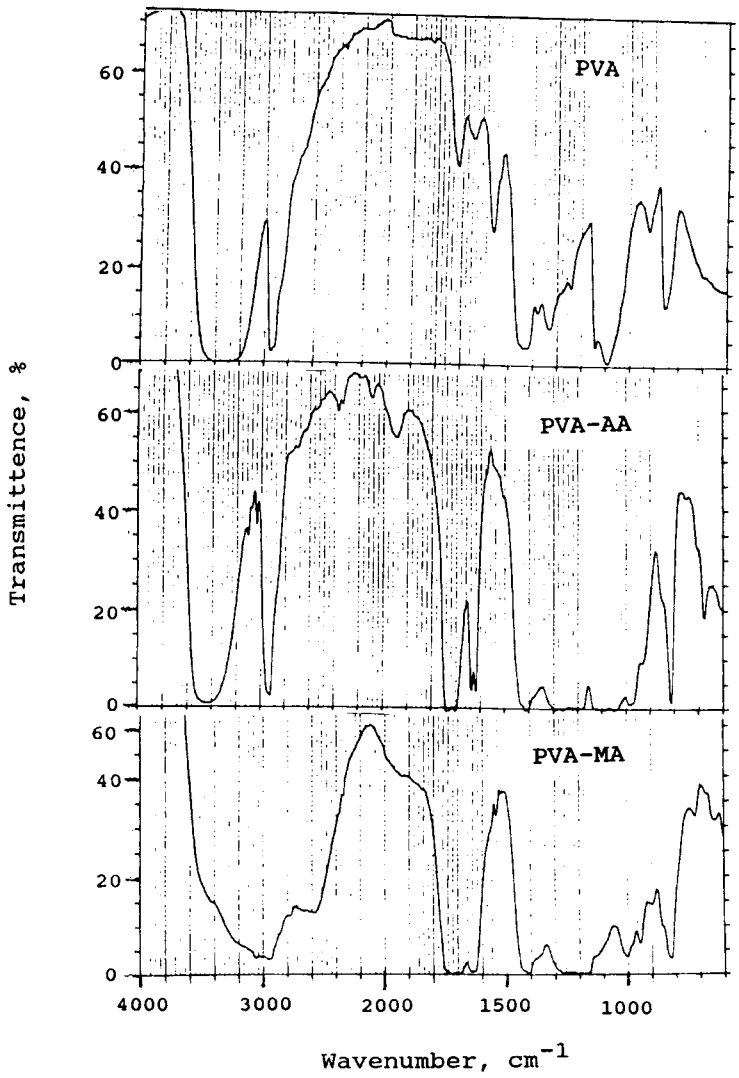

Figure 1 IR spectra of PVA, PVA-AA, and PVA-MA.

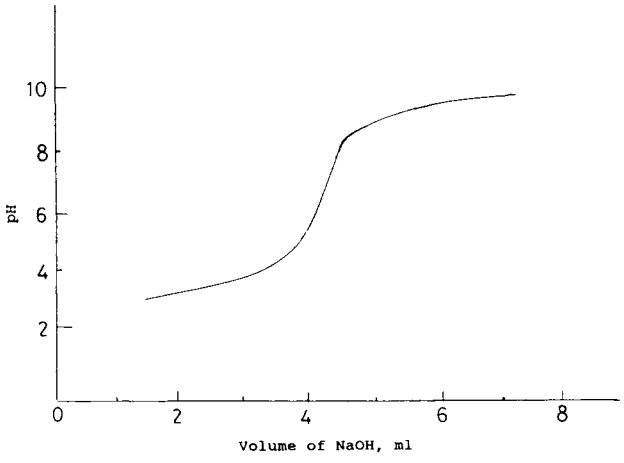

Figure 2 Titration curve of PVA-MA.

Characteristics of the Two Copolymers

The physical properties of the hydrogel films with various compositions for poly[HEMA-co-(PVA-AA)] are shown in Figure 3. As shown in this figure, the copolymer with higher PVA-AA content had Young's modulus higher than those with low (or no) PVA-AA content. Corresponding to this change, tensile strain decreased with increasing PVA-AA concentration. The water content of the copolymer on the other hand decreased with increasing PVA-AA content. We believed that PVA-AA not only provided double bonds for chain extension with HEMA but also served as the crosslinking species (as macromolecular crosslinking agent). As a result, the copolymeric hydrogel film is stronger than its

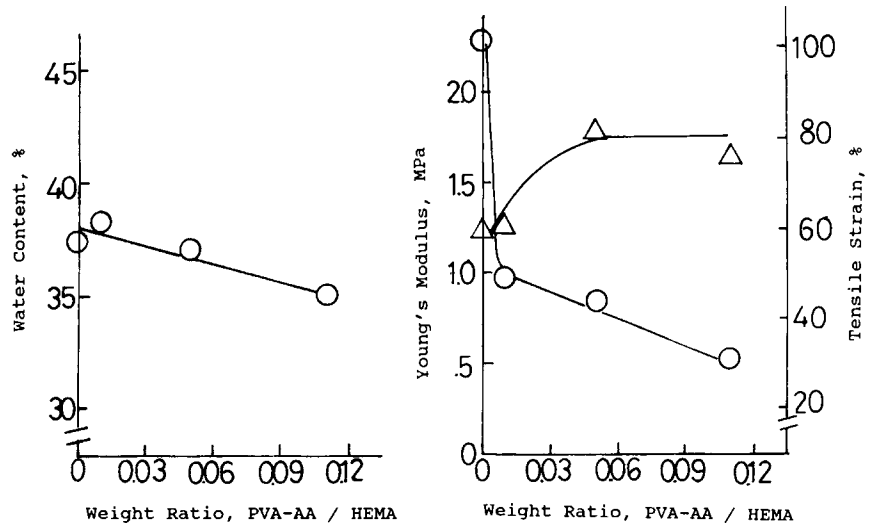

Figure 3 Effect of PVA-AA content on the physical properties of poly[HEMA-co-(PVA-AA)]: (a) water content and (b) Young's modulus (— △ —) and tensile strain (— ○ —). The compositions of the copolymers are listed in Table I (items 1, 3, 4, and 5).

poly(HEMA) counterpart. For example, the Young's modulus of the hydrogel films with high PVA-AA content is 1.57 MPa, higher than 1.17 MPa observed for poly(HEMA).

The physical properties of another copolymer poly[HEMA-co-(PVA-MA)] were however different (Fig. 4). The water content of this copolymer increased with increasing the content of PVA-MA. This could be attributed to the highly ionized carboxylic acids existing in the polymeric material. The negative-charged group repelled each other, leaving space for water molecules in the polymeric network. PVA-MA had a great effect on the mechanical strength of the copolymer. As shown in Figure 4(b), the Young's modulus decreased significantly, but the tensile strain increased with the presence of PVA-MA in the hydrogel network.

This proposed effect of the negative-charged car-

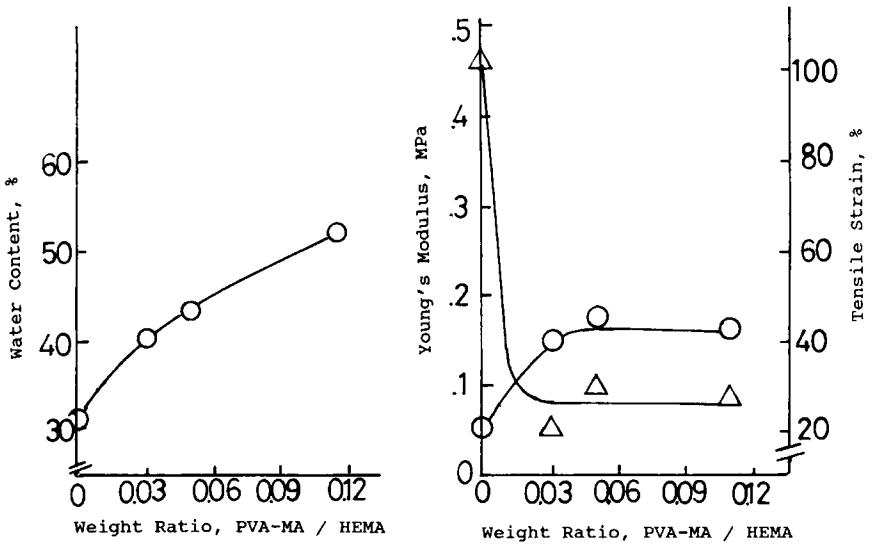

Figure 4 Effect of PVA-MA content on the physical properties of poly[HEMA-co-(PVA-MA)]: (a) water content and (b) Young's modulus (— △ —) and tensile strain (— ○ —). The compositions of the copolymers are listed in Table I (items 2, 12, 13, and 14).

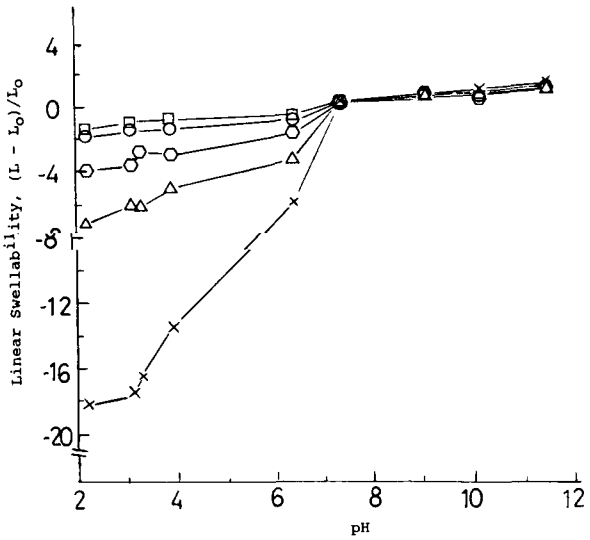

Figure 5 Effect of PVA-MA content on the linear swellability of poly[HEMA-co-(PVA-MA)]. The concentration of TMPTMA is 0.6% (in weight part) and the weight ratios of PVA-MA to HEMA are: 0.005 (— □ —), 0.010 (— ○ —), 0.031 (— o —), 0.053 (— △ —), and 0.111 (— × —).

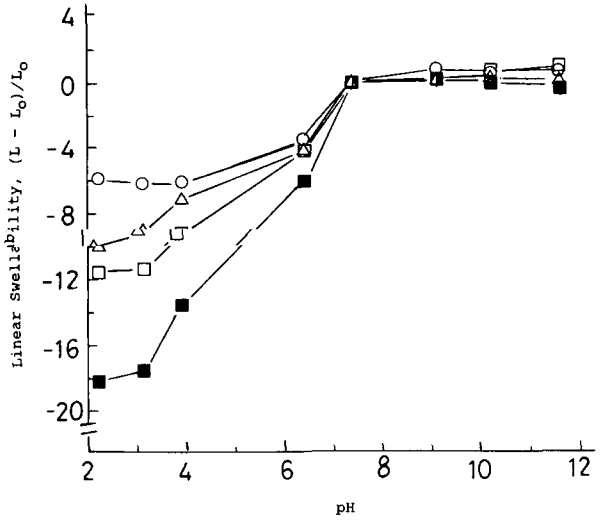

Figure 6 Effect of TMPTMA content on the linear swellability of poly[HEMA-co-(PVA-MA)]. The weight ratio of PVA-MA to HEMA was 0.111 and the concentrations of TMPTMA used are: 0.6% (— ■ —), 2.4% (— □ —), 7.2% (— △ —) and 9.6% (— ○ —).

boxyl ions existing in the network structure of the copolymer was sustained by the effect of pH on the swellability of poly[HEMA-co-(PVA-MA)]. The linear swelling capability of the hydrogels of poly[HEMA-co-(PVA-MA)] is shown in Figure 5. The length of the hydrogel increased with increasing pH value between pH 2 and 7. The swellability curve titrated by pH change appeared to shift to the more alkaline pH (compared Fig. 5 with Fig. 2). This result is not unexpected because the maleic group has been converted to malic group after polymerization. The malic acid has an pKa of 3.4, which is higher than the first pKa of the maleic acid. Figure 5 also showed that the extent of the swellability increased with increasing content of PVA-MA in the hydrogel film. Higher crosslinking nevertheless hindered the swelling ability of the hydrogel (Fig. 6). The length of the hydrogel remained almost constant at the pH higher than 7.0, indicating that all carboxylic groups have been ionized at this pH. It is conceivable that the negative-charged carboxyl ions repel each other, resulting in an increase of the skeletal length (and pore size) of the hydrogel matrix.

The surface contact angles, water contents, and urea mass transfer rates of the three hydrogels are listed in Table II. As shown in this table, the contact angle of poly[HEMA-co-(PVA-AA)] is higher than that of poly-HEMA. However, the film became more hydrophilic by substituting PVA-AA with PVA-MA, due to the presence of negative charge on the carboxyl group. Consistent with the fact of larger porosity created by the repelling carboxylic ions, the water content of poly[HEMA-co-(PVA-MA)] are higher than that of poly[HEMA-co-(PVA-AA)]. All three films have about the same urea transfer rate.

Table II Physical Properties of the Hydrogels

	Contact Angle	Water Content	Urea Transfer Rate (cm^2/s)
Poly-HEMA[a]	75°	32%	6.6×10^{-5}
Poly [HEMA-co-(PVA-AA)][b]	86°	29%	3.7×10^{-5}
Poly [HEMA-co-(PVA-MA)][c]	75°	43%	1.3×10^{-5}

[a] See item 2 in Table I for composition.
[b] See item 6 in Table I for composition.
[c] See item 14 in Table I for composition.

We have demonstrated that when PVA-AA was introduced to copolymerize with the HEMA, the material became stronger but maintained the hydrogel characteristics. This material therefore has a better mechanical property than the soft poly-HEMA hydrogel. The new material can be used in construction of hydrogel-based draining tube[12] for body fluid to replace the current most used silicone tubing. While poly[HEMA-co-(PVA-MA)] were softer, this copolymeric material has a great potential in biomedical applications such as controlled drug release.[13] Although the pore size of poly[HEMA-co-(PVA-MA)] was regulated most effectively between pH 4 and 6, the copolymers effective in other pH range could be obtained by coupling acids of various chain length to the PVA molecules. The potential biomedical application of the two copolymers is currently under investigation in our laboratory.

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