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Swelling Process and Order−Disorder Transition of Hydrogel Containing Hydrophobic Ionizable Groups

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ABSTRACT: A moderately water-swollen hydrogel with molecularly-ordered aggregate structure was prepared by copolymerizing acrylic acid with the hydrophobic 16-acryloylhexadecanoic acid (AHA) and 12-acryloyldodecanoic acid (ADA). X-ray diffraction indicated that the swelling of the network occurs first by disordering of a layer structure and then by the elimination of side-chain crystallization. Changes in the degree of swelling are produced by either changes of pH or the addition of ethanol to the aqueous gel. The swelling data are consistent with the X-ray diffraction results.

Introduction

We have previously synthesized a water-swollen hydrogel with a molecularly-ordered structure by copolymerizing acrylic acid (AA) with the hydrophobic *n*-stearyl acrylate (SA).[1] The poly(SA-*co*-AA) gel underwent reversible order−disorder transition with a change in temperature and dramatically changed its Young's modulus at a certain temperature.[2] Polyelectrolyte gels with organized structure have been prepared by incorporating positively-charged surfactant molecules[3,4] (*n*-alkylpyridinium ions) to a polysulfonic network, whereupon the size of the alkyl chains and the concentration of the surfactant played a crucial part in the organization.[5] Thermal and electrical properties of polypeptide gel based on formation of a charge-transfer complex in dimethyl sulfoxide were also studied.[6]

Water-swollen hydrogels prepared from synthetic polymers are generally amorphous and have no particular ordered structure on the molecular level, and as far as we know, this is the first example showing an order−disorder transition in a synthetic polymer gel.

In this paper we have synthesized a water-swollen hydrogel containing 12-acryloyldodecanoic acid (ADA) and the hydrophobic 16-acryloylhexadecanoic acid (AHA). Polymer gels with these moieties underwent reversible order−disorder transitions with a change of temperature, pH, and solvent composition. The aggregate structure associated with the swelling behavior was studied by X-ray diffraction, and it was found that the swelling of the network first leads to the destruction of organized aggregate layers and then to the disappearance of side-chain crystallization.

Experimental Section

Materials. AHA was synthesized by esterifying acryloyl chloride (Tokyo Kasei) with 16-hydroxyhexadecanoic acid (Tokyo Kasei; 99%) in tetrahydrofuran (THF) in the presence of triethylamine at 4 °C for 12 h. THF-soluble matter was collected, and the product was recrystallized from methanol and dried under vacuum. ADA was prepared in a manner similar to that of AHA using 12-hydroxydodecanoic acid (Aldrich; 97%). The chemical structure of these products was confirmed by ^{1}H NMR, ^{13}C NMR (JEOL GSX-400, 400 MHz), and IR spectroscopy. Acrylic acid (AA; Wako) was distilled at 30 °C under 900 Pa before use. α,α′-Azobis(isobutyronitrile) (AIBN; Tokyo Kasei) used as a radical initiator and *N,N′*-methylenebis(acrylamide) (MBAA; Wako) used as a cross-linking reagent were recrystallized from an ethanol solution.

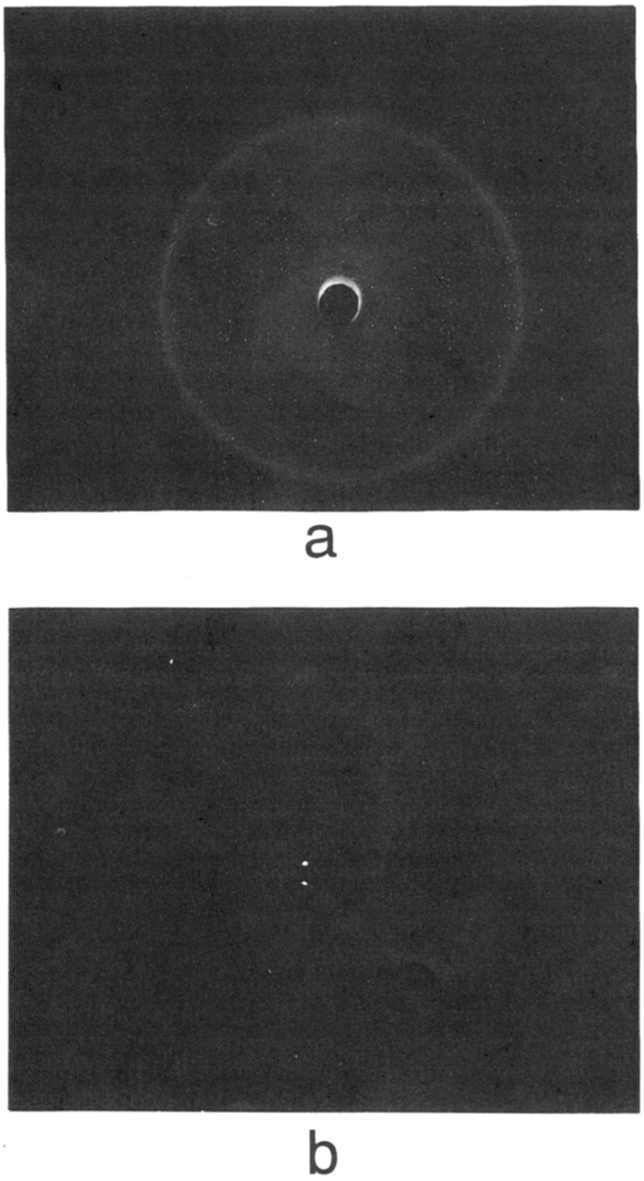

Figure 1. Wide-angle X-ray diffraction (WAXD) patterns of copolymer gels swollen in water. Sample thickness: 2 mm. (a) Poly(AHA-*co*-AA) gel with $F = 0.33$; q (degree of swelling) $= 1.12$. (b) Poly(ADA-*co*-AA) gel with $F = 0.33$; $q = 1.45$.

Preparation. The poly(AHA-*co*-AA) gel was prepared by radical copolymerization in the presence of 1.5×10^{-1} M MBAA in ethanol. The total monomer concentration was kept at 3.0

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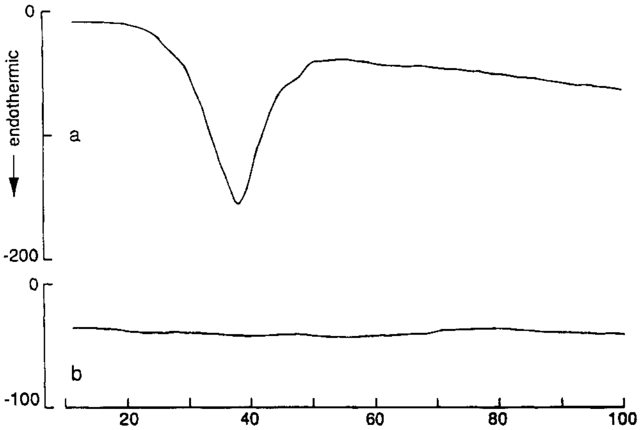

Figure 2. DSC thermograms of copolymer gels swollen in water. Samples are the same as those in Figure 1.

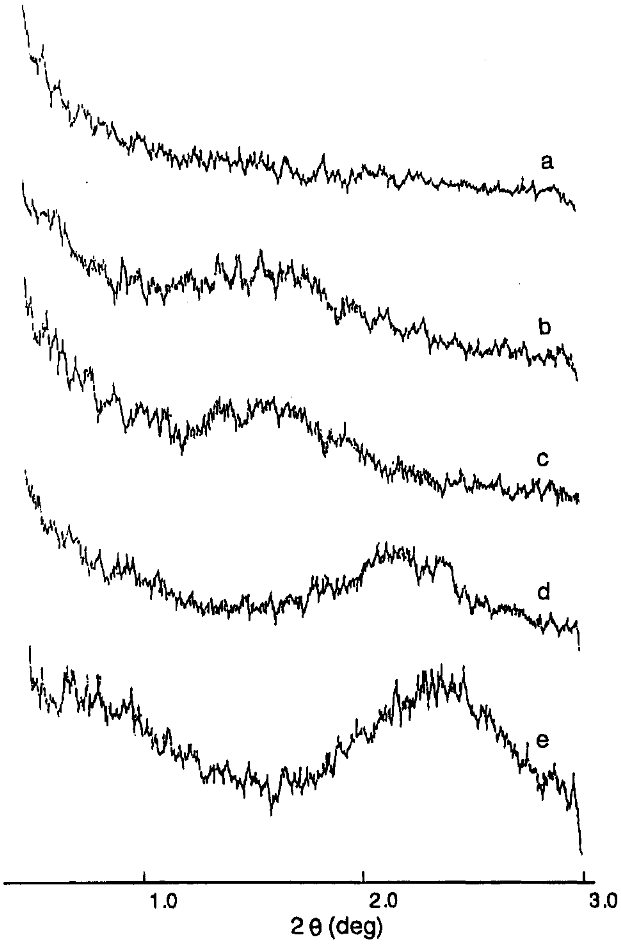

Figure 3. SAXD patterns of water-swollen and dry poly(AHA-*co*-AA) gels with different F. Sample thickness: 2 mm. (a) $F = 0.17$; $q = 1.27$. (b) $F = 0.33$; $q = 1.12$. (c) $F = 0.40$; $q = 1.16$. (d) $F = 0.50$; $q = 1.13$. (e) $F = 0.50$; dry.

M. Polymerization was carried out at 55 °C for 24 h, and during this period nearly 100% of monomer was polymerized and formed a chemically cross-linked polymer gel. The poly(ADA-*co*-AA) gel was prepared similarly to the poly(AHA-*co*-AA) gel by using ADA. After polymerization, the gels were immersed in a large amount of ethanol for more than 3 days to remove the monomers, un-cross-linked polymers, and initiator and then in water for a week until they reached equilibrium.

Measurements. The mole fraction F of AHA units in the poly(AHA-*co*-AA) gel [or ADA units in the poly(ADA-*co*-AA) gel] was determined by ^{1}H NMR from the intensity ratio of the peaks for α-proton of AHA (2.17 ppm) and α-proton of AA (2.66 ppm).

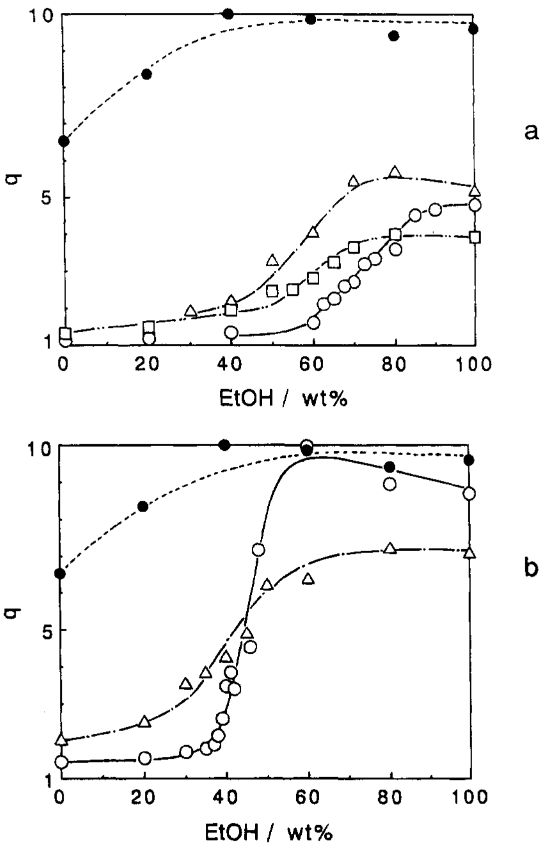

Figure 4. Degree of swelling (q) of poly(AHA-*co*-AA) (a) and poly(ADA-*co*-AA) (b) gels with different F as a function of ethanol–water composition. Temperature: 25 °C. (a) (●) $F = 0$ (PAA gel); (△) $F = 0.17$; (□) $F = 0.25$; (○) $F = 0.33$. (b) (●) $F = 0$ (PAA gel); (△) $F = 0.17$; (○) $F = 0.33$.

The ordered structures of poly(AHA-*co*-AA) and poly(ADA-*co*-AA) gels were studied by X-ray scattering. The wide- and small-angle X-ray diffraction (WAXD and SAXD) studies of the poly(AHA-*co*-AA) gel in various ethanol–water mixtures and at various pH values used an X-ray diffractometer (XD-610, Shimadzu Co. Ltd.) with Ni-filtered Cu Kα radiation (40 kV, 30 mA). The order–disorder transitions for the gel both in the swollen state and in the dry state were analyzed using a differential scanning calorimeter (DT-40, Shimadzu Co. Ltd.). The samples were hermetically sealed in aluminum pans and scanned under nitrogen from 10 to 100 °C with a heating rate of 1 °C/min. The sample weight was varied between 7 and 15 mg, and no weight loss was recorded during the experiments.

The degree of swelling (q), the weight ratio of the swollen and dry gel, was determined in various ethanol–water mixtures and varying pH at 25 °C.

Results and Discussion

Swollen poly(AHA-*co*-AA) gels with various F were studied by WAXD. The poly(AHA-*co*-AA) gel with $F = 0.17$ showed no diffraction peak, while those with $F = 0.33$, 0.40, and 0.50 showed diffraction peaks at $2\theta = 21.8°$ corresponding to a lattice spacing (d_1) of 0.41 nm (Figure 1). By contrast, the poly(ADA-*co*-AA) gel showed no peaks for any F value, indicating the importance of sufficient size and concentration of the alkyl side chains.

Figure 2 shows DSC thermograms for water-swollen poly(AHA-*co*-AA) gel (a) and poly(ADA-*co*-AA) gel (b) with $F = 0.33$. The poly(AHA-*co*-AA) gel showed an endothermic peak at 38.3 °C, which corresponds to the melting of side-chain crystallization in poly(AHA), whereas the poly(ADA-*co*-AA) gel showed no endothermic peak. This indicates that an ordered structure is formed in the moderately swollen state if the hydrophobic alkyl groups are long enough to align side-by-side.

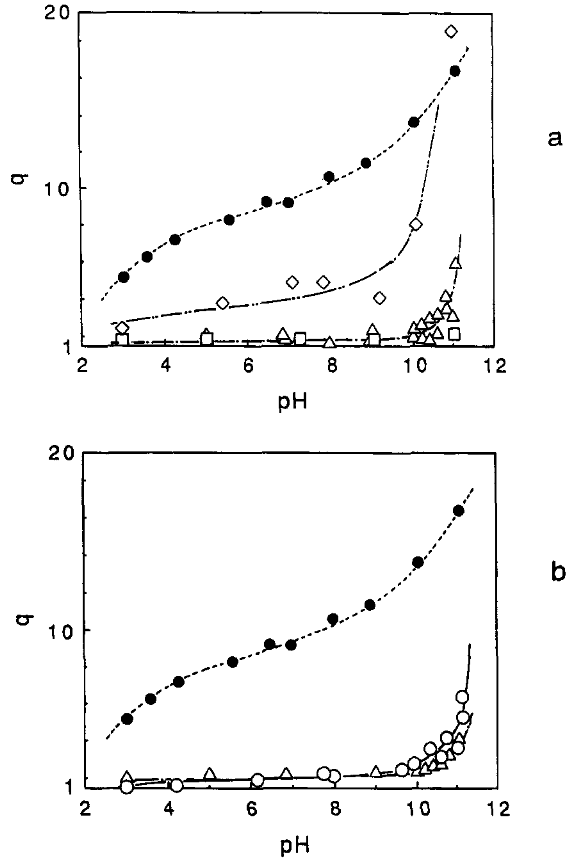

Figure 5. Degree of swelling (q) of poly(AHA-*co*-AA) (a) and poly(ADA-*co*-AA) (b) gels with different F as a function of pH. Temperature: 25 °C. (a) (●) $F = 0$ (PAA gel); (◇) $F = 0.08$; (△) $F = 0.17$; (□) $F = 0.25$. (b) (●) $F = 0$ (PAA gel); (◇) $F = 0.17$; (○) $F = 0.33$.

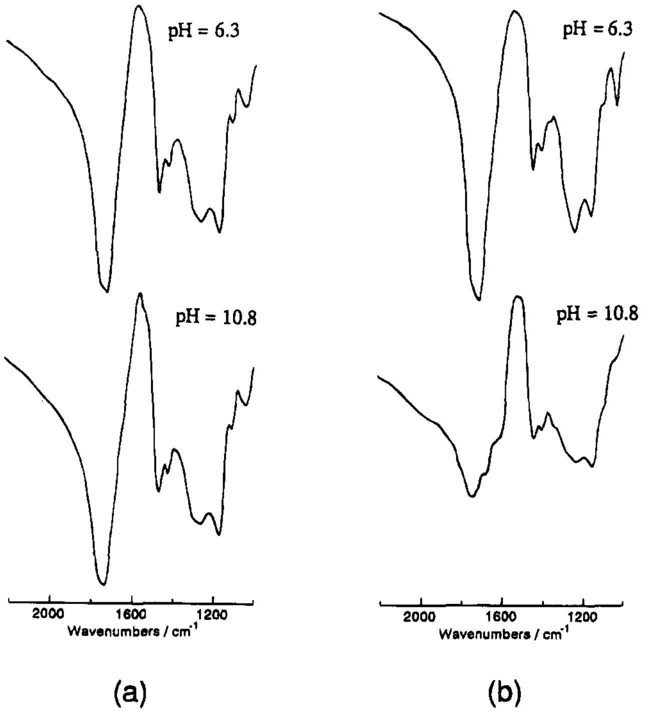

Figure 6. Infrared spectra of poly(AHA-*co*-AA) with $F = 0.17$ (a) and PAA (b).

Side-chain crystallization of acrylate and methacrylate polymers has been systematically investigated by Platé and Shibaev, who emphasized the importance of the cooperative nature of alkyl side-chain crystallization both in the condensed phase and in solution.[7,8] According to the literature,[9] stearyl side chains align tail-to-tail perpendicularly to the main chains. A similar tail-to-tail alignment can be assumed in the present case;

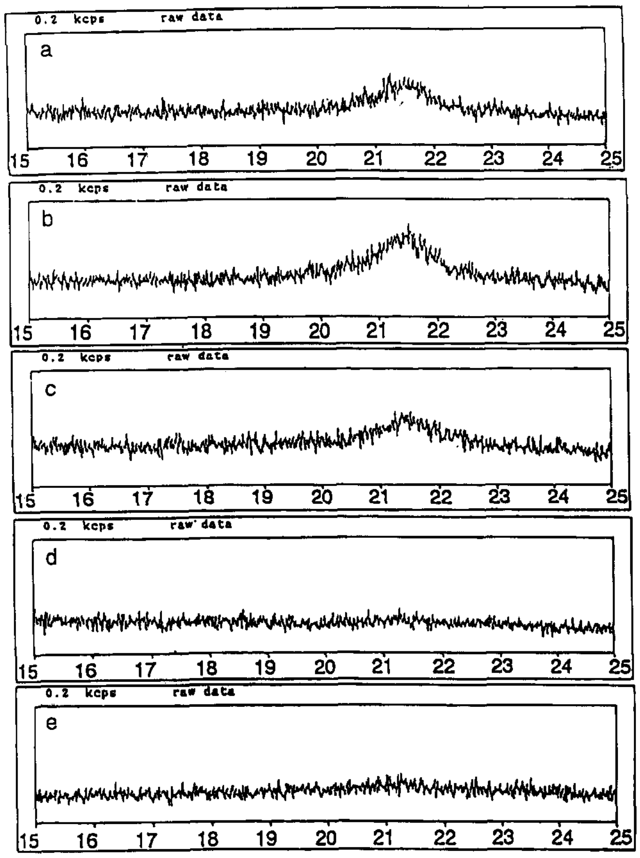

Figure 7. WAXD patterns of the poly(AHA-*co*-AA) gel ($F = 0.50$) swollen in various ethanol–water mixtures. Sample thickness: 2 mm. Temperature: 25 °C. (a) Water; $q = 1.13$. (b) 25 wt % ethanol; $q = 1.19$. (c) 50 wt % ethanol; $q = 1.32$. (d) 75 wt % ethanol; $q = 1.65$. (e) 100% ethanol; $q = 2.74$.

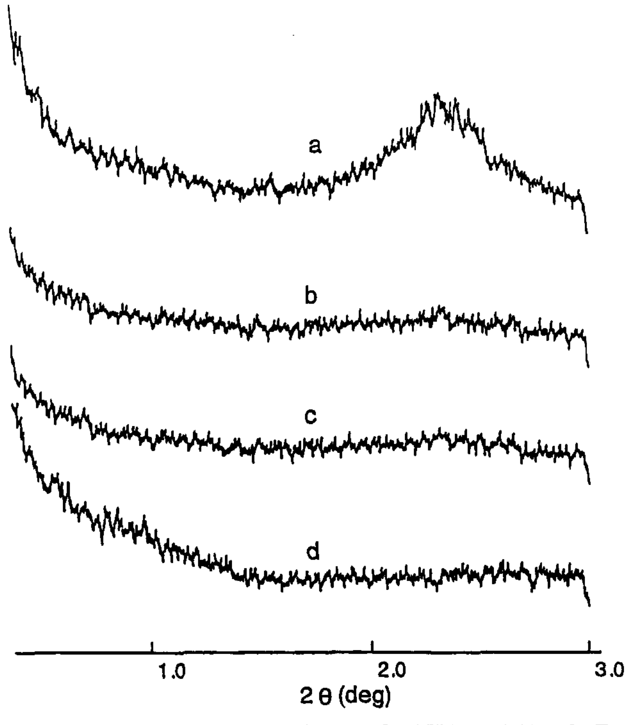

Figure 8. SAXD patterns of the poly(AHA-*co*-AA) gel ($F = 0.50$) swollen in various ethanol–water mixtures. Sample thickness: 2 mm. Temperature: 25 °C. (a) Water; $q = 1.13$. (b) 10 wt % ethanol; $q = 1.18$. (c) 25 wt % ethanol; $q = 1.19$. (d) 50 wt % ethanol; $q = 1.32$.

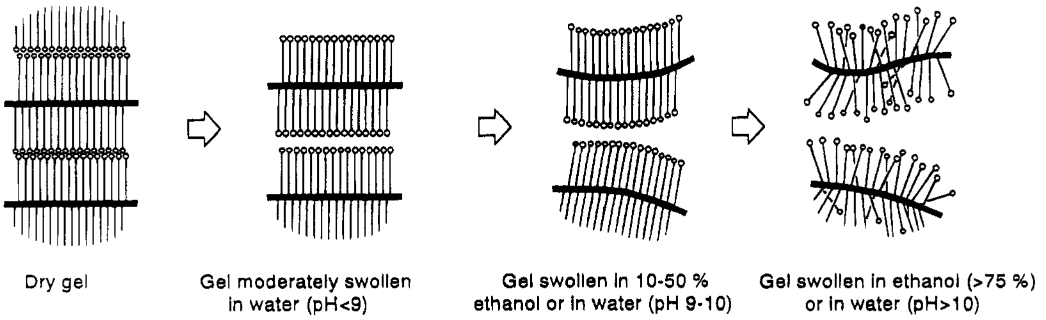

Figure 9. Schematic illustration of the change in organized structure of the poly(AHA-*co*-AA) gel by swelling in various media.

i.e., the diffraction should be attributed to the hexagonal packing of the long alkyl side chains of the hexadecanoic acid residues. The diffraction peak of the wet and dry gels ($F = 0.50$) corresponds to a spacing of 0.41 nm, characteristic of the hexagonal packing of the long alkyl side groups. It is essentially the same as that in the swelling gel and the dry polymers.

Small-angle X-ray diffraction (SAXD) by the swollen and dry copolymer gels is shown in Figure 3. SAXD of the dry gel with $F = 0.40$ and 0.50 appeared at $2\theta = 2.30°$ and 2.38°, i.e., lattice spacings of 3.80 and 3.71 nm, suggesting that the long alkyl side groups from a layered structure with a thickness of ca. 3.7–3.8 nm having a tilt of 53° to the main chain.[9] The swollen poly(AHA-*co*-AA) gel with $F = 0.33$, 0.40, and 0.50 showed diffraction peaks at $2\theta = 1.56°$, 1.62°, and 2.22° which correspond to lattice spacings of 5.66, 5.45, and 3.97 nm, respectively. The layer spacing in the swollen gel is larger than that in the dry sample and decreases with an increase in F. This indicates that water molecules in the polymer gel are preferentially absorbed between two aggregate layers of hexadecanoic acid groups aligned to the main chain. The AA units seem to enhance water absorption between the hexadecanoic acid groups.

These copolymer gels abruptly change their volume with a change in the solvent composition and pH. Figure 4 shows the degree of swelling (q) of poly(AHA-*co*-AA) (a) and poly(ADA-*co*-AA) (b) gels as a function of ethanol–water composition. The PAA gel ($F = 0$) increased its volume sharply when a relatively small amount of ethanol was added to water. On the contrary, q of poly(AHA-co-AA) gels remained as low as 2.0 at low alcohol concentration but showed extensive swelling when the ethanol concentration reached 40% and increased their volume several fold at higher ethanol contents. The ethanol concentration at which the swelling starts increased with an increase in F. A similar behavior was observed for the poly(ADA-*co*-AA) gel, but the swelling started at a lower ethanol concentration and the values were larger.

Figure 5 shows the pH dependence of q of poly(AHA-*co*-AA) (a) and poly(ADA-*co*-AA) (b) gels with various F. The PAA gel increased the volume with an increase of pH, while an incorporation of a small amount of AHA units strongly suppressed the swelling. The gel with $F = 0.17$ showed practically no swelling even at pH = 10. Similar results were obtained for the poly(ADA-*co*-AA) gel. These results suggest that hydrophobic interactions between alkyl side chains are strong enough to inhibit ionization of carboxylic groups even in the alkaline medium. In fact, the carboxylic groups of poly(AHA-*co*-AA) are largely in the undissociated state, showing a strong peak at 1720 cm^{-1} in water (pH = 6.3) and in the alkaline solution of pH = 10.8, in contrast with PAA which is mostly ionized at pH = 10.8 (Figure 6).

On the basis of these swelling data, the change in aggregate structure with a change in the solvent and pH has been studied by WAXD and SAXD. Figure 7 shows WAXD of the poly(AHA-*co*-AA) gel swollen in various ethanol–water compositions. A distinct diffraction peak at $2\theta = 21.8°$ or $d_1 = 0.41$ nm can be observed until the ethanol concentration is 50% but disappeared at an ethanol concentration 75% or higher. This result coincides with the result of Figure 4 which indicates that the copolymer gel starts swelling at an ethanol concentration higher than 60%. Interestingly, as shown in Figure 8 the SAXD peak of the same sample disappears at an ethanol concentration as low as 10%. These results indicate that a small concentration of ethanol eliminates the layered structure organization due to the long alkyl groups. This is also the case when the pH of the medium is changed. The SAXD pattern disappears when the gel is immersed in water of pH = 9, but the WAXD peak corresponding to $d_1 = 0.41$ nm is still present at pH = 9 and disappears only at pH > 11. These results are consistent with the swelling data shown in Figure 5.

It is evident that water molecules in the moderately-swollen polymer gel are presumably absorbed between the layers separated by the long alkyl groups attached to the main chain, increasing the layer spacing. An extensive volume increase of the gel observed at high pH or at high ethanol concentration occurs on elimination of side-chain crystallization. The process of the swelling and the change in structure of the poly(AHA-*co*-AA) gel are schematically illustrated in Figure 9.

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