Order–Disorder Transition of a Hydrogel Containing an *n*-Alkyl Acrylate

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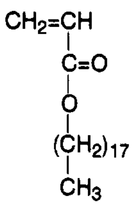
ABSTRACT: A moderately water-swollen hydrogel with a molecularly ordered structure was prepared by copolymerizing an acrylic monomer with a hydrophobic long alkyl side group—*n*-stearyl acrylate (SA)—with acrylic acid (AA). The long alkyl ester side chains of the gel form lamellar layers with a thickness of ca. 5 nm, and the lamellar distance of the swollen gels is nearly 0.8 nm larger compared to that of their dry state. This indicates that water molecules in the polymer gel are preferentially adsorbed between two aggregates of stearyl groups perpendicularly aligned to the main chain. We have also found that the poly(SA-*co*-AA) gel undergoes a reversible order–disorder transition with change in temperature and a dramatic change in its Young's modulus at a certain temperature.

Introduction

A polymer gel consists of an elastic cross-linked network with a fluid filling the interstitial space of the network, and a fundamental study on polymer gels has intensively been made in recent years.[1–3]

Water-swollen hydrogels are generally amorphous in nature and have no particular ordered structure at the molecular level except for some biological gels where higher ordered aggregates are observed in the "junction zones".[4] This might be one of the reasons why synthetic polymer gels suffer from a lack in mechanical toughness.

We have attempted to synthesize a water-swollen hydrogel with a molecularly ordered structure by copolymerizing an acrylic monomer with a hydrophobic long alkyl side group—*n*-stearyl acrylate (SA)—with acrylic acid (AA). We have found that poly(SA-*co*-AA) gel undergoes a reversible order–disorder transition with change in temperature and a dramatic change in its tensile modulus at a certain temperature. The crystallizing ordering of the long side chain of acrylate and methacrylate polymers has already been systematically investigated by Platé and Shibaev, who emphasized the importance of the cooperative nature of the side alkyl side chain both in the condensed phase and in solutions.[5–7] However, no attempt has been made to study the ordered structure of cross-linked polymer gels in the swollen state.



$CH_2{=}CH{-}C({=}O){-}O{-}(CH_2)_{17}{-}CH_3$

Stearyl acrylate: SA
(Octadecyl acrylate)

Experimental Section

Materials. Stearyl acrylate (SA, octadecyl acrylate) (Tokyo Kasei Kogyo Co. Ltd.) was repeatedly recrystallized from ethanol solution. Acrylic acid (AA) (Tokyo Kasei Kogyo Co. Ltd.) was distilled at 313 K under 933 Pa before use. α,α'-Azobis(isobutyronitrile) (AIBN) (Tokyo Kasei Kogyo Co. Ltd.) used as a radical initiator and *N,N'*-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries Ltd.) used as a cross-linking reagent were recrystallized from ethanol solution. Deuterated dimethyl sulfoxide (DMSO-d_6) (Tokyo Kasei Kogyo Co. Ltd.) used for NMR measurements was used without further purification.

Preparation. Poly(SA-*co*-AA) gel with various SA–AA compositions, F (F is defined as the mole fraction of SA in the total monomer), was prepared by radical copolymerization. The total monomer concentration in ethanol was kept at 3.0 mol dm^{-3} in the presence of 3.0×10^{-2} mol dm^{-3} MBAA. Polymerization was carried out at 323 K for 24 h and during this period nearly 100% of the monomer was polymerized and formed chemically cross-linked polymer gel. After polymerization, the gel was 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 it reached an equilibrium state.

Un-cross-linked poly(SA-*co*-AA) polymers were prepared by the same procedure as the poly(SA-*co*-AA) gel without using MBAA.

The sample for establishing the monomer–copolymer composition relation were obtained by copolymerizing the monomer mixture no more than 5–10%. The obtained polymers were purified and dried in vacuo.

Measurements. f, which is defined as the mole fraction of SA unit in poly(SA-*co*-AA) was determined by ^{1}H NMR measurement (JEOL GSX-400, NMR spectrometer, 400 MHz) of the intensity ratio of the peaks for the α-proton of SA (2.17 ppm) and the α-proton of AA (2.66 ppm). The reactivity ratios r_1 and r_2 for SA and AA, respectively, were evaluated by the Fineman–Ross method using the result of the ^{1}H NMR measurements.

The wide-angle X-ray diffraction study of the water-swollen poly(SA-*co*-AA) gel and the corresponding dry polymer gel was made using an X-ray diffractometer (XD-610, Shimadzu Co. Ltd.) with Ni-filtered Cu Kα radiation (40 kV, 30 mA). The melting and crystallization temperatures of the gels and the correspond un-cross-linked polymers were measured using a differential scanning calorimeter (DT-40, Shimadzu Co. Ltd.). For the X-ray and DSC measurements of the un-cross-linked polymers, a calculated amount of water was added to compare with the swollen gel samples. The sample were hermetically sealed in aluminum pans and scanned under a N_2 atmosphere from 290 to 343 K with a heating rate of 1 K/min. The melting and crystallization temperatures were calibrated against the melting transition peak of spectroscopic grade cyclohexane. The sample weight was varied between 4 and 10 mg, and no weight loss was recorded during the experiments.

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Table 1. Specific Characteristics of Poly(SA-*co*-AA)

				melting			crystallization		
F	q	d_1 (nm)	d_2 (nm)	ΔT_m (°C)	$\Delta H_m{}^a$ (kJ mol^{-1})	$\Delta S_m{}^a$ (J mol^{-1} K^{-1})	ΔT_c (°C)	$-\Delta H_c{}^a$ (kJ mol^{-1})	$-\Delta S_c{}^a$ (J mol^{-1} K^{-1})
0 G[b]	1283	amorphous							
0.005 G	440								
0.05 G	79.5								
0.1 G	8.1								
0.15 G	1.9	0.40	6.22						
DG[c]			5.45						
P[d]									
DP[e]		0.39							
0.25 G	1.6	0.39	5.88	49.3	30.6	94.7	45.0	32.2	99.9
DG			4.99	50.8	24.0	74.0	43.5	24.8	78.3
P				49.7	29.6	91.7	46.7	34.3	106.1
DP			5.07						
0.5 G	1.0	0.40		50.4	20.7	64.0	46.6	23.6	73.9
P		0.40		49.7	7.3	22.3	43.1	10.4	32.7
0.75 G	1.0	0.40		51.8	20.3	62.6	44.2	22.5	70.7
P		0.39		48.4	14.3	44.5	43.9	13.6	42.8
1.0 G	1.0	0.40		49.8	22.2	69.1	43.2	21.5	68.1
P		0.39		48.9	22.0	68.2	43.4	18.4	58.1

[a] ΔH_m, ΔS_m, ΔH_c, and ΔS_c are in units per mole of SA. [b] G: swollen gel. [c] DG: dry gel. [d] P: Un-cross-linked polymer. [e] DP: dry polymer.

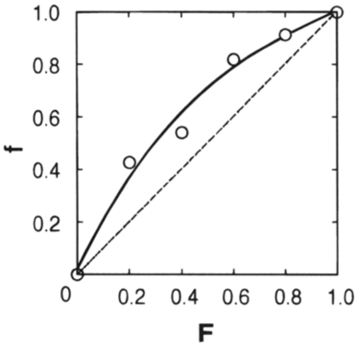
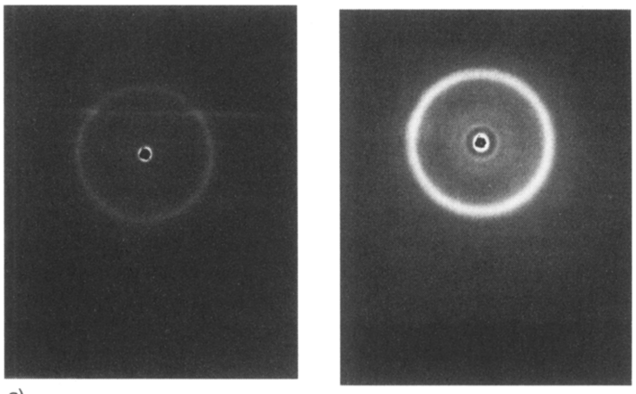


Figure 1. Monomer–copolymer composition curve for the copolymerization of SA and AA. F and f are defined in the text.



a) b)

Figure 2. Wide-angle X-ray diffraction patterns of poly(SA-*co*-AA) gel: (a) $F = 0.15$; (b) $F = 0.25$.

The mechanical properties of the poly(SA-*co*-AA) gel ($F = 0.25$, 0.55 mm thick, 4.3 mm wide, and 25 mm long) were measured with a tensile tester (TOM-500, Shinko Communication Industry Co. Ltd.). Young's modulus, E, was determined as the slope of the stress–strain curve where the strain rate was 1.0 mm min^{-1}.

Results and Discussion

Figure 1 shows the monomer–copolymer composition curve for the copolymerization of SA and AA. As shown in this figure, SA units are incorporated into the copolymer preferentially to AA units. From this result, monomer reactivity ratios of SA (r_1) and AA (r_2) were calculated as 3.0 and 0.5, respectively.

From these results, the number of SA units in a successive sequence of an SA and that of an AA in the copolymer were calculated,[8] and it was found that the numbers of SA units and AA units for the copolymer with $F = 0.25$ were 2 and 2.5, respectively. This suggests that the monomer sequence of the copolymer consists of two SA units and two or three AA units ideally in the beginning of the copolymerization.

The degree of swelling (q), which is defined as the weight ratio of swollen to dry gel, strongly depends on the copolymer composition. PAA gel ($F = 0$) showed q as high as 1283, while q of the copolymer gel rapidly decresed with increasing SA content: the q of the gel with $F = 0.05$, 0.10, 0.15, and 0.25 became 80, 8.1, 1.9, and 1.6, respectively. Polymer gels with $F > 0.5$ showed practically no swelling (Table 1). This is obviously due to extensive aggregate formation of hydrophobic long alkyl side groups in water.

To study the molecular structure of the gel, a wide-angle X-ray diffraction (WAXD) study of the swollen samples with various F was made.

PAA gel and poly(SA-*co*-AA) gels with $F = 0.005$, 0.05, and 0.01 (sample thickness 2.4 mm) showed no diffraction peaks through the whole 2θ scanning range. This indicates that the PAA gel and these copolymer gels are amorphous. When $F = 0.15$, a weak diffraction pattern appeared at $2\theta = 21.8°$, which is equivalent to a lattice spacing (d_1) of 0.40–0.41 nm (Figure 2a). The gel with $F > 0.25$ showed clear and strong diffraction at $2\theta = 22.5°$ or $d_1 = 0.39$ nm (Figure 2b). The lattice spacing changed no more than 0.01 nm when F of the gel changed from 0.25 to 1.0.

According to the literature,[7,9] this diffraction is attributed to interplanar spacing (100) of the crystalline state formed by the long alkyl side chain of poly(stearyl acrylate). The (100) interplanar spacings of the dry gel as well as the dry un-cross-linked copolymer with various copolymer compositions were found to be 0.39–0.40 nm, indicating that the side-by-side spacing between the long alkyl side groups of the swollen gel is essentially the same as that of the dry polymers.

A small-angle X-ray diffraction (SAXD) analysis was made for the water-swollen copolymer gels with various F values (Figure 3). The poly(SA-*co*-AA) gel with $F =$

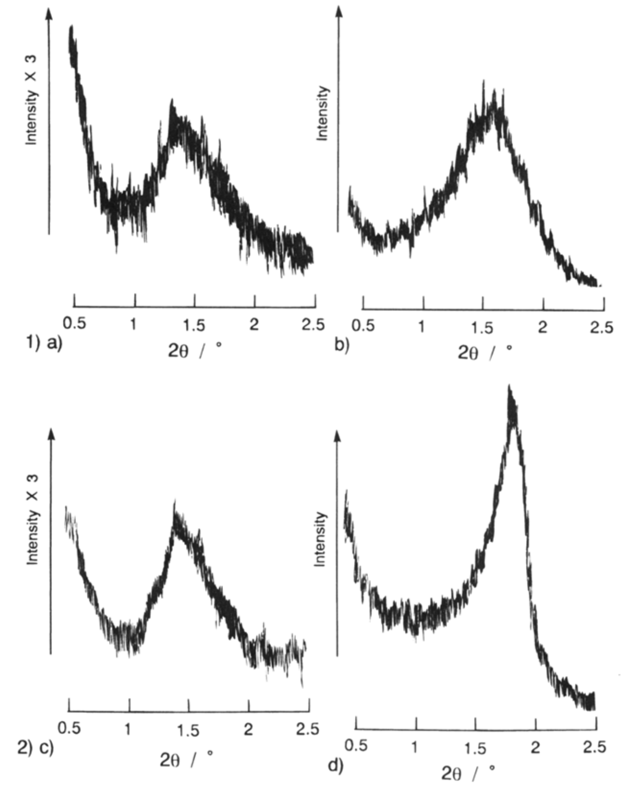


Figure 3. Small-angle X-ray diffraction of poly(SA-*co*-AA) gel. (1) $F = 0.15$: (a) water-swollen gel; (b) dry gel. (2) $F = 0.25$: (c) water-swollen gel; (d) dry gel.

0.15 showed a diffraction peak at $2\theta = 1.42°$, which corresponds to a lattice spacing (d_2) of 6.22 nm. The gel with $F = 0.25$ showed a diffraction peak at $2\theta = 1.50°$, which corresponds to $d_2 = 5.88$ nm. These gels were allowed to dry, and SAXD measurement was made in a similar manner. The dry cross-linked gel with $F = 0.15$ exhibited a diffraction peak at $2\theta = 1.62°$ or a lattice spacing of 5.45 nm. The copolymer gel with $F = 0.25$ exhibited a diffraction peak at $2\theta = 1.78°$, corresponding to $d_2 = 4.99$ nm. The un-cross-linked copolymer with $F = 0.25$ showed at $2\theta = 1.74°$, which is equivalent to a lattice spacing of 5.07 nm.

Assuming the stearyl group is in the extended β-sheet conformation and aligned perpendicularly to the main chain, the stearyl length is calculated as 2.57 nm. These results suggest that the long alkyl ester side chains form lamellar layers with a thickness of ca. 5 nm making a tail-to-tail alignment perpendicurly to the main chains. This is quite reasonable, since adjacent SA units in the chain backbone are not able to take the meso configuration (or isotactic diad) in the flat plane but take only racemic (or syndiotactic diad) configurations.

One should notice here that the lamellar distance (d_2) of the swollen gels is nearly 0.8 nm larger compared to that of their dry state (Figure 4). This indicates that water molecules in the polymer gel are preferentially adsorbed between two aggregates of stearyl groups perpendicularly aligned to the main chain. This should be due to the hydrophilic carboxyl groups of copolymerized acrylic acid units, because d_2 of the swollen gel with $F = 0.15$ was 0.4 nm larger than that of the gel with $F = 0.25$.

To clarify the ordered structure of the gel, we carried out DSC measurements and confirmed that these gels melt and crystallize with a change in temperature (Figure 5). As suggested from the X-ray results, the endothermic and exothermic peaks for the gel with $F =$ 0.15 were weak and those of the copolymer gels with $F = 0.25$ were intense and sharp. In all copolymer gels, hysteresis was observed whereupon the melting temperature was higher than the crystallization temperature. The transition temperature did not depend much on the copolymer composition (Figure 6). The enthalpy and entropy changes of melting as well as the crystallization of the copolymer gels are shown in panels a and

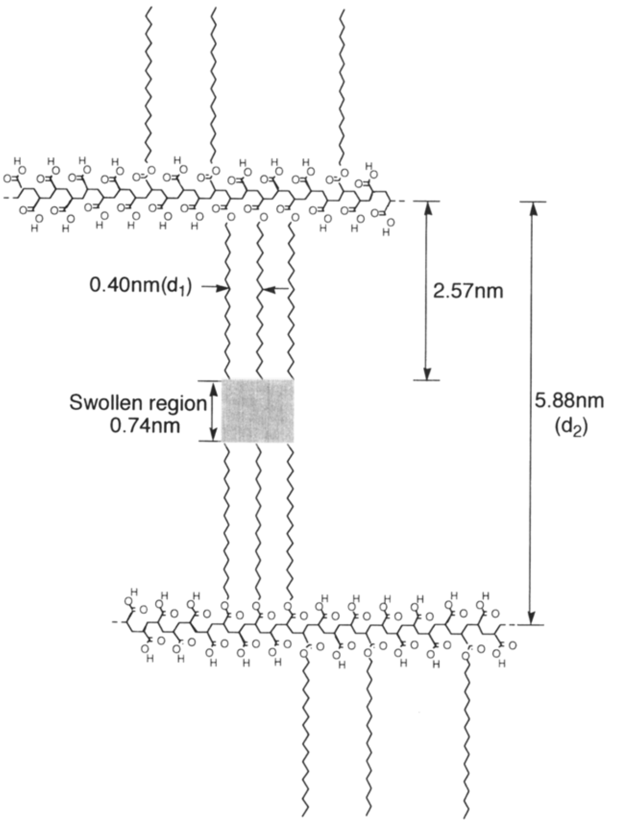
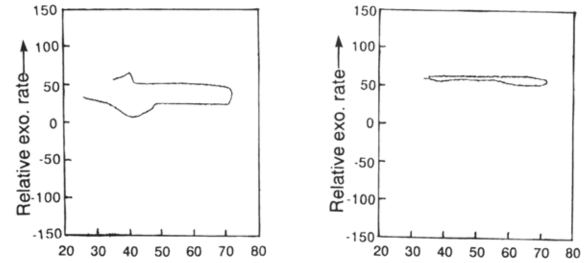
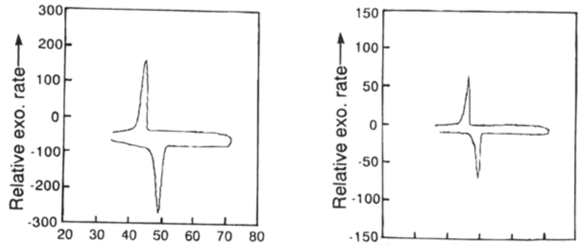


Figure 4. Schematic illustration of the structure of poly(SA-*co*-AA) gel ($F = 0.25$).



(a) F=0.15Gel

(b) F=0.15 Polymer



(c) F=0.25 Gel

(d) F=0.25 Polymer

Figure 5. DSC thermograms of poly(SA-*co*-AA) gels and corresponding un-cross-linked polymers: (a) gel, $F = 0.15$; (b) un-cross-linked polymer, $F = 0.15$; (c) gel, $F = 0.25$; (d) un-cross-linked polymer, $F = 0.25$.

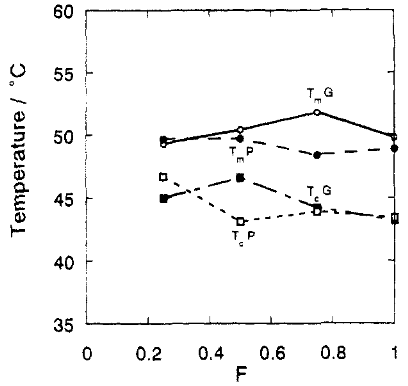


Figure 6. Dependences of melting (T_m) and crystallizing (T_c) temperatures on the copolymer composition (F) for poly(SA-*co*-AA) gel and the corresponding un-cross-linked polymer.

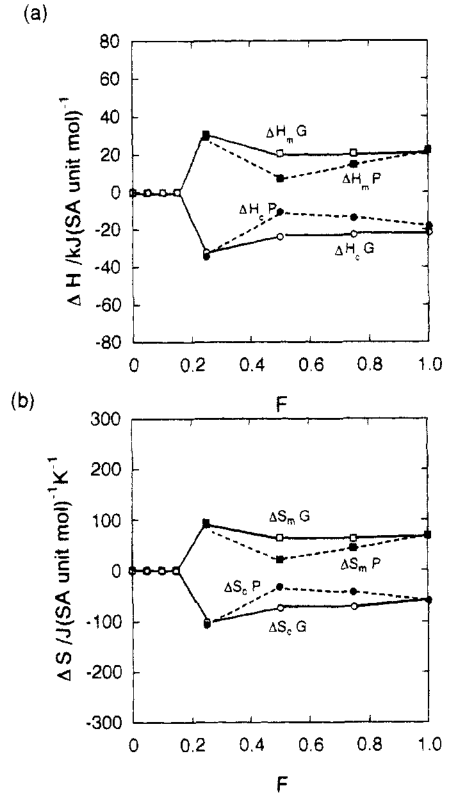


Figure 7. Dependences of (a) enthalpy and (b) entropy changes of melting and crystallization on the copolymer composition (F) for poly(SA-*co*-AA) gel and the corresponding un-cross-linked polymer. (a) ΔH_mG, melting for the gel; ΔH_cG, crystallization for the gel; ΔH_mP, melting for the polymer: ΔH_cP, crystallization for the polymer. (b) ΔS_mG, melting for the gel, ΔS_cG, crystallization for the gel; ΔS_mP, melting for the polymer; ΔS_cP, crystallization for the polymer.

b of Figure 7, respectively. The enthalpy and entropy changes are expressed per mole of stearyl acrylate unit. The results show that the enthalpy and entropy changes of the copolymer gel are somewhat larger than those of the corresponding copolymer, suggesting a better arrangement of stearyl groups in the gel compared with those in the un-cross-linked polymers.

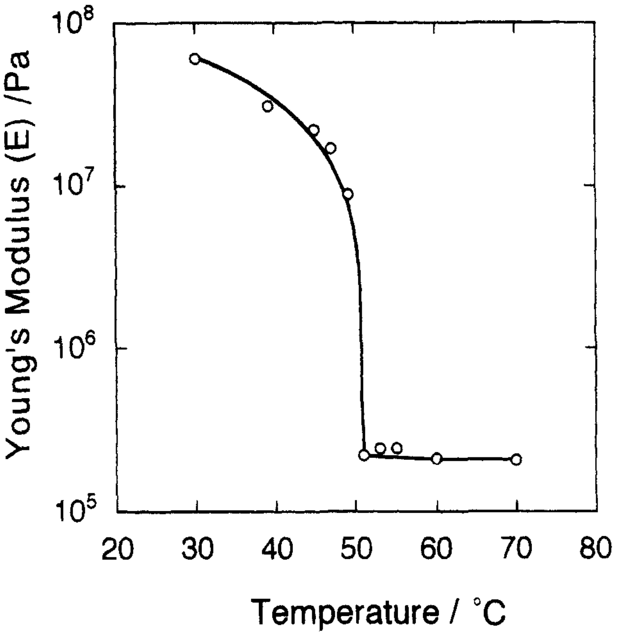


Figure 8. Temperature dependence of Young's modulus (E) of poly(SA-*co*-AA) gel (F = 0.25).

Young's modulus, E, of the poly(SA-*co*-AA) gel as a function of temperature is shown in Figure 8. E decreased gradually with increasing temperature from 30 to 47 °C and decreased abruptly from 1.7×10^7 to 2.2×10^5 Pa above 49 °C. The temperature at which E decreased abruptly coincides with the melting temperature of the gel obtained by DSC measurement. The gel showed a typical jelly-like softness above that temperature. The drastic change observed in mechanical property is reversible and cyclically reproduced by repeated temperature changes.

The described crystallization–melting behaviors were observed for other copolymer gels prepared from hexadecyl acrylate (HA) and acrylic acid, but no crystallized structure was observed in the copolymer gel of dodecyl acrylate and acrylic acid.

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