Fluorinated Water-Swollen Hydrogels with Molecular and Supramolecular Organization

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ABSTRACT: Moderately water-swollen hydrogels were prepared by copolymerizing *n*-stearyl acrylate (SA), 2,2,2-trifluoroethyl acrylate (TFEA), and acrylic acid (AA), and the effects of water and TFEA on the molecular and supramolecular structure were investigated. An incorporation of TFEA brought about a decreased d_2 spacing (long-range ordering) presumably due to a local render amorphous while d_1 (short-range ordering) was kept constant. Enhanced effects of water and stretching on the supramolecular organization were demonstrated. The transition temperature at which Young's modulus abruptly changes could be controlled by changing the TFEA content of the gel.

Introduction

He et al.[1−3] reported that a multiblock copolymer composed of soft segments and hydrophobic hard segments showed the thermoreversible gelation by the order−disorder transition of hard segments.

We reported in the previous papers that water-swollen hydrogels prepared by copolymerizing acrylic acid (AA) with a hydrophobic acrylate containing long alkyl side groups such as *n*-stearyl acrylate (SA) [poly(SA-*co*-AA) gel],[4] 16-acryloylhexadecanoic acid (AHA) [poly(AHA-*co*-AA) gel],[5] and hexadecyl acrylate (HA) [poly(HA-*co*-AA) gel] can form molecular- and supramolecular-ordered structures which undergo reversible order−disorder transition at the melting temperature.[6] Below the transition temperature, the poly(SA-*co*-AA) gel is crystalline and rigid with a Young's modulus of more than 10^7 Pa, while it becomes sufficiently soft to be easily deformed above that temperature. If the deformed gel is cooled, it becomes rigid, again retaining its deformed shape. However, the gel recovers to the original shape, showing a shape memory behavior if it is once again heated above the transition temperature. Using this behavior, a shape memory gel was developed.[7] It was found that the cross-linking suppressed the formation of ordered structure but there existed an optimum cross-linking.[8]

However, the transition temperature of the shape memory hydrogel could not be controlled because the size and the structure of the crystalline domain did not change even by changing the chemical composition of the copolymer gel due to strong phase separation nature of the crystalline domain from hydrophilic swelling region. Besides, the response was not quick enough, and a permanent strain often remained after repeated operations. To solve these problems, we attempted, in this paper, to incorporate elastomeric copolymer units—2,2,2-trifluoroethyl acrylate (TFEA) in the poly(SA-*co*-AA) gel—expecting to modulate the transition temperature by changing the copolymer composition as well as to obtain quick and reproducible responses. As a result, we successfully obtained a shape memory gel, the transition temperature of which could be modulated in a temperature range of 38−52 °C by changing the gel composition. The effects of incorporation of TFEA units on the molecular and supramolecular structure were also investigated. It was found that water incorporation into the hydrogel enhanced the formation of these structures.

Experimental Section

Materials. Stearyl acrylate (SA, *n*-octadecyl acrylate) (Tokyo Kasei Kogyo Co. Ltd.) was repeatedly recrystallized from ethanol solution. 2,2,2-Trifluoroethyl acrylate (TFEA) (Daikin Kaseihin Hanbai Co. Ltd.) and acrylic acid (AA) (Tokyo Kasei Kogyo Co. Ltd.) were distilled at 313 K under 933 Pa before use. α,α′-Azobis(isobutyronitrile) (AIBN) (Tokyo Kasei Kogyo Co. Ltd.) and *N*,*N*′-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical industries Ltd.) used as a radical initiator and a cross-linking agent, respectively, were recrystallized in the ethanol solution.

Gel Preparation. Poly(SA-*co*-TFEA-*co*-AA) gels with various compositions were prepared by radical polymerization in the presence of 3.0×10^{-2} M MBAA and AIBN in ethanol. The total monomer concentration was kept at 3.0 M. The SA content (S) in the copolymer poly(SA-*co*-TFEA-*co*-AA) gel was kept constant as 0.25, while the TFEA content was varied (F is defined as $F = [\mathrm{TFEA}]/([\mathrm{TFEA}] + [\mathrm{AA}])$. Polymerization was carried out at 323 K for 24 h, and nearly 100% of monomer has been polymerized forming chemically cross-linked polymer gel. After polymerization, the gel was kept in a large amount of ethanol for more than 3 days to remove unreacted monomer, soluble polymer, and residual initiator and then in water for a week until it reached an equilibrium state. The equilibrium degree of swelling (q) was determined as the weight ratio of swollen to dry gel.

Measurements. The reactivity ratios were determined for the SA/AA and TFEA/AA copolymer compositions using ^{1}H NMR measurements (JEOL GSX-400, NMR spectrometer, 400 MHz).

The wide-angle X-ray diffraction (WAXD) patterns of the water-swollen gels were taken by an imaging plate (rint 2000, Rigaku Co. Ltd.) with Ni-filtered Cu Kα radiation (40 kV, 200 mA). Small-angle X-ray diffractions (SAXD) were measured by an X-ray diffractometer (rint 2000, Rigaku Co. Ltd.) with the same radiation as WAXD.

The melting and crystallization temperatures of the gels were measured by a differential scanning calorimeter (DSC) (DSC 22C, Seiko Densi Kogyo Co. Ltd.). The samples were hermetically sealed in aluminum pans and scanned under N_2 atmosphere from 283 to 343 K with a heating rate of 1 K/min.

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Melting and crystallization temperatures and the energy calibration were determined using the melting transition peaks of In and Sn. The sample weight was varied between 5 and 10 mg, and no weight loss was recorded during the experiments.

Young's modulus of these gels was measured using a tensile tester (Orientec Corp. RTC-1150A).

Results and Discussion

1. Structure. (a) Effect of TFEA. As reported previously,[4] poly(SA-*co*-AA) gel forms an organized structure through side-by-side interaction of SA units with a spacing of 0.4 nm (d_1) and a supramolecular long-range ordering of the main chains with a spacing of 5.9 nm (d_2). The crystalline size and the melting temperature were not affected by changing the SA content. To study the effect of incorporation of TFEA units on the short- and long-range structures of poly(SA-*co*-TFEA-*co*-AA) gels, wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD) were used. The elastic nature of these gels allowed us to carry out the experiments using stretched samples. Figure 1 shows typical WAXD patterns of stretched samples (strain = 1.0) in the water-swollen state (hydrogels). When the stretched specimen is placed in the vertical direction, intensive diffraction peaks corresponding to short-range ordering d_1 appear on the meridian line for all F samples, indicating that SA side chains are oriented vertically to the extended main chain direction. From Figure 1, we found that $d_1 = 0.40{-}0.42$ nm, and these values are not changed by the presence of TFEA.

We evaluated the degree of orientation of alkyl chains from the intensity ratio (I_v/I_h) of the vertical direction (I_v) to the horizontal direction (I_h), for various F specimens from Figure 1. I_v/I_h was calculated as 2−2.5 and decreases with an increase in F. This suggests that TFEA units dispersed in the SA crystalline domain partly destroy the SA packing and decrease the SA alignment.

Figure 2 shows the SAXD patterns for the stretched samples in the water-swollen state (strain = 1.0) taken for horizontal and vertical directions. One can seen that peaks are observed only for the samples placed horizontal to the stretching direction, indicating that the main chain is orientated along the stretching direction. With the increase in F, the diffraction peak shifted to a higher angle, i.e., to decreased d_2 spacing (Figure 3). As reported before,[4] stearyl groups are aligned perpendicularly to the main chain to give lamellar packing of the main chains with a spacing of d_2. If the stearyl groups take the most extended conformation in the gel, d_2 should be calculated as 2×2.57 nm = 5.14 nm, which is shorter than d_2 of $F = 0$ ($d_2 = 5.38$ nm) but longer than those of $F = 0.2$, 0.4, 0.6, 0.8, and 1.0. Therefore, the decrease in d_2 by incorporating TFEA might be associated with a partial destruction of the extended conformation of side chains as Kajiyama et al. reported.[9] The decreased sharpness of the samples of $F = 0.8$ and 1.0 compared with $F = 0$ and $F = 0.2$ also supports the conclusion that the partial render amorphous occurred by incorporation of TFEA.

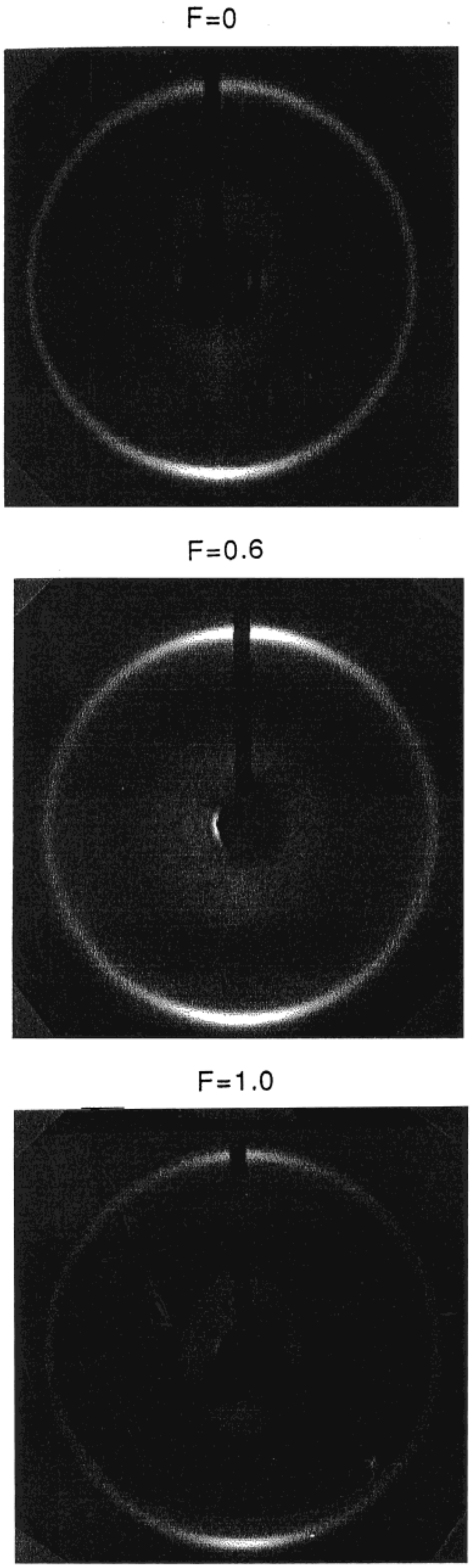

Figure 1. WAXD patterns of stretched poly(SA-*co*-TFEA-*co*-AA) gels (strain = 1). F denotes the molar fraction of TFEA in the gels.

(b) Effect of Stretching. The nonstretched poly(SA-*co*-TFEA-*co*-AA) gels showed the same $d_1 = 0.40{-}0.42$ nm ($2\theta = 21.1{-}22.0°$) as the stretched samples and no orientation by incorporating TFEA at any F. However, as shown in Figure 3, d_2 of stretched gel is smaller than those of nonstretched gel, indicating an improved packing of SA units by the stretching. SAXD peaks for the stretched gel for $F = 0$, 0.2, and 0.4 are sharper compared with those of the nonstretched gel. It should be emphasized that for the stretched gels intensive and clear peaks are observed even for the samples of $F =$

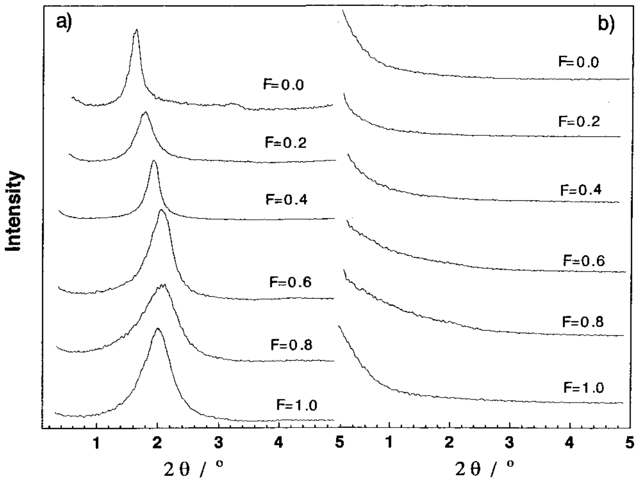

Figure 2. SAXD patterns for stretched poly(SA-*co*-TFEA-*co*-AA) gels (strain = 1) of horizontal (a) and vertical (b) directions.

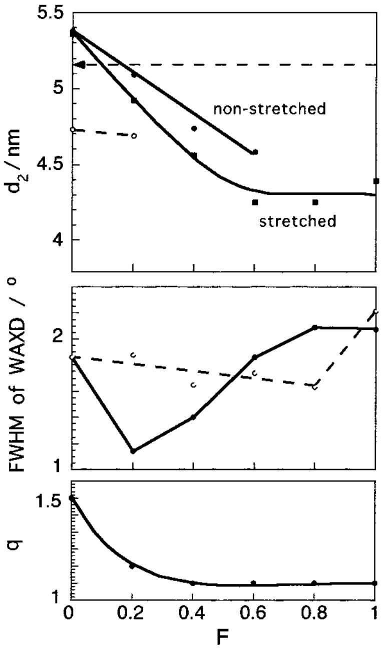

Figure 3. d_2, fwhm, and q as a function of F: full line, wet sample; dotted line, dry sample. Arrow at the vertical axis indicates the estimated double length of stearyl side chain.

0.8 and $F = 1.0$, which did not show any peak for nonstretched samples.

(c) Effect of Water. As shown in Figure 3, the equilibrium degree of swelling (q) of the gel is strongly dependent on the TFEA content and decreases with an increasing F, which should be attributed to the strong hydrophobicity of TFEA. The effect of water on the molecular packing (d_1) as well as on the supramolecular structure (d_2) was further studied by comparing the structure of the sample in the wet and dry states.

Using the data of WAXD patterns for nonstretched gels, the full width at half-maximum (fwhm) of the dry or wet gel was calculated and shown in Figure 3. The fwhm of the dry sample is constant at 1.85° regardless the change in F while the fwhm for the water-swollen hydrogel decreases from 1.85° of $F = 0$ to 1.15° of $F = 0.2$ and then increased gradually with an increasing F. This indicates that incorporation of an appropriate amount of water ($q = 1.2$) does not destroy the crystalline structure of the gel, but even increases the crystallinity presumably due to enhanced hydrophobic interaction between side groups. This result is in agreement with that observed for poly(SA-*co*-AA) gel, poly(HA-*co*-AA) gel, and poly(AHA-*co*-AA) gel,[8] which also showed the highest crystallinity when $q = 1.2$.

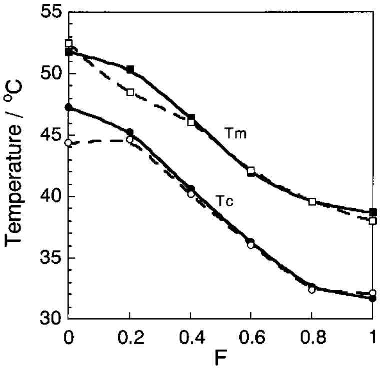

Figure 4. Transition temperature of poly(SA-*co*-TFEA-*co*-AA) gels as a function of F. T_m and T_c denote the temperature of melting and crystallization, respectively. Full line, wet sample; dotted line, dry sample.

As described, the nonstretched swollen gels of $F = 0$, 0.2, 0.4, and 0.6 show a clear d_2 spacing, but no distinct d_2 spacing was observed for $F = 0.8$ and 1.0. For the dry state, d_2 was observed only for the samples of $F = 0$ and $F = 0.2$, showing values of 4.73 and 4.69 nm ($2\theta = 1.87°$ and $1.88°$), which was much shorter than those of swollen samples, and no SAXD peak appeared for the samples of $F = 0.4$, 0.6, 0.8, and 1.0. This indicates that the incorporation of water not only increases the crystallinity but also enhances the supramolecular organization.

2. Thermal Property. The effect of TFEA on the transition temperature was studied by DSC. All the samples showed very sharp peaks associated with the melting−crystallization transition. The transition temperature of the poly(SA-*co*-TFEA-*co*-AA) gels decreased monotonously with an increase in F (Figure 4) for dry samples as well as for wet samples. As previously reported,[4−6] although the melting temperature of cross-linked poly(SA-*co*-AA) was independent of the SA content, that of the cross-linked poly(SA-*co*-MA) (MA: methyl acrylate) decreased with an increasing in MA due to the decrease in the crystalline domain size.[10] Since the fwhm of the d_1 diffraction peak of the dry samples did not change with F, as shown in Figure 3, and the crystalline domain size of poly(SA-*co*-TFEA-*co*-AA) gel did not change, the decrease in the melting temperature with an increase in F should not be attributed to the change in the crystal domain size, but to the sequential structure of the crystal domain, i.e., local render amorphous due to the presence of TFEA.

To experimentally prove this, the miscibility of TFEA with SA in the SA crystalline aggregates was examined by the monomer reactivity ratios in the copolymer. Copolymerization of SA and AA, or TFEA and AA, was carried out varying the monomer ratios in ethanol and methanol, respectively, and the copolymer composition was determined by ^{1}H NMR measurement. The reactivity ratios were calculated using the Finemann−Ross and Kelen−Tudos methods and were found to be r_1(SA) = 3, r_2(AA) = 0.5 and r_1(TFEA) = 1.6, r_2(AA) = 0.7. From these values, we can calculate r_1(TFEA) = 0.8 and r_2(SA) = 1.3, which suggests that TFEA units are well mixed and dispersed in the SA aggregates. Dispersed TFEA with its short side chain in the crystal-

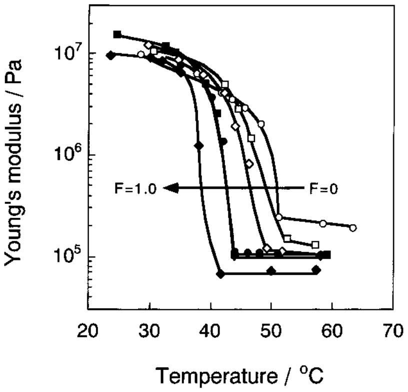

Figure 5. Temperature dependence of Young's modulus of the poly(SA-*co*-TFEA-*co*-AA) gels: (○) $F = 0$; (□) $F = 0.2$; (◇) $F = 0.4$; (●) $F = 0.6$; (■) $F = 0.8$; (◆) $F = 1.0$.

line domain might lead to voids and increased thermal motion. This might induce a decreased side-by-side chain interaction of SA units, especially near the main chain, and induce the local render amorphous as reported in the literature[9] to bring about a decreased d_2. It is reported[11−13] that a decrease in melting temperature of 10 °C is equivalent to the shortening of alkyl chain length by as much as two carbons. The local render amorphous might also account for the decreasing d_2 spacing with an increase in F, as shown in Figure 3.

3. Mechanical Property. One of the most characteristic features of the hydrogels with organized structure is the drastic change in Young's modulus (E) near the transition temperature. Figure 5 shows Young's modulus as a function of temperature for the gels with various F. One can see that the gels abruptly decrease E by nearly 2 orders of magnitude around each transition temperature, and the higher the F, the larger the change in E due to the elastomeric nature of TFEA units.

Thus, the obtained fluorinated water-swollen hydrogels with molecular and supramolecular organization show an enhanced mechanical property with a controlled transition temperature, producing as shape memory gels with improved function.

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