Effects of Carboxyls Attached at Alkyl Side Chain Ends on the Lamellar Structure of Hydrogels

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ABSTRACT: Two kinds of water-swollen hydrogels composed of three monomers—poly(stearyl acrylate (C18A)-*co*-*n*-alkyl acrylates (C*n*A)-*co*-acrylic acid (AA)) and poly(16-acryloyloxyhexadecanoic acid (AHA)-*co*-C*n*A-*co*-AA) (*n* is the number of carbon atoms of side chains: $n = 14, 16, 18, 20, 22$)—were synthesized, and their structures were investigated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD). Both gels formed the crystalline structure with the lamellae. In the case of poly(C18A-*co*-C*n*A-*co*-AA) gels, both the lamellar thickness, d_2, and the melting temperature, T_m, increased with the increase in *n*, suggesting that C18A and C*n*A form molecularly mixed crystalline domains. On the other hand, d_2 of poly(AHA-*co*-C*n*A-*co*-AA) gels was much smaller than that of poly(C*n*A-*co*-AA) gels, and T_m was constant regardless of *n*. An abrupt decrease in T_m was observed for poly(AHA-*co*-C18A-*co*-AA) gels at an AHA composition of 0.8. These results indicate that carboxyls attached at alkyl side chain end of AHA significantly shorten and stabilize the lamellae of the hydrogel due to the cooperative hydrogen bonding and rearrangement of the lamellar structure occurred.

Introduction

In the previous papers, we have reported that water-swollen hydrogels prepared by copolymerizing acrylic acid (AA) with hydrophobic acrylate monomers with long alkyl side groups such as *n*-octadecyl acrylate (C18A) [poly(C18A-*co*-AA) gel],[1] hexadecyl acrylate (C16A) [poly(C16A-*co*-AA) gel],[2] and 16-acryloyloxyhexadecanoic acid [poly(AHA-*co*-AA) gel][3,4] could form the organized structure which was disordered by changing temperature, pH, or the solvent composition. The organized structure is composed of a short- and long-range ordering which correspond to the side-by-side stacking of side chains and the lamellar structure, respectively. It was found that water incorporated in the gel plays a crucial role for this organization since water gives the main chain mobility which allows to reorganize the hydrophobic side chains.[5] These gels showed the Young modulus as high as 10^7-10^8 Pa in the ordered state[1,6,7] but changed to the amorphous state in an organic solvent such as ethanol or tetrahydrofuran. If the gel swollen in the organic solvent is placed on the water surface, it performed the rotation as fast as 4.0×10^2 rpm for a few hours and produced an electric power (chemical motor).[8,9]

In the present study, the hydrogels are derived from three kinds of monomers—AHA, *n*-alkyl acrylates (C*n*A; *n* is the carbon number of alkyl group: 14, 16, 18, 20, 22), and AA—and the effects of carboxyls of AHA and the side chain length of C*n*A on the structures of the hydrogels are investigated. We previously reported that the hydrogen bonding of carboxyls attached at the carboxybiphenyl mesogen in the liquid crystalline hydrogels enhances the ordering and stabilizes the mesophase structure.[10] Carboxyls of AHA, therefore, may enhance the structural ordering of the crystalline domain of *n*-alkyl side chains in the hydrogels. It is another interest to know whether two different long alkyl side chains incorporated into the hydrogels form the mixed ordered domain or individual two domains separately.

It has been reported that the long alkyl side chain of comblike polymers or gels form the crystalline domain.[11−14] However, as far as we know, the structure and property of the hydrogels containing different kinds of alkyl side chains have not been investigated.

Experimental Section

Materials. 16-Acryloyloxyhexadecanoic acid (AHA) used as a monomer was prepared by the procedures described in the preceding paper.[3] Acrylic acid (AA; TCI) used as a monomer was distilled under reduced pressure. Hexadecyl acrylate (C16A; Osakayukikagaku) and octadecyl acrylate (C18A; Kyoeisha Chemical Co., Ltd.) used as monomers were recrystallized before use. Acryloyl chloride (Junsei Chemical Co., Ltd.), tetradecanol (TCI), eicosanol (TCI), docosanol (TCI), and triethylamine (TCI) were used as received. α,α′-Azobis(isobutylonitrile) (AIBN; TCI) used as a radical initiator was recrystallized from ethanol before use. Adipoyldihydrazide (ADH, TCI) used as a cross-linking agent, *N*-hydoroxysuccinimide used as a condensation reagent, and dicyclohexylcarbodiimide used as a condensation accelerator were used as received. Tetrahydrofuran (THF; TCI) and dimethylacetamide (DMAc; Junsei Chemical Co., Ltd.) used as solvents were distilled after standing overnight in sodium metal and calcium hydride, respectively.

Synthesis of Monomers (Dococyl Acrylate (C22A)). Docosyl acrylate (C22A) was synthesized by the following procedure. A homogeneous THF solution (150 mL) of docosanol (6.0 g) and triethylamine (3.85 mL) was added dropwise under nitrogen to a THF solution (20 mL) of acryloyl chloride (2.33 g) with stirring over several hours at 0 °C and then at room temperature for 24 h. After the triethylamine hydrochloride generated as a result of reaction was removed and THF was evaporated, the solid material was washed by water and methanol and then dried in vacuo (yield: 65%). Tetradecyl acrylate (C14A) and eicosyl acrylate (C20A) were synthesized by an analogous procedure as docosyl acrylate (yield: 80% and 85%, respectively).

Synthesis of Hydrogels. The poly(C*n*A-*co*-AA) gels ($n = 14, 16, 18, 20, 22$) were prepared by the following procedure.

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First, 3.0 mol L^{-1} concentration of C*n*A and AA in DMAc were polymerized in the presence of 1 mol % AIBN as an initiator at 60 °C for 24 h under nitrogen, and during this period nearly 100% of the monomer was polymerized. ADH was added into polymerization solutions in the presence of dicyclohexylcarbodiimide and *N*-hydroxysuccinimide to give a chemically cross-linked polymer gel. The gels were immersed in a large amount of DMAc for 3 days and then water for 10 days to remove unreacted chemicals. The poly(AHA-*co*-AA) gel was prepared by analogous procedures as the poly(C*n*A-*co*-AA) gels. The copolymer composition, *F*, was defined as $F_{CnA} = [CnA]/([CnA] + [AA])$ or $F_{AHA} = [AHA]/([AHA] + [AA])$.

The poly(C18A-*co*-C*n*A-*co*-AA) gels and poly(AHA-*co*-C*n*A-*co*-AA) gels ($n = 14, 16, 18, 20, 22$) were prepared by the following procedure. The linear polymers poly(C18A-*co*-C*n*A-*co*-AA)'s and poly(AHA-*co*-C*n*A-*co*-AA)'s were prepared by radical polymerization of three monomers by the analogous procedure as the poly(CA-*co*-AA)'s. These polymers composed of three monomers were called as terpolymers in this article. The gels were prepared by cross-linking individual corresponding terpolymers in the analogous procedures as the poly(C*n*A-*co*-AA) gels. In all the hydrogels, the molar composition of AA to total monomers was kept as 0.66. The composition of acrylates with alkyl side chains, *F*, was defined as $F_{CnA} = [CnA]/([CnA] + [C18A])$, $F_{C18A} = [C18A]/([CnA] + [C18A])$, or $F_{AHA} = [AHA]/([CnA] + [AHA])$ without accounting for AA content in the terpolymer.

Measurements. Wide-angle X-ray diffraction (WAXD) patterns were taken with a flat-plate camera mounted on a Shimazu X-ray generator (XD-610) emitting Ni-filtered Cu Kα radiation (40 kV, 40 mA) in transmission geometry. The distance from the sample to the film was determined by calibration with silicone powder. Small-angle X-ray diffraction (SAXD) patterns were recorded on a Rigaku X-ray diffractometer (RINT-2000) (40 kV, 200 mA) in transmission geometry. A 2θ (θ: diffraction angle) scanning speed of 1° $\min^{-1}$ with a sampling interval of 0.01° was used.

The transition temperature was measured at a scanning ratio of 5 °C $\min^{-1}$ under nitrogen by differential scanning calorimeter DSC (DSC22C, Seiko). The samples of about 10 mg were hermetically sealed in aluminum pans, and no weight loss was recorded during the experiments. Temperature and enthalpy calibration were made using melting peaks of In and Sn.

The degree of swelling, *q*, was defined as the weight ratio of a swollen gel to the dried one.

Results and Discussion

Poly(C*n*A-*co*-AA) Gels and Poly(C18A-*co*-C*n*A-*co*-AA) Gels. As reported in the previous papers, the poly(C18A-*co*-AA) gels with F_{C18A} higher than 0.25 form the crystalline domain of the lamellar structure even in the water-swollen state.[1,2] The hydrogels show a WAXD diffraction at $2\theta = 21.7°$ (θ: the diffraction angle) corresponding to a spacing of 0.41 nm (d_1) which is attributed to the side-by-side arrangement of alkyl side chains.[1,2] Since the diffraction in the WAXD image of a stretched sample of the poly(C18A-*co*-AA) gel appears on the meridian line parallel to the stretching direction,[15] the C18A side chain is concluded to be aligned perpendicularly to the main chains. Formation of the crystalline domain is largely due to the strong hydrophobic interaction of side chains in the presence of water. We have previously evaluated that monomer reactivity ratios of C18A (r_1) and AA (r_2) were 3.0 and 0.5, respectively. Since acrylate monomers with long alkyl side chains such as teradecyl acrylate (C14A), hexadecyl acrylate (C16A), eicosyl acrylate (C20A), and docosyl acrylate (C22A) have similar structures and electron environments around the double bond with C18A, we can assume that the reactivity ratios of C*n*A and AA were 3.0 and 0.5, respectively. Therefore, C*n*A may be randomly sequenced in the hydrogels. Figure 1 shows the WAXD pattern of the poly(C22A-*co*-AA) gel with F_{C22A} of 0.33, showing a strong diffraction ring with a d_1 spacing of 0.41 nm ($2\theta = 21.7°$). Similar diffractions with d_1 spacing of 0.41 nm are obtained for all other copolymer gels.

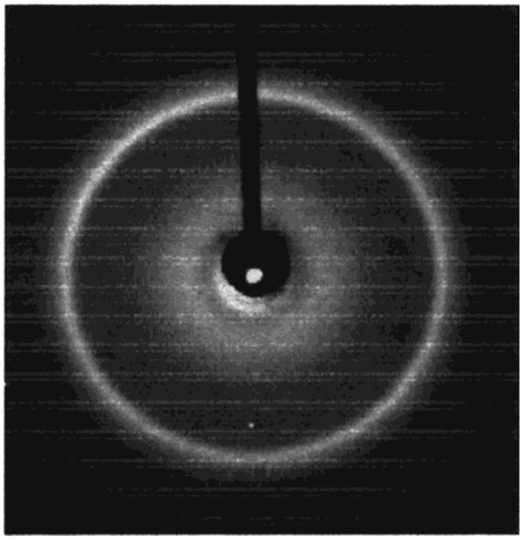

Figure 1. Wide-angle X-ray diffraction pattern of the poly(C22A-*co*-AA) gel with F_{C22A} of 0.33.

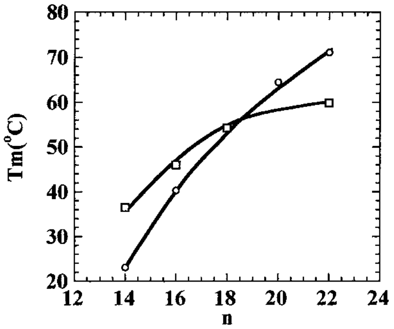

Figure 2. Melting temperatures of the poly(C*n*A-*co*-AA) gels (○) and the poly(C18A-*co*-C*n*A-*co*-AA) gels with F_{CnA} of 0.50 (□) (AA content is 0.66).

DSC thermograms of the poly(C*n*A-*co*-AA) gels with F_{CnA} of 0.33 show a clear endothermic peak in a range from 22 °C for the poly(C14A-*co*-AA) gel to 66 °C for the poly(C22A-*co*-AA) gel. Since the WAXD diffraction disappears and amorphous halo appears above individual endothermic temperatures, it is found that these peaks are due to the melting of crystalline domains. The melting temperatures (T_m) increases almost linearly from 22.5 to 71.5 °C with increasing *n* from 14 to 22 as shown in Figure 2, indicating that crystals of longer *n*-alkyl side chains have increased thermal stability.

The length of *n*-alkyl side chains should also influence on the long-range ordering of the crystalline domain. As reported previously, the SAXD pattern of the poly(C18A-*co*-AA) gel show a diffraction with a spacing of $d_2 = 5.98$ nm ($2\theta = 1.48°$) which is attributed to the bilayer spacing where the long alkyl side groups form a tail-to-tail alignment. We have taken SAXD patterns of the poly(C*n*A-*co*-AA) gels and found distinct diffractions at a certain diffraction angle. Figure 3 shows the d_2 values as a function of *n*. d_2 increased from 5.60 to 7.30 nm with increasing *n* from 14 to 22, indicating that the longer C*n*A side chain forms the thicker bilayer structure. Assuming that C*n*A side chains take an

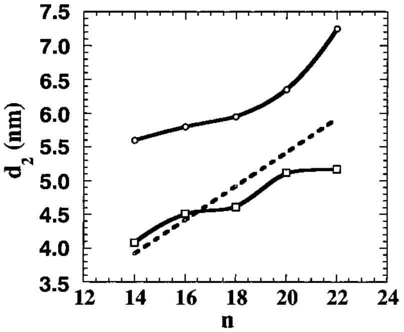

Figure 3. d_2 spacings of the poly(C*n*A-*co*-AA) gels with F_{CnA} of 0.33 (○) and the poly(AHA-*co*-C*n*A-*co*-AA) gels with F_{AHA} of 0.66 (□) (AA content is 0.66). Dashed line shows double lengths of C*n*A side chains calculated assuming the extended β-sheet conformation.

extended β-sheet conformation aligning perpendicularly to main chains, we calculated side chain lengths of the poly(C*n*A-*co*-AA) gels as 3.92, 4.42, 4.92, 5.42, and 5.92 nm for *n* of 14, 16, 18, 20, and 22, respectively. These calculated values are shown in Figure 3 as a dashed line which are much smaller than d_2 values experimentally obtained. The difference between calculated and experimental values might correspond to the thickness of main chain backbone which is in the amorphous state. Thus, the lamellar structure of the gel consists of two parts: one is the bilayer domain of C*n*A side chains (domain A), and the other is an amorphous domain composed of main chain backbones (domain B). Thus, the thickness of domain B for the case of poly(C18A-*co*-AA) gel would be calculated as $5.98 - 4.92 = 1.06$ nm.

Now another problem arises: what happens if two kinds of C*n*A with different side chains are copolymerized? To investigate the effects of the second *n*-alkyl acrylate monomer on the structures, the terpolymer poly(C18A-*co*-C*n*A-*co*-AA) gels with F_{CnA} of 0.50 were synthesized. (Note: in this and all other terpolymers AA contains 66 mol % in monomer feed. Therefore, C18A and C*n*A content in this terpolymer are 0.165, respectively.) The obtained terpolymer gels were cloudy and stiff. Since the reactivities of C*n*A monomers are similar to each other, the sequence of crystallizable monomer (C*n*A and C*m*A) in the terpolymers maybe random. Their WAXD patterns show only one diffraction ring with d_1 of 0.41 nm, indicating that the crystals with the same side by side arrangement as the poly(C18A-*co*-AA) gel are formed. DSC thermograms showed only one melting peak at an intermediate position between T_m of the poly(C18A-*co*-AA) and poly(C*n*A-*co*-AA) gels (Figure 2). These results suggest that a crystalline domain composed of C18A and C*n*A side chains are able to form one crystalline domain mixed molecularly each other due to their similar chemical structures.

T_m of the mixed crystalline domain in the terpolymer gels should depend on the composition of each monomer units, and we have synthesized the poly(C18A-*co*-C22A-*co*-AA) gels varying the C22A composition, keeping constant the AA composition, and the relationship between T_m and F_{C22A} was investigated (Figure 4). T_m of the terpolymer gels increased almost proportionally with increase in F_{C22A}, demonstrating again that side chains of C18A and C22A are miscible on the molecular level.

Associated with this, the bilayer thickness should also change with the copolymer composition. SAXD patterns of all the terpolymer gels with various F_{C22A} showed distinct diffractions, and d_2 was plotted against *n* (Figure 5). Similarly to T_m, d_2 increased from 5.98 to 7.20 nm with an increase in F_{C22A}. This result means that d_2 values of terpolymers are simply determined by the average of two *n*-alkyl components: C18A and C22A. Summarizing these data, one can conclude that the poly(C18A-*co*-C22A-*co*-AA) terpolymer gels form a lamellar structure with a constant d_1 spacing (0.41 nm), and their T_m and d_2 vary almost proportionally with their composition.

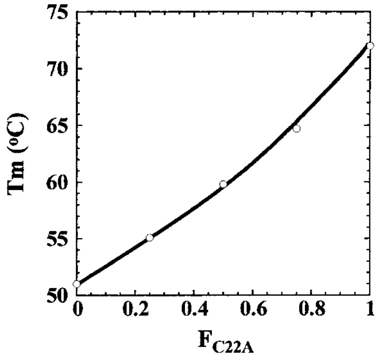

Figure 4. Melting temperatures of the poly(C18A-*co*-C22A-*co*-AA) gels as a function of F_{C22A}.

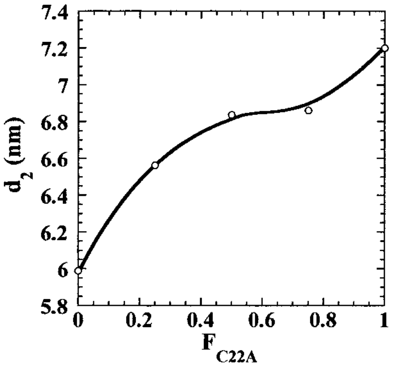

Figure 5. d_2 spacings of the poly(C18A-*co*-C22A-*co*-AA) gels as a function of F_{C22A}.

Poly(AHA-*co*-AA) Gel and Poly(AHA-*co*-C*n*A-*co*-AA) Gels. AHA has a pentadecyl side chain with the carboxyl group at the chain end. The carboxyl has hydrophilic nature and able to form the hydrogen bonding each other. This may exert a significant effect on the structure of the crystalline domain. Since structures and electron environments around the double bond of AHA are similar to that of C*n*A, it can be assumed that the reactivity of AHA monomer is the same with those of C*n*A monomers to give the random sequence. First, we have synthesized the poly(AHA-*co*-AA) gels and confirmed that they form the lamellar structure with a d_1 spacing of 0.41 nm and d_2 spacing of 4.26 nm. This d_2 value was much smaller than d_2 (5.74 nm) of the poly(C16A-*co*-AA) gel which was derived from the monomer with the same alkyl size but no carboxyls. Thus, the carboxyls attached at the side chain end significantly shorten d_2 spacing, presumably due to the hydrogen bonding of these carboxyls. In fact, T_m of the poly(AHA-*co*-AA) gel was 72.0 °C and was much higher than that of poly(C16A-*co*-AA) gel (40.3 °C) due to the stabilized structure by carboxyls. Therefore, a series of terpolymer gels—the poly(AHA-*co*-C*n*A-*co*-AA) where *n* was varied as 14, 16, 18, 20, and 22—have been synthesized keeping AA content as 66 mol % and F_{AHA} as 0.66, and their structural and thermal behavior were

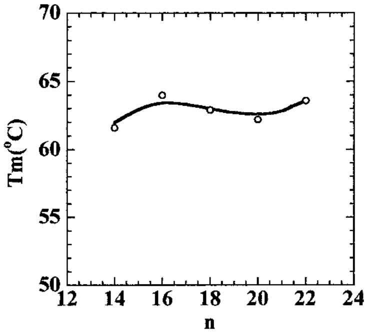

Figure 6. Melting temperatures of the poly(AHA-*co*-C*n*A-*co*-AA) gels with F_{AHA} of 0.66 as a function of *n*. Note: melting temperature of the poly(AHA-*co*-AA) gel is 72 °C.

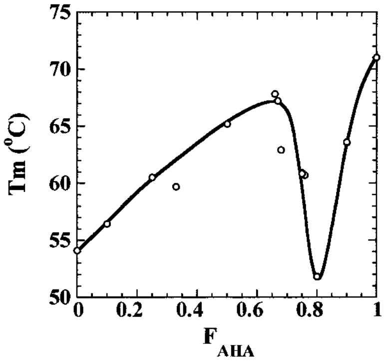

Figure 7. Melting temperatures of the poly(AHA-*co*-C18A-*co*-AA) gels as a function of F_{AHA}.

investigated. Their WAXD patterns showed the diffraction with a spacing of $d_1 = 0.41$ nm. However, DSC thermograms showed a constant T_m peak of 63 ± 1.2 °C regardless of *n* as shown in Figure 6. This is a strong contrast with the case of the poly(C*n*A-*co*-AA) gels in which T_m increases proportionally with an increase in *n* (Figure 2). The obtained T_m was higher than that of any poly(C18A-*co*-C*n*A-*co*-AA) gels and about 9 °C lower than that of the poly(AHA-*co*-AA) gel.

The effects of carboxyls on d_2 of terpolymer gels were also studied. As shown in Figure 3, experimental d_2 values of these terpolymer gels are much smaller than those of the poly(C*n*A-*co*-AA) gels. Thus, the presence of AHA units significantly decreases the d_2 spacing due to carboxyls.

The effects of composition of AHA on T_m or d_2 were studied using the poly(AHA-*co*-C18A-*co*-AA) gels. T_m of the poly(C18A-*co*-AA) gel and the poly(AHA-*co*-AA) gel were 54 and 72 °C, respectively.[1,3] The higher T_m of the poly(AHA-*co*-AA) gel than that of poly(C18A-*co*-AA) gel suggests the increased stabilization of the crystalline domains due to the hydrogen bonding of carboxyl groups. Interestingly, the poly(AHA-*co*-C18A-*co*-AA) gels below $F_{AHA} = 0.66$ show only one T_m which raised with increase in F_{AHA} (Figure 7). This is the same case as the poly(C18A-*co*-C22A-*co*-AA) gel in Figure 4 and suggests C18A and AHA units are molecularly miscible, forming one crystalline domain. However, when AHA content increases, T_m abruptly decreased from 67.8 to 51.8 °C and then increased up to 72.0 °C for the poly(AHA-*co*-AA) gel. There is a possibility that the decrease in crystalline domain size caused the decrease in T_m. In that case, ΔH should decrease with T_m. However, ΔH showed constant values of about 10.0 kJ/mol in the composition range of $F_{AHA} = 0.66-1.0$ where T_m dropped. Therefore, the possible reason for T_m decrease is the decrease in the structural ordering rather than the decrease in the crystalline domain size. Since the presence of AHA significantly decreases d_2, C18A side chains can no more be stacked in the crystalline domain and may form an eutectic crystal which usually induces a strong decrease in T_m.[16]

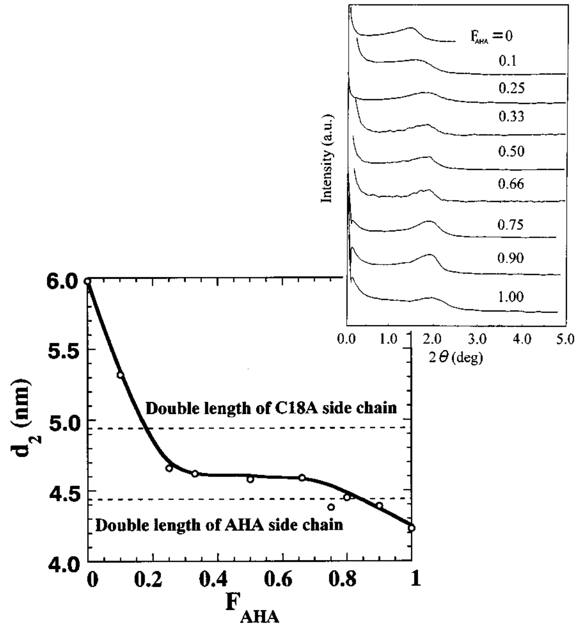

Figure 8. Change in d_2 spacings of the poly(AHA-*co*-C18A-*co*-AA) gels as a function of F_{AHA}.

To clarify this assumption, we have investigated d_2 dependence on the composition. The SAXD patterns of the terpolymer gels showed a distinct diffraction regardless of F_{AHA}. d_2 sharply decreased from 5.98 to 4.66 nm when F_{AHA} increase from 0 to 0.25 and became almost constant (4.66−4.58 nm) in the range from $F_{AHA} = 0.25$ to 0.66 and then decreased again to 4.23 nm when F_{AHA} increased from 0.75 to 1.00 (Figure 8). As described before, the lamellar structure of poly(C18A-*co*-AA) gel consists of two parts: domain A, which is composed of stretched side chains with a calculated thickness of 4.92 nm, and domain B, composed of the coiled main chain backbones with a thickness of 1.06 nm. One observed no second-order diffraction peak, but d_2 spacing showed the bilayer ordering. We have previously found that poly(C18A-*co*-AA) gel and poly(AHA-*co*-AA) gel formed the lamellar structure with the bilayer ordering. Therefore, we can assume that the poly(C18A-*co*-AHA-*co*-AA) gel formed the lamella structure. As described before, a significant decrease of d_2 from 5.98 to 4.66 nm at $F_{AHA} = 0.25$ could be associated with the intra- and/or intermolecular cooperative hydrogen bonding of carboxyls locating at the side chain ends. The hydrogen bonding should be particularly strong in the hydrophobic crystalline domains and bring about "true up" of the side chain end of C18A units as schematically illustrated in Figure 9b. Since side chain length of AHA is calculated as 2.21 nm assuming the stretched β-sheet conformation, thickness of main chain backbones is calculated as 0.24 nm, which is much thinner than that of the poly(C18A-*co*-AA) gel. Here, the extra length of side chain of C18A might be partly adjusted by the coiled main chain backbone. When F_{AHA} further increased and the lamellae is more thinned and stabilized by the hydrogen bonding, the extra length of side chains of C18A cannot be any more adjusted by the coiled main

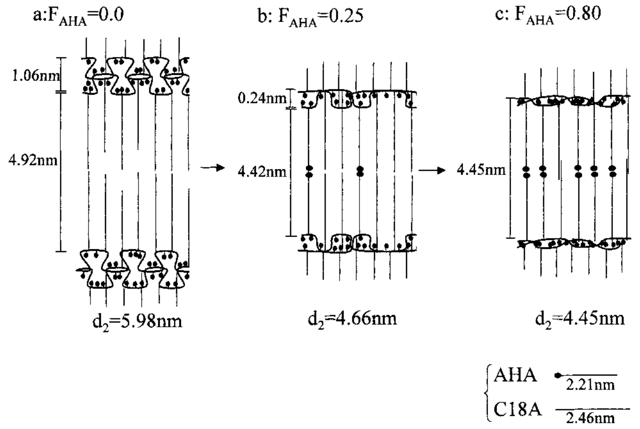

Figure 9. Schematic illustration of bilayer structures of the poly(C18A-*co*-AHA-*co*-AA) gel with various F_{AHA}.

chain backbone, because the lamellae in this state is too small and too stable to be placed and C18A side chains would be "overlapped" each other structure (Figure 9c). The abrupt decease in T_m might be associated with this rearrangement of C18A side chains. When $F_{AHA} = 1.00$, d_2 dips below the double length of the calculated AHA side chain. As seen from the broad SAXD peak of $F_{AHA} = 1.00$ in Figure 8, the structural ordering is low. This suggest that the AHA side chain maybe partially coiled. Therefore, d_2 value dips below the calculated double length assuming the fully extended conformation. In the previous paper, we demonstrated that an introduction of water as much as 5% in the poly(C18A-*co*-AA) gel causes a stretching of the side chains and aligns perpendicularly to the main chain to give rise a crystallization.[5] The role of water is to give the side chains the mobility for the alignment perpendicular to the main chains.[5] Similarly, "true up" of the side chain ends and the adjustment of the side chains may also be occurring in this case.

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