Ordered Structure of Poly(fluoroalkyl α-fluoroacrylate)s

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Introduction. Recently, physicochemical and structural investigations of fluoroalkyl acrylate/methacrylate polymers have received a great deal of attention.[1-6] In poly(fluoroalkyl acrylate) [-{$CH_2CHCOOCH_2(CF_2)_pH/F\}_q$-] (P*n*FA, *n* is the number of F atoms in the fluoroalkyl group) and poly(fluoroalkyl methacrylate) [-{$CH_2C(CH_3)$-$COOCH_2(CF_2)_pH/F\}_q$-] (P*n*FM; see Figure 1), it has been reported that the fluoroalkyl side chains crystallize in the polymer matrix to form lamellar structures which consist of single- or double-layer packings of the side chains, when the number of CF_2 moieties (p) is larger than 6. Our concern has been in understanding how the introduction of an F atom influences the structure and properties of acrylate polymers and, in particular, how the crystallization and mesogenicity of the fluoroalkyl side chains respond to the chemical structure of acrylate polymers. This paper reports our recent findings that poly(fluoroalkyl α-fluoroacrylate) [-{$CH_2CFCOOCH_2(CF_2)_pH/F\}_q$-] (P*n*FF; see Figure 1) has a crystalline phase even in the short fluoroalkyl homologs.

Experimental Section. P*n*FF, P*n*FM, and P*n*FA (*n* = 3–9) were prepared by a radical polymerization of the corresponding monomer in 1,3-bis(trifluoromethyl)benzene, using AIBN as an initiator and a chain-transfer agent as a molecular weight regulator in a Pyrex tube, into which the monomer and 1,3-bis(trifluoromethyl)benzene were sealed during deairing under liquid nitrogen, where the reaction temperature was 323 K for PnFF and 343 K for P*n*FM/P*n*FA. The products were finally heated at 453–533 K under a reduced pressure for 24 h to remove unreacted monomers and other volatiles. The polymers were used without further purification for the measurements. Weight-average molecular weights determined by a gel permeation chromatography ranged from 1.8×10^5 to 7.7×10^5. Isotacticities of P*n*FF, P*n*FM, and P*n*FA were 0.11–0.13, 0.056–0.069, and 0.017–0.031, respectively, and the syndiotacticities were 0.37–0.41, 0.52–0.56, and 0.37, respectively, as determined by NMR spectroscopy. The sheet samples were prepared by compression molding at a temperature above T_g and then heated enough above their melting points and cooled below T_g at a rate of about 0.3 K/min. The oriented samples were obtained by uniaxially drawing to a ratio of 3–4 at a temperature above T_g.

Thermal analyses were performed at a heating rate of 10 K/min using a differential scanning calorimeter (Perkin-Elmer; DSC-7). X-ray diffraction patterns were measured with a X-ray diffractometer (Rigaku Denki Co.; RU-3 and RAD-rA) at room temperature, using monochromatic CuKα radiation (40 kV, 70/100 mA). The diffracted X-rays were detected by a photographic flat film at a distance of 90 mm from the surface of the sheet samples by use of a normal-beam-transmission technique. The photograph was taken under vacuum to suppress air scatterings. Moreover, to confirm the values of the Bragg spacings,

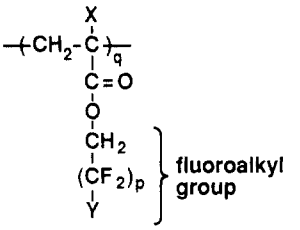

Figure 1. Chemical structures of samples. X = H: poly(fluoroalkyl acrylate) (P*n*FA). X = CH_3: poly(fluoroalkyl methacrylate) (P*n*FM). X = F: poly(fluoroalkyl α-fluoroacrylate) (P*n*FF). Y = H or F. *n*: no. of F atoms. When Y = H, *n* is an even number and $n = 2p$. When Y = F, *n* is an odd number and $n = 2p + 1$.

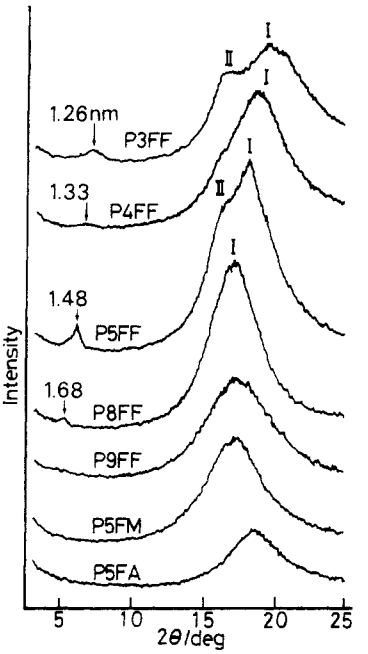

Figure 2. X-ray scattering intensity–Bragg angle (2θ) curves at room temperature.

the X-ray scatterings were also measured by a reflection method, and the scattering intensities were detected by a scintillation counter with a pulse-height analyzer. For the uniaxially oriented sheets, X-ray scattering measurements were performed along the equatorial and meridianal directions, respectively, after adjusting the drawing direction to the meridianal direction.

Results and Discussion. Figure 2 shows wide-angle X-ray diffractive intensity–Bragg angle (2θ) curves for P*n*FF homologs and the others, and diffraction patterns for P5FF and P4FF are illustrated in Figure 3. The X-ray diffraction patterns of P*n*FF (*n* = 3–8) show a few Debye rings and so, apparently, indicate a presence of crystallites even in the short fluoroalkyl P*n*FF homologs. P4FF and P8FF exhibit two Debye rings (inner ring and outer ring denoted as I), while P3FF and P5FF have three rings as the result of the appearance of another outer ring denoted as II. On the other hand, in P5FM and P5FA, only one diffuse scattering halo is observed near $2\theta = 17.3$ and 18.4°, respectively, which was also confirmed on the X-ray diffraction photographs. These results indicate that P5FM and P5FA are mostly amorphous and scarcely form crystallites, being well consistent with the past results reported by several researchers.[1,2] The crystallites in the short fluoroalkyl P*n*FF homologs have the following interesting structural features.

(1) The Bragg spacings of the innermost rings (low-angle scatterings) are 1.26 nm for P3FF, 1.33 nm for P4FF,

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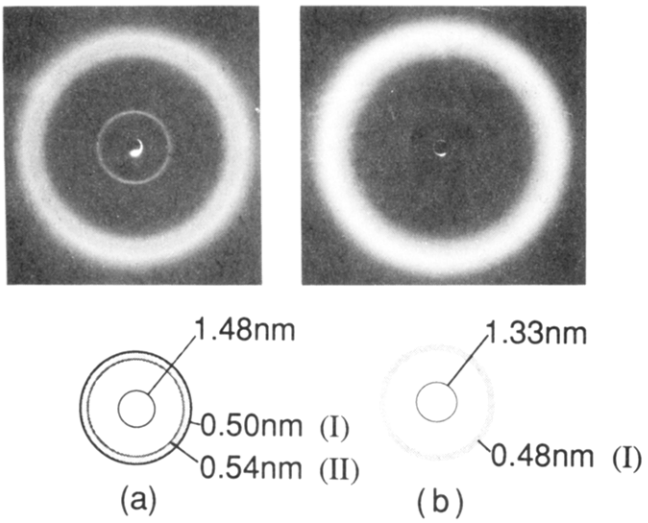

Figure 3. X-ray diffraction patterns of (a) P5FF and (b) P4FF at room temperature.

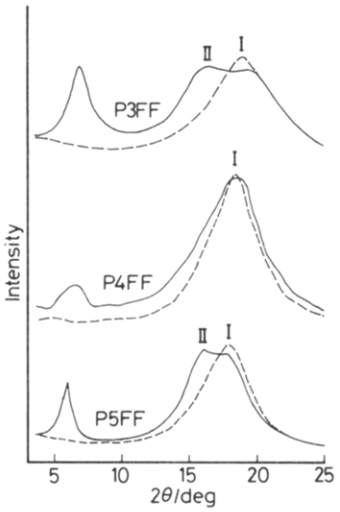

Figure 4. X-ray scattering curves at room temperature for uniaxially drawn samples. P3FF, P4FF, and P5FF: perpendicular (—) and parallel (- - -) patterns to the drawing direction.

1.48 nm for P5FF, and 1.68 nm for P8FF; each value is nearly twice as long as each side-chain length. Therefore, it was concluded that these samples have a double-layer packing structure of fluoroalkyl side chains. This is noteworthy, since this double-layer packing has been found only in P*n*FA/P*n*FM with crystallizable longer fluoroalkyl side chains,[2,3,5] for example, in P17FA/P17FM [the fluoroalkyl = $-CH_2CH_2(CF_2)_8F$].

(2) P3FF and P5FF have two outer rings (diffraction peaks) I and II at 0.45 and 0.54 nm and 0.50 and 0.54 nm, respectively, while P4FF and P8FF have only one outer ring I at 0.48 and 0.52 nm, respectively. Figure 4 shows X-ray scattering patterns for uniaxially drawn films at room temperature. The small-angle peak (the inner ring) is strengthened perpendicular to the drawing (meridianal) direction, which indicates that the fluoroalkyl side chains arrange almost perpendicular to the main chains. In the outer ring I in P3FF and P5FF, the intensity is a little more intense in the meridianal direction than in the equatorial direction. This can be understood, based on that the outer ring I comes from the lateral ordering between the fluoroalkyl side chains in each layer. The anisotropic X-ray results on the inner rings and outer ring I of the drawn films strongly support that the main backbone chains arrange parallel to the drawing direction

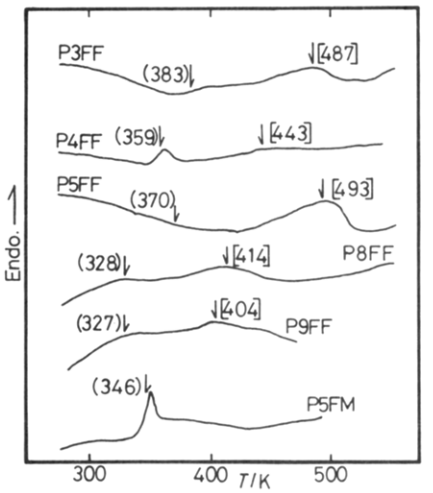

Figure 5. DSC heating curves at a rate of 10 K/min. ( ): T_g, [ ]: the melting point of the crystallites.

and the fluoroalkyl chains are packed in the perpendicular direction. The anisotropy of outer ring II in P3FF and P5FF is novel and interesting, although the origin is not well-assigned at present. The intensity of outer ring II is more intense in the equatorial direction than in the meridianal (drawing) direction. The above results lead us to the conclusion that the main backbone chains arrange each other to form an ordered packing in P3FF and P5FF. In P*n*FM and P*n*FA homologs, it has been reported that the long fluoroalkyl side chains are packed to form lamellar crystals, when the number of CF_2 moieties is larger than 6, as already mentioned. Our present results show that the short fluoroalkyl P*n*FF homologs such as P3FF and P5FF form the crystallites and that their crystallites consist of three-dimensional ordering in which the main backbone chains, themselves, participate in addition to the side chains forming lamellar packings.

(3) P4FF has a $-CF_2H$ end group in the fluoroalkyl side chain, while P5FF has a $-CF_3$ end group. This is only one difference in chemical structure between these two polymers. However, the structure of the crystals is largely different between the two. As seen in Figures 2 and 3, P4FF has only one outer ring I while P5FF has two outer rings, I and II. Inferring from the X-ray scattering results, the crystallinity appears to be smaller in P4FF than P3FF and P5FF and is much more decreased in P9FF, although the fluoroalkyl side chain of P9FF has the $-CF_3$ end group. These phenomena are also seen in DSC heating curves shown in Figure 5. On our unpublished recent data,[7] P17FF [the fluoroalkyl = $-CH_2CH_2(CF_2)_8F$] had a crystalline structure again. Therefore, the ordered packings of both main chains and side chains seem to be sensitively influenced by the length and chemical structure of the fluoroalkyl side chains.

This paper reports that P*n*FF has the crystallites formed by both main and side chains even in the short fluoroalkyl homologs such as P3FF and P5FF. Further structural studies of P*n*FF homologs will be published elsewhere in the near future.

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