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DSC AND X-RAY STUDIES ON SIDE-CHAIN CRYSTALLIZATION OF COMB-LIKE POLYMERS

Fluorinated *n*-alkyl acrylate and methacrylate polymers

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Abstract

Thermal properties of acrylate and methacrylate monomers containing long-fluorocarbon chains ($H(CF_2)_nCH_2OCOCH=CH_2$, (F_nA) and $H(CF_2)_nCH_2OCOC(CH_3)=CH_2$, ($F_nMA$), where $n=6$, 8, 10) and their comb-like polymers have been investigated by differential scanning calorimeter (DSC) and X-ray diffraction. The comb-like polymers ($PF_{10}A$ and $PF_{10}MA$) with sufficiently long-fluorocarbon chains showed a simple melting and crystallizing behavior. For the fusion of $PF_{10}A$ in 1st heating, enthalpy change ΔH_f was 18 kJ mol^{-1} and entropy change ΔS_f was 45 J K^{-1} mol^{-1}, while for $PF_{10}MA$ the values ΔH_f and ΔS_f were 5.3 kJ mol^{-1} and 14 J K^{-1} mol^{-1}, respectively. Melted PF_8A crystallized slowly, whereas PF_8MA with same fluorocarbon chain and also both of PF_6A and PF_6MA with shorter fluorocarbon chains can hardly crystallize by the aggregation of side-chains. Effects of the length of side-chain and the flexibility of main chain on the side-chain crystallization of comb-like polymers are clear. Crystallization process of the methacrylate monomers was sensitively affected by the scanning rate of DSC measurement and the length of fluorocarbon chains.

Keywords: comb-like polymer, DSC, fluorocarbon chain, side-chain crystallization, X-ray diffraction

Introduction

Thermal properties of comb-like polymers are influenced by the chemical nature of side chains, such as length, flexibility, bulkiness, polarity, etc., and by the flexibility of main chain [1–5]. Fluorocarbon chain is thicker than that of hydrocarbon chain and less flexible, since the van der Waals radius of fluorine atom is too large to allow a precise trans zig-zag planar conformation of $-(CH_2-CF_2)_n-$ chain, as in the poly(tetrafluoroethylene) crystal. The comb-like polymers containing long fluorocarbon chains in the side chains have been interested from the viewpoint of new functional polymers with special electrical and chemical properties, and also self-organizing property [7]. Budovskaya *et al.* formed some monomer molecules containing long fluorocarbon chains which have a tendency to make a layered structure [8] and the functional groups for polymerization would be arranged in an optimum orientation allowing a conformational freedom. In this study, thermal properties of acrylate and methacrylate monomers containing long fluorocarbon chains and their polymers have been examined by differential scanning calorimetry (DSC)

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and small angle X-ray diffraction. Effect of fluorocarbon-chain length and steric effect of methyl group at α-position of vinyl group on the packing mode of monomer molecules and its long side chains of the comb-like polymers have been investigated on the basis of enthalpy change for fusion ΔH_f and entropy change for fusion ΔS_f estimated by DSC measurements.

Experimental

These monomers were purchased from Daikin Kaseihin-hanbai: 1H,1H,11H-icosafluoroundecyl methacrylate: $H(CF_2)_{10}CH_2OCOC(CH_3)=CH_2$, $F_{10}MA$, *m.p.* 37.2–38.2°C; 1H,1H,11H-icosafluoroundecyl acrylate: $H(CF_2)_{10}CH_2OCOCH=CH_2$, $F_{10}A$, *m.p.* 44.5–45.4°C; 1H,1H,9H-hexadecafluorononyl methacrylate: $H(CF_2)_8CH_2OCOC(CH_3)=CH_2$, F_8MA, *m.p.* 14.8°C; 1H,1H, 9H-hexadecafluorononyl acrylate: $H(CF_2)_8CH_2OCOCH=CH_2$, F_8A, *m.p.* 19°C; 1H,1H,7H-dodecafluoroheptyl methacrylate: $H(CF_2)_6$–$CH_2OCOC(CH_3)=CH_2$, F_6MA, *m.p.* 34.6°C. $F_{10}MA$ and $F_{10}A$ were used after purification by recrystallization from the ethanol solution, but F_8A, F_8MA and F_6MA were used as received, because melting points of these monomers are too low for a usual recrystallization. The polymers of these monomers, abbreviated as $PF_{10}MA$, $PF_{10}A$, PF_8MA, PF_8A and PF_6MA, were obtained by γ-ray-irradiation post-polymerization (1–3 Mrad in liq. N_2). The polymerized samples of 0.5–1.0 g were dissolved in acetone of 1–2 ml and poured into CCl_4 of 60–80 ml at room temperature [9, 10], and the purified polymers by reprecipitation method were used for DSC and X-ray diffraction measurements without thermal disturbance.

Thermal properties of monomers and their polymers were measured using a Seiko Instruments Model DSC20 differential scanning calorimeter. Temperature and energy calibration of the DSC apparatus was checked using indium as a standard of a scanning rate of 2 or 5°C min^{-1} and the samples in the range of 4–5 mg were hermetically sealed in Al pans (50 μl). X-ray diffraction patterns were measured with a Rigaku diffractometer (RAD-B, CuK_α radiation 0.15405 nm).

Results and discussion

In Fig. 1 the DSC curves for first heating (melting) and first cooling (crystallization) with $F_{10}A$, $F_{10}MA$ and F_8A monomer and the corresponding comb-like polymers are shown. The simple phase transition behaviour of $F_{10}A$ and $PF_{10}A$ is shown in Fig. 1(A), whereas the melting point of comb-like polymer (118.2°C) is 73°C higher than that of monomer (45.4°C). Although molar heat of fusion for constitutional unit of $PF_{10}A$ ($\Delta H_f=18$ kJ mol^{-1}) was almost same with that of its monomer $F_{10}A$ ($\Delta H_f=18$ kJ mol^{-1}), the entropy change for $PF_{10}A$ ($\Delta S_f=45$ J K^{-1} mol^{-1}) was smaller than that for $F_{10}A$ ($\Delta S_f=56$ J K^{-1} mol^{-1}). Here, ΔH_f was estimated from the peak area, A (cm^2) in DSC curve, using a following equation, $\Delta H_f=A/m\times 60/B\times Y(25)$, where m is mass of sample (mg), B is chart speed (cm min^{-1}), Y is range of recorder (mJ s^{-1}). As an approximation guess, ΔS_f was obtained from $\Delta H_f/T_m$, however, for T_m the peak value was taken. The entropy difference indicates that comb-like arrangement of fluorocarbon side-chains in poly-

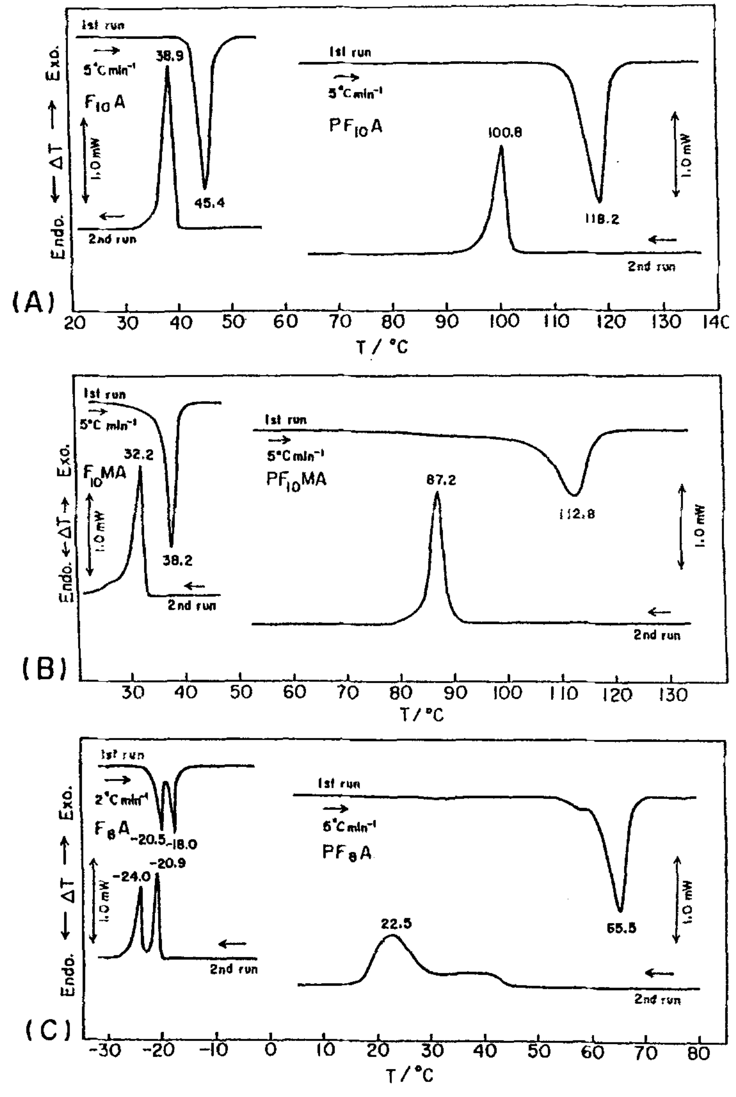

Fig. 1 DSC curves for F$_{10}$A, F$_{10}$MA and F$_8$A and their polymers: (A) F$_{10}$A and PF$_{10}$A, (B) F$_{10}$MA and PF$_{10}$MA, (C) F$_8$A and PF$_8$A

meric PF$_{10}$A restricts the rotational motion of main chain in the crystallization process. The comb-like polymers can not achieve an energy minimum of compact packing. As shown in Fig. 2(A), in the small angle X-ray diffraction pattern of PF$_{10}$A, the first order and second order diffraction peaks appeared at $2\theta=4.96^\circ$ (very strong) and 10.0° (week) indicating a layered structure of 1.78 nm distance, and a very strong peak appeared at $2\theta=17.96^\circ$, which corresponds to a hexagonal packing of fluorocarbon chains (d=0.49 nm) and is larger than the dimension of hexagonal packing of hydrocarbon chains (d=0.42 nm) [11, 12]. In contrast, the

X-ray diffraction pattern of PF$_{10}$MA (Fig. 2(B)) was relatively broad and week. The crystal of PF$_{10}$MA seems to be defective in construction. Figure 3 shows illustrations for polymerization process (A) and arrangements of F$_{10}$A and PF$_{10}$A (B) in the lamellar structure. In addition, the $-CH=CH_2$ groups are arranged regularly in layered crystal of F$_{10}$A and they have fairly large freedom for local motion. This situation can be considered as an optimum condition for the solid-state polymerization *via* γ-radiation [11, 12].

The replacement of α-hydrogen atoms with methyl groups, the thermal properties of polymer crystals, which may be affected by a lower degree of freedom of main chain, was examined. Figure 1(B) shows DSC curves for F$_{10}$MA and PF$_{10}$MA. Their melting and crystallization peaks resemble with those for F$_{10}$A and PF$_{10}$A. The melting points of F$_{10}$MA and PF$_{10}$MA are lower than those of corresponding F$_{10}$A and PF$_{10}$A by 5–7°C. In the case of PF$_{10}$MA, the difference between melting temperature and crystallization temperature is 25°C and larger (7°C) than that for PF$_{10}$A of 18°C. The super cooling suggests that the rate of self-organization of this comb-like polymers is retarded by the restriction of conformational freedom of the main chain for PF$_{10}$MA owing to a steric effect of the α-methyl groups. Furthermore, the enthalpies of fusion and crystallization of PF$_{10}$AM were $\Delta H_f=5.3$ kJ mol^{-1} and $\Delta H_c=5.9$ kJ mol^{-1}, and the entropies of the two physical transitions are $\Delta S_f=14$ JK^{-1} mol^{-1}, $\Delta S_c=16$ JK^{-1} mol^{-1}. The difference in entropy changes for fusion with respect to the difference of a methyl group is remarkable: PF$_{10}$A; $\Delta S_f=45$ JK^{-1} mol^{-1} *vs.* PF$_{10}$MA: $\Delta S_f=14$ JK^{-1} mol^{-1}, although the values of entropy changes for the monomers are rather similar, F$_{10}$A: $\Delta S_f=56$ JK^{-1} mol^{-1}, F$_{10}$MA: $\Delta S_f=48$ JK^{-1} mol^{-1}. The side chain crystallization of comb-like polymers affected by a steric effect of α-methyl groups on the main chain flexibility is evident.

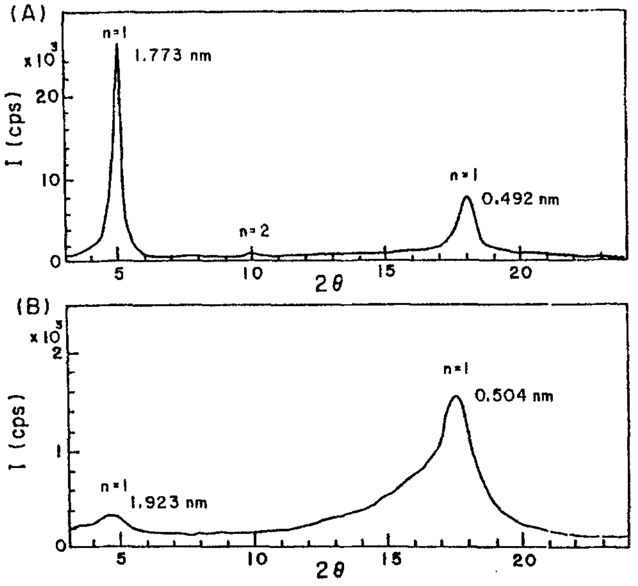

Fig. 2 X-ray diffraction patterns for comb-like polymers: (A) PF$_{10}$A and (B) PF$_{10}$MA

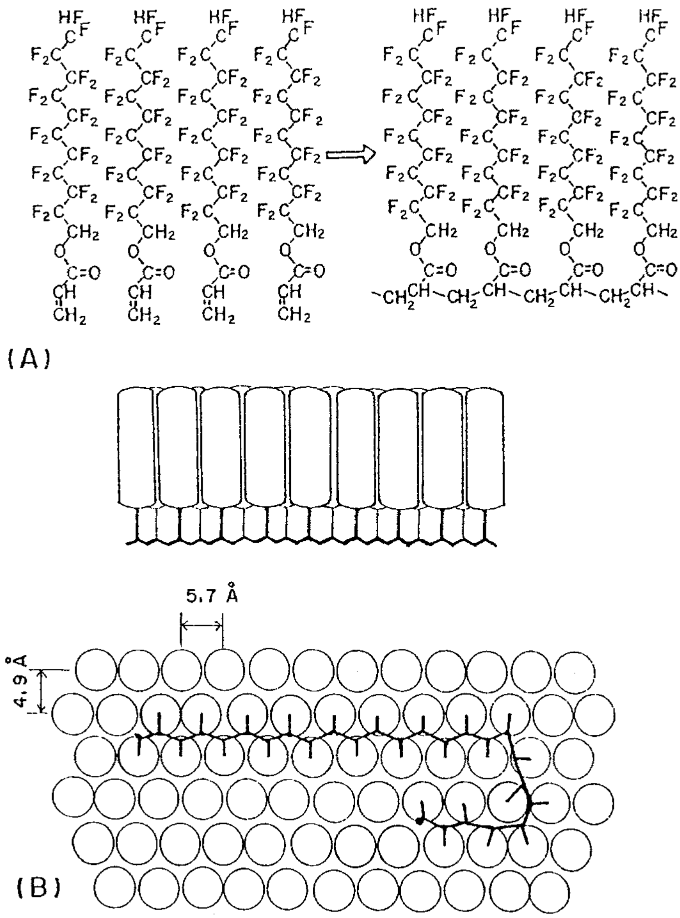

Fig. 3 Illustration for polymerization process (A) and arrangements of $F_{10}A$ and $PF_{10}A$ (B)

As shown in Fig. 1(C), F_8A exhibited two endothermic peaks indicating an enantiotropic phase transition, such as crystal⇔mesophase⇔liquid. In addition, when F_8A was reheated immediately after an exothermic peak at higher temperature a corresponding endothermic peak appeared with good reproducibility. These DSC results indicate the characteristic thermal property of F_8A, because an acrylate monomer having appropriate long alkyl chain tend to exhibit a polymorphism [3, 4, 12]. A melting peak of PF_8A appeared at 65°C and a broad crystallization peak appeared at 22°C, whereas the shape of these peaks was changed to normal in successive DSC measurements. It can be seen from this result that the side chain crystallization of PF_8A is not so easy, because the degree of ordering in crystal may be directly related to the number of CF_2 groups, as reported by Budovskaya *et al.* [8]. Although PF_8MA and PF_6MA are a powder or a bulk solid at room temperature, DSC measurements of PF_8MA and PF_6MA could not give a clear informa-

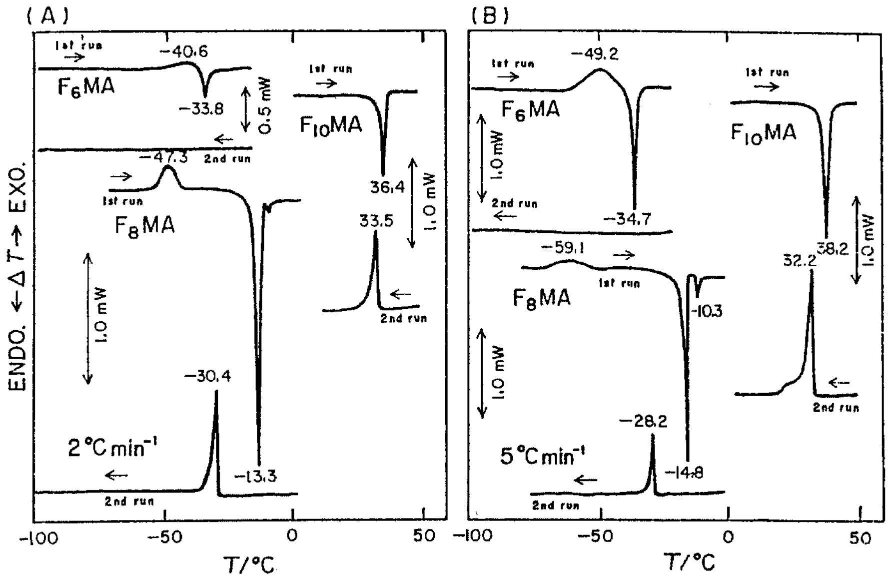

Fig. 4 Effect of scanning rate on the thermal behaviour of F_6MA, F_8MA and $F_{10}MA$: (A) 2°C min^{-1}, (B) 5°C min^{-1}

tion, probably because the side-chain crystallization is not possible for these comb-like polymers.

Finally, effect of scanning rate on the thermal behaviour of F_6MA, F_8MA and $F_{10}MA$ was examined. As shown in Fig. 4, phase transition temperature shifted irregulary with the increase of scanning rate, $F_{10}MA$ is the only normal monomer; a sufficient long fluorocarbon chain make the difference. With F_6MA and F_8MA, the scanning rate acted reversely on the exothermic peaks, which should be ascribed to crystal growth during heating at lower scan rate (2°C min^{-1}). In the case of F_8MA, a relatively clear exothermic peak at –47.3°C and a big endothermic peak at –13.3°C are seen at the heating curve of 2°C min^{-1}, whereas a broad exothermic peak at –59.1°C and a sharp endothermic peak at –14.8°C accompanied with a shoulder at –10.3°C are seen at the heating curve of 5°C min^{-1}. With F_6MA no crystallization peak appeared in the cooling curves of 2 and 5°C min^{-1}, although the melting peaks were clearly observed. From the fact that even a small difference (2.5 times) in scanning rates affected evidently on the thermal behavior of these monomers, it is clarified that the relaxation time of monomer molecules in the crystallization process are influenced by the balance between a coagulation force among fluorocarbon chains and a repulsive force of methacrylic acid residues having bulky α-methyl group.

The $-CH_2-$ group between the fluorocarbon chain and acrylic and methacrylic acid residues may act as a flexible spacer for a compact packing of the stiff long-fluorocarbon chains.

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