Aggregation state and mesophase structure of comb-shaped polymers with fluorocarbon side groups

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The aggregation states of a series of comb-shaped polymers with perfluoroalkyl side chains were investigated. The main chains of the comb-shaped polymers were poly(fumarate), poly(acrylate) and poly(methacrylate). D.s.c. and w.a.x.d. measurements and p.o.m. observations over a wide temperature range showed that all the poly(fluoroalkylfumarates) (PFAF) investigated were amorphous polymers, but poly(fluoroalkylacrylate) (PFAA) and poly(fluoroalkylmethacrylate) (PFAMA) having a heptadecafluorodecyl (C_8F_{17}) group in the side chain were in a mesomorphic state at room temperature. The type of mesophases can be most likely classified as an ordered smectic liquid crystalline (LC) structure in the Smectic B (S_B) modification for PFAA and an unordered smectic LC structure in the Smectic A (S_A) modification for PFAMA. Increasing the main chain flexibility in going from poly(fumarate) to poly(methacrylate) and poly(acrylate) enhances the probability of ordered structure formation.

(Keywords: poly(fluoroalkylfumarate); poly(fluoroalkylacrylate); poly(fluoroalkylmethacrylate); mesomorphic state; smectic phase; liquid crystalline order)

INTRODUCTION

The so-called comb-shaped polymers occupy a special position among a large number of polymers. They differ from ordinary branched polymers due to the fact that they have many side chains; for example, each monomeric unit can contain such a chain. It is important that the length of these side groups is significantly greater than their cross-section. Only under this condition can the unique properties of comb-shaped polymers occur (for example, the autonomous behaviour of the side chains, their capacity to form layered structures, and to crystallize regardless of the main chain configuration)[1].

Closely spaced side chains within the same backbone create the conditions for their interaction, which is very similar to what takes place for a group of small molecules of similar structure. On the other hand, the presence of the main chain with its inherent flexibility and intermolecular interactions leads to the dual character of the ordering and properties of the system as a whole.

The autonomous nature of the behaviour of the side chains of comb-shaped polymers makes it possible to create liquid-crystalline (LC) polymers by incorporating mesogenic groups in the side chains. To date several hundred polymeric compounds with mesogenic groups have been synthesized. These mesogenic segments are usually a component of common low-molecular-weight liquid crystals (Shiff bases, cholesterol esters, substances containing substituted phenyl, diphenyl and diphenylbenzoate groups, etc.). Comb-shaped polymers having fluorocarbon segments in the side chains have attracted particular attention due to the very low values of their surface energy[2–6]. On the other hand, molecular models show that the general shape of the normal fluorocarbon chain is nearly cylindrical. Since the van der Waals radius of fluorine is larger than that of hydrogen, the fluorine atoms attached to a planar zigzag carbon chain would be overcrowded. This slight overcrowding is relieved by rotation at each chain-bond with a slight opening of the bond angles[7,8] to 116°. Fluorocarbon molecules (for instance, PTFE) appear to be very stiff, and are unlikely to be much influenced by the weak intermolecular forces which are similar in magnitude to those between hydrocarbon molecules[8]. Thus, the low-molecular-weight fluorocarbon molecules of normal structure and perfluoroalkyl groups (no less than C_5–C_6) have an anisodiametric, rod-like shape, and in this respect they are to some extent unique substances with extremely low intermolecular forces which can form LC structures.

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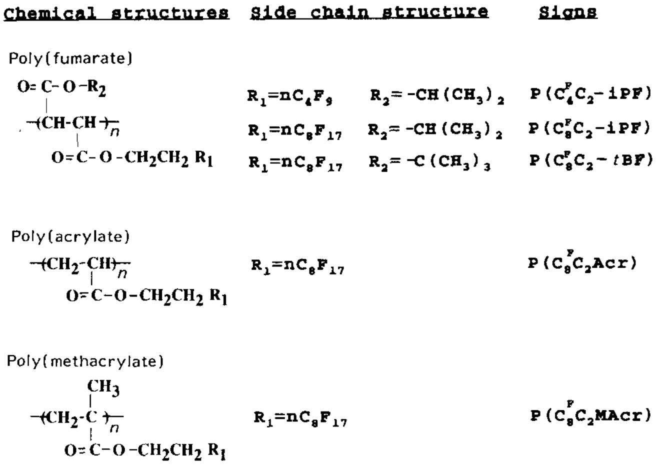

Figure 1 Chemical structure of poly(fluoroalkylfumarates), poly(fluoroalkylacrylate) and poly(fluoroalkylmethacrylate)

In the present work, the aggregation states of a series of comb-shaped polymers such as poly(acrylates), poly(methacrylates) and disubstituted poly(fumarates) containing perfluoroalkyl groups in their side chains have been investigated. We will apply the term liquid crystalline state (including the concept of a glassy or frozen LC state in ref. 1) to the thermodynamically stable phase state of polymers characterized by spontaneously appearing anisotropic properties (particularly optical anisotropy) in the absence of a three-dimensional crystal lattice.

EXPERIMENTAL

Materials

Poly(fluoroalkylfumarates) (PFAF), poly(fluoroalkylacrylate) (PFAA) and poly(fluoroalkylmethacrylate) (PFAMA) were prepared by radical polymerization. The polymerization procedure is similar to that for poly(alkylfumarate)[9,10]. *Figure 1* shows the chemical structure of poly(3,3,4,4,5,5,6,6,6-nonafluorohexyl isopropyl fumarate) ($P(C_4^FC_2\text{-iPF})$), poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl isopropyl fumarate) ($P(C_8^FC_2\text{-iPF})$), poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl *t*-butyl fumarate) ($P(C_8^FC_2\text{-}t\text{BF})$), poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate) ($P(C_8^FC_2\text{Acr})$), poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate ($P(C_8^FC_2\text{MAcr})$). Polymer films for physico-chemical investigation were prepared by casting polymer solution on a clean glass plate at room temperature. The solvent used was 1,1,2-trifluorotrichloroethane.

Physico-chemical characterization

Wide-angle X-ray diffraction (w.a.x.d.) patterns were recorded on a photographic film using Cu K_α radiation from an X-ray generator (RU-200, Rigaku Co., Ltd). D.s.c. thermograms were obtained using a differential scanning calorimeter (DSC8230, Rigaku Co., Ltd) at a heating rate of 5 K min^{-1} under a dried nitrogen purge. Optical anisotropy in the film was observed with a polarizing optical microscope under crossed nicols.

RESULTS AND DISCUSSION

Poly(fluoroalkylfumarates)

Figure 2 shows the d.s.c. thermograms for poly(fluoroalkylfumarates). All polymers presented in *Figure 2* are distinguished from each other by either the length of the side fluorocarbon group or the alkyl substituent of the second ester group. These polymers have only one common feature: the spacer fragment in the side fluorocarbon groups is the same (two methylene units). *Figure 2* indicates that all investigated poly(fumarates) are essentially amorphous. The endothermic peaks observed for the cast films of $P(C_4^FC_2\text{-iPF})$ and $P(C_8^FC_2\text{-iPF})$ disappeared after annealing (the first run). It can be seen that the d.s.c. curves of annealed films change their baseline slopes in the region 303–313 K. It should be noted that poly(fluoroalkylfumarates) are brittle materials at room temperature but above 303–313 K they became ductile. Also, at the temperature of 313 K, $P(C_4^FC_2\text{-iPF})$ and $P(C_8^FC_2\text{-iPF})$ can be elongated up to 700% and 400%, respectively. Though further study is necessary in order to characterize the thermal transition of PFAF at this temperature region, it may be confirmed that the slope change of the d.s.c. baseline is associated with the glass transition temperature.

The w.a.x.d. patterns of PFAF showed three diffuse rings as in *Figure 3*. For example, in the case of $P(C_8^FC_2\text{-}t\text{BF})$ and $P(C_8^FC_2\text{-iPF})$ these three rings correspond to Bragg spacing (d_1, d_2 and d_3) of 0.53, 0.99, 2.71 and 0.53, 0.95, 2.4 nm, respectively. The first and third diffraction maxima are more intense than the

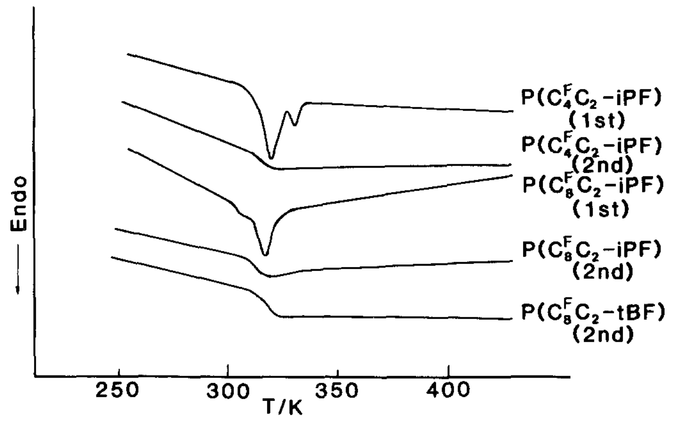

Figure 2 D.s.c. thermograms for poly(fluoroalkylfumarates)

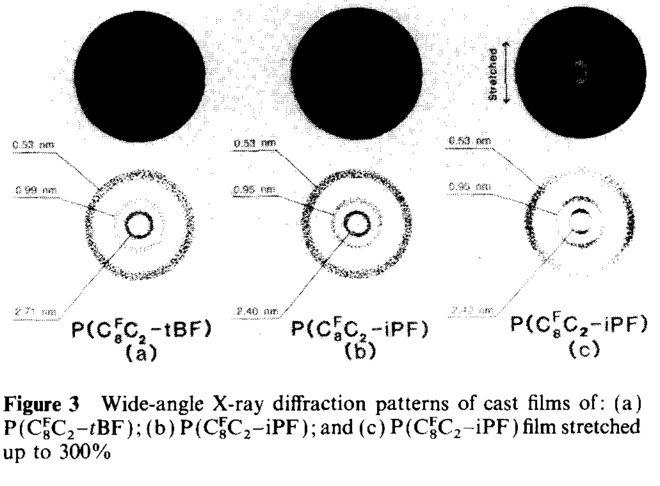

Figure 3 Wide-angle X-ray diffraction patterns of cast films of: (a) $P(C_8^FC_2\text{-}t\text{BF})$; (b) $P(C_8^FC_2\text{-iPF})$; and (c) $P(C_8^FC_2\text{-iPF})$ film stretched up to 300%

second. The value of d_1 is very close to the value of the interchain distance in the amorphous region of poly(tetrafluoroethylene)[11]. As was shown in our previous report[2], the value of the second diffraction maximum d_2 observed in the small-angle region depends on the length of the side chain of poly(dialkylfumarates). It should be noted that this type of change in d_2 reflects the specific features of the structure of all comb-shaped polymers. Usually, the dependence of d_2 on the number, n, of carbon atoms in the side alkyl chain is linear[12,13].

$$d_2 = d_0 + na \qquad (1)$$

The presence of a large spacing and its linear dependence on n indicates that the main chains of comb-shaped polymers in the amorphous state are arranged in a certain order with respect to each other at distances close or equal to the length of the side chains, the latter being oriented perpendicularly to the longitudinal axis of the macromolecule[1]. In such a situation, d_0 should correspond to the so-called effective diameter of the main chain, including the spacer in the alkyl group, and also, should correspond to the increment in the length of the side chain per CH_2 group ($a = 0.127$ nm for the methylene chain in the planar zigzag conformation).

The extrapolation of the value of d_2 to $n = 0$ for PAF[2] for $n = 4$, 6 and 8 leads to the value of the main chain diameter, $d_0 = 1.04$ nm. The figure of 1.04 nm agrees with that obtained by the CPK (Coury–Pauling–Koltun) molecular models, but the value of a obtained exceeds 0.127 nm and equals 0.15 nm. Large values of a were also obtained for such polymers as, for instance, poly(*N*-alkyl maleimides) and poly(phenyl methacrylic esters) of n-alkoxybenzoic acids, which have a relatively complex and rigid linkage[14,15]. Consequently, by analogy with the comb-shaped polymers discussed above, this diffraction maximum can be attributed to the interaction of the side fluorocarbon groups. The increase in d_1 (from[2] 0.47 nm to 0.53 nm (*Figure 3*)) in going from PAF to PFAF reflects the difference in van der Waals radii of hydrogen and fluorine (0.11–0.12 nm and 0.135 nm, respectively). The values of the second diffraction maximum d_2 and the third d_3 are essentially dependent on the length of the side chain being equal to[2] 0.76, 1.3 nm and 0.95, 2.4 nm for $P(C_4^FC_2$–iPF) and $P(C_8^FC_2$–iPF), respectively. The value of d_3 for $P(C_8^FC_2$–*t*BF) is 2.71 nm. This slight increase of d_3 reflects the increase of the main chain diameter in going from the i-propyl substituent to the more bulky *t*-butyl one.

The w.a.x.d. pattern of the oriented sample of $P(C_8^FC_2$–iPF), which was obtained by uniaxially drawing the cast film at 313 K to a draw ratio of 3 (*Figure 3*), shows that two inner rings on the meridian are more intense than those on the equator (the drawing direction is parallel to the meridian). In contrast, the outer ring is slightly more intense on the equator than on the meridian. It may be concluded from this w.a.x.d. data that $P(C_8^FC_2$–iPF) is oriented in the process of uniaxially drawing while the main chains are situated almost perpendicular to the drawing direction. Under polarizing optical microscopy (p.o.m.), the cast film of $P(C_8^FC_2$–iPF) looks optically isotropic, but optical anisotropy appears after uniaxial drawing. These observations agree with the w.a.x.d. measurements and indicate that $P(C_8^FC_2$–iPF) is oriented during uniaxial drawing. The intensity of the optical anisotropy (brightness of the field of vision) for the stretched film fixed between two glass plates maintained a practically constant value in the temperature range from room temperature to around 313 K, and then decreased by a factor of about two at higher temperatures than 313 K. The w.a.x.d. pattern obtained at 313 K also showed the orientation of polymeric chains, but the profile was more diffuse in comparison with *Figure 3c*, which can be explained by a reduction in orientational order. The optical anisotropy of a specimen decreased drastically and almost diminished in the vicinity of 343 K. Therefore, the p.o.m., d.s.c. and w.a.x.d. studies of uniaxially drawn films of $P(C_8^FC_2$–iPF) made in the temperature range 293–373 K allow us to conclude that there are two temperature regions, in the vicinity of 313 K and 343 K respectively, in which a distinct change in the thermal molecular motion of the polymer chains takes place.

Poly(fluoroalkylacrylate) and poly(fluoroalkylmethacrylate)

Figure 4 shows the w.a.x.d. patterns of the cast $P(C_8^FC_2Acr)$ and $P(C_8^FC_2MAcr)$ films at room temperature. The intensity curve for $P(C_8^FC_2Acr)$ showed four diffraction peaks corresponding to a Bragg spacing of 0.50, 1.07, 1.62 and 3.33 nm. Annealing and quenching the $P(C_8^FC_2Acr)$ did not markedly change the positions of diffraction maxima but increased and decreased, respectively, their intensity. The diffraction ring at 0.50 nm corresponds to the intermolecular distance between the side fluorocarbon groups. The spacing of the innermost diffraction (3.33 nm) is twice as long as the expected side chain length estimated by the use of c.p.k. molecular models, and the spacing of the next (1.62 nm) is equal to the side chain length (the second-order diffraction of 3.33 nm). The p.o.m. observations showed that the $P(C_8^FC_2Acr)$ film was composed of optically anisotropic domains at room temperature. The optical texture of $P(C_8^FC_2Acr)$ was a so-called fine-grained texture which consisted of a set of birefringent regions.

The w.a.x.d. pattern of the $P(C_8^FC_2MAcr)$ cast film also showed four Debye rings as shown in *Figure 4*, corresponding to a Bragg spacing of 0.53, 1.04, 1.55,

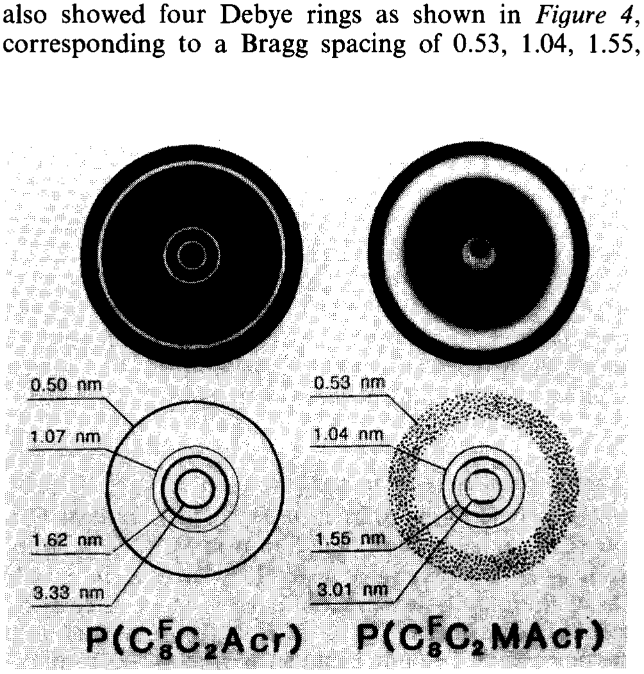

Figure 4 Wide-angle X-ray diffraction patterns of cast films of: (a) $P(C_8^FC_2Acr)$; and (b) $P(C_8^FC_2MAcr)$ at room temperature

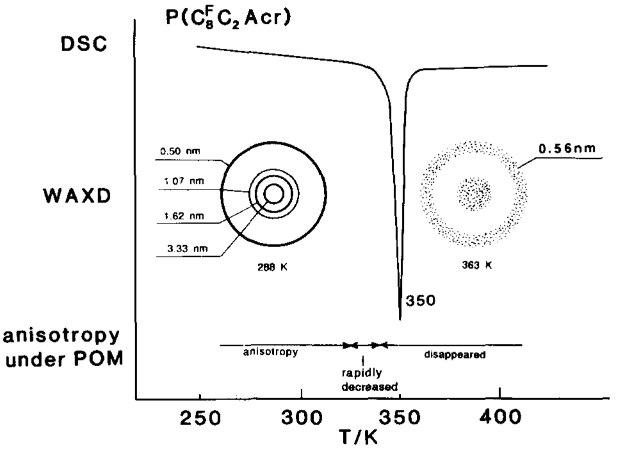

Figure 5 D.s.c. thermogram, optical anisotropy and w.a.x.d. pattern of P(C$^F_8$C$_2$Acr)

3.01 nm. The slight orientation in the small angle reflection might be due to the gravitational effect or surface induced orientation by the cell window. The spacing of the innermost diffraction (3.01 nm) is slightly smaller than twice the length of the expected side chain (3.33 nm). The ratio of the spacing of the three inner diffractions is about 3 : 2 : 1. The outer ring corresponding to the intermolecular distance between C_8F_{17} groups was very intense but diffuse. Three inner rings on the meridian were more intense than those on the equator. Optical anisotropy was also observed for this specimen, but in contrast to P(C$^F_8$C$_2$Acr), the optical texture of P(C$^F_8$C$_2$MAcr) is uniform. All these results indicate that there is some orientation of polymeric chains in the P(C$^F_8$C$_2$MAcr) cast films. The presence of diffraction maxima corresponding to the long spacings reflects the existence of layered structures in the P(C$^F_8$C$_2$MAcr) and P(C$^F_8$C$_2$Acr) films.

Figure 5 shows a d.s.c. thermogram, the temperature dependence of the w.a.x.d. pattern and the birefringence of P(C$^F_8$C$_2$Acr). The d.s.c. curve of P(C$^F_8$C$_2$Acr) shows one sharp endothermic peak at 350 K in the range of 273–423 K. P.o.m. observation revealed that 350 K is also the clearing point temperature. The w.a.x.d. patterns of P(C$^F_8$C$_2$Acr) obtained at 288, 318 and 338 K showed that there was no marked change in the values of spacings corresponding to all four diffraction maxima, but all sharp Debye rings were converted into a diffuse ring of 0.56 nm and an amorphous halo in the small angle region above 350 K.

The w.a.x.d. and p.o.m. data presented in *Figure 5* indicate that the endothermic peak at 350 K seems to be due to the mesomorphic–isotropic phase transition. The enthalpy of phase transition, ΔH_{cl} measured from the d.s.c data is 20.35 J g^{-1}. According to the classification given in ref. 1, the structure of P(C$^F_8$C$_2$Acr) below 350 K seems to be ordered smectic liquid crystalline which can be classified as Smectic B (S_B) type. The structure of the S_B mesophase is characterized by the arrangement of the side chains in layers where the axes of the side chains are perpendicular to the plane of the layers with ordering of the side chains in layers. The X-ray patterns of polymers in the S_B modification, in addition to a number of small-angle reflections, usually exhibit a narrow and relatively intense wide-angle reflection[16,17].

The w.a.x.d. patterns of P(C$^F_8$C$_2$Acr) are characterized both by the large spacing, indicating the existence of layered structure, and by the sharp diffraction at 0.50 nm corresponding to the intermolecular distance between the side fluorocarbon groups, indicating that side chains are ordered in layers. As shown above, the magnitudes of large spacings correlate with the length of the side chain. The fine-grained optical texture of P(C$^F_8$C$_2$Acr) and the elevated value of ΔH_{cl} (20.35 J g^{-1}) also correspond to those observed for LC polymers with ordered smectic mesophase[1]. However, it should be remembered that in practice it is frequently very difficult to draw a boundary between the crystalline and the LC state in ordered smectic phases.

Thermal properties of P(C$^F_8$C$_2$MAcr) are shown in *Figure 6*. In the range 273–523 K, the d.s.c. curve for P(C$^F_8$C$_2$MAcr) shows three endothermic peaks (a large, sharp one at 366 K and two small peaks at 321 and 388 K), one endothermic shoulder at ca. 346 K and endothermic deflection from the base line at ca. 493 K. According to w.a.x.d. measurements, sharp Debye rings corresponding to the large spacings merged in a diffuse halo in the small angle region above 380 K. On the other hand, all data presented in *Figure 6* indicate that P(C$^F_8$C$_2$MAcr) is in a mesomorphic state below this temperature due to the presence of layered reflections in w.a.x.d. patterns, and optical anisotropy under p.o.m. Therefore, the peak at 388 K may be attributed to the mesomorphic–isotropic phase transition. The type of mesophase of P(C$^F_8$C$_2$MAcr) can be most likely classified as the smectic phase in the S_A modification. Comparison of the smectic layer width of 1.55 nm with the calculated side chain length (1.62 nm) indicates that the side chains of P(C$^F_8$C$_2$MAcr) are arranged in a single-layer packing in the temperature range 366–388 K. As the intensity of the diffraction ring corresponding to single-layer spacing is not markedly changed for w.a.x.d. patterns measured below and above 366 K, the phase transition at 366 K can be identified as the transition of a smectic LC region with double-layer packing from a mesomorphic to an isotropic state (melting of a smectic region with double-layer packing). At temperatures below 366 K the coexistence of single-layer and double-layer packing is observed. It is supposed that the coexistence of at least two types of packing is apparently one of the features of the structure of LC polymers with mesogenic side groups[1] and this phenomenon has already been confirmed in particular, for P(C$^F_8$C$_2$Acr), as shown in *Figure 4*.

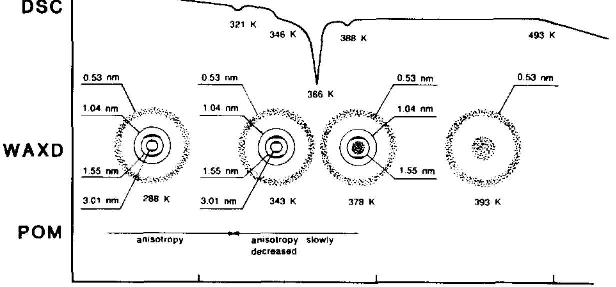

Figure 6 D.s.c. thermogram, optical anisotropy and w.a.x.d. pattern of P(C$^F_8$C$_2$MAcr)

Similar results have also been published for other LC polymers[18–21]. The total enthalpy of the phase transition at 366 and 388 K is 6.5 J g^{-1}. This is in agreement with values obtained by other authors for LC polymers with an S_A structure[1].

The peak at 321 K may be attributed to the transition from a glassy (frozen) LC structure of $P(C_8^FC_2MAcr)$ side chains to an LC state, but this interpretation should be considered as rather preliminary. More accurate conclusions concerning the nature of the transition at 321 K, as well as the endothermic shoulder at ca. 346 K and the endothermic deflection of the d.s.c. curve at ca. 493 K, could be made on the basis of further detailed investigation of the molecular motion of $P(C_8^FC_2MAcr)$.

CONCLUSION

Comb-shaped polymers with various types of main chain polymers (poly(fumarate), poly(acrylate) and poly(methacrylate)) with side chains of perfluoroalkyl groups have been investigated. D.s.c. and w.a.x.d. measurements and p.o.m. observations showed that all investigated poly(fluoroalkylfumarates) were amorphous polymers, but $P(C_8^FC_2MAcr)$ and $P(C_8^FC_2Acr)$ manifested a mesomorphic state at room temperature. The role of mesogenic groups in these cases is played by perfluoroalkyl C_8F_{17} groups. This is the first report of an LC structure of the comb-shape polymers having a perfluoroalkyl mesogenic group in the side chain.

Main chain flexibility increases in the order of poly(fumarate), poly(methacrylate) and poly(acrylate). As a consequence the aggregation state of the investigated polymers at room temperature changes as follows: amorphous state for $P(C_8^FC_2{-}iPF)$, unordered smectic for $P(C_8^FC_2MAcr)$, and ordered smectic LC (or even crystalline state) for $P(C_8^FC_2Acr)$. Increasing the flexibility of the main chain increases the probability of an ordered structure formation.

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