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Room-temperature transitions and melting of tetrafluoroethylene–hexafluoropropylene copolymers with low comonomer contents [1]

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Abstract

Differential scanning calorimetry has been used to study the room-temperature transitions and melting of native and melt-crystallized tetrafluoroethylene–hexafluoropropylene (TFE–HFP) copolymers from aqueous dispersion polymerization, with low comonomer contents (between 0.15 and 0.8 mol% of HFP). At least three clear room-temperature transitions are observed for the native polymers suggesting, according to previous evidence, the coexistence of two crystalline components. Also the behaviour after annealing at the melting temperature of the melt-crystallized samples has been investigated. Conclusions are drawn concerning the morphology of the native and melt-crystallized polymers. An interpretation of the melting peaks in the light of the suggestions given by the room-temperature transitions is suggested.

INTRODUCTION

Polytetrafluoroethylene (PTFE) presents a high melting temperature and a very high melt viscosity and, hence, requires special processing techniques such as powder sintering and paste extrusion whereas tetrafluoroethylene and hexafluoropylene (TFE–HFP) copolymers with very low comonomer contents have useful mechanical and chemical properties and require less stringent processing conditions, e.g. lower extrusion pressures.

It is well known that at atmospheric pressure, PTFE displays two crystal–crystal transitions at 19°C (transition 1) and at 30°C (transition 2) [1,2]. Below 19°C, PTFE is generally thought to crystallize in a well-ordered triclinic phase [1,3,4], whereas between 19 and 30°C, it forms a well-known, partially ordered, hexagonal phase [1,2]. Above 30°C and up

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to the melting point (equilibrium melting temperature, $T_m^\circ = 332°C$ [5]), a pseudo-hexagonal, very disordered phase is stable [1,2,5]. These results have been obtained by X-ray diffraction and calorimetric measurements on the melt-crystallized polymer. Differential scanning calorimetry (DSC) has revealed another transition at 17°C (transition 1′) for native PTFE from aqueous dispersion polymerization [6,7]. Our previous in-depth examination by DSC and wide-angle X-ray scattering (WAXS) of the room-temperature transitions of native PTFE and the effect of the heating rate and of the thermal history of these transitions [8–11], showed that transition 1′ is not due to kinetic effects, suggesting the coexistence in the native polymer of two crystalline components with different morphologies that are presumably responsible for the transitions observed. Three DSC peaks are clearly evident; however another small, unresolved peak, 2′, may be present near that at 30°C. We suggested that the first two peaks 1′ and 1, correspond to the triclinic–hexagonal transitions and the last two, 2 and 2′, to the hexagonal–pseudo-hexagonal transition of the two crystalline components, respectively. Weeks et al. [4] studied the room-temperature transitions of TFE–HFP copolymers, starting from a content of 1.6 mol% of HFP (FEP copolymers) and showed that the two transitions move toward lower temperature and merge to a single, broad transition for higher comonomer contents. From X-ray diffraction results, it has been suggested that the structures of the copolymer phases are similar to those of the homopolymer with an extra longitudinal disorder. Furthermore, the hexagonal phase exists only in narrow ranges of temperature, pressure and HFP concentration [12]. A previous study performed by us on TFE–HFP copolymer with 0.3 mol% of HFP drew conclusions analogous to those for PTFE [13]. The main differences are the higher content in the copolymer of the low-transient component, which is responsible for transitions 1′ and 2′, and the behaviour after annealing near the equilibrium melting temperature, probably related to the different melt-crystallizing abilities of the copolymer and homopolymer [14,15].

Native PTFE morphology has been extensively studied. An electron microscopy study by Luhmann and Feiring revealed rod-like, roughly spherical and, in the case of very low molecular weight material, small hexagonal particles [16]. The rod-like and the hexagonal particles were single crystals, while the spherical particles were aggregates. DSC, too, yielded three room-temperature transitions. The authors attribute the lower of the first two transitions to the hexagonal particles, and the second to the rod-like and spherical particles. Rahl et al. [17] studied the morphology of native and melt-crystalized PTFE. For the first, a ‘folded ribbon’ morphology (the lamellae fold a number of times on themselves) has been proposed. Electron diffraction showed that the ribbons are single crystals with the chain axis parallel to the long axis of the ribbons. Then, in these ‘folded ribbons’, linear and folded regions coexist. For the melt-crystallized polymer, the presence of extended-chain crystals with very thick lamellae has been proposed. In contrast, a lamellar morphology has been proposed for melt-crystallized FEP copolymers [18, 19].

The melting behaviour of PTFE has been much reported in the literature [5, 6, 20, 21]. A double melting peak has been observed for the native polymer, while only one is observed for the melt-crystallized polymer, which has a lower enthalpy of fusion than the native polymer. Various interpretations have been suggested for the nature of the double melting peak. In particular, we note that of Suwa et al. [20] who hypothesized the coexistence of two crystalline states in PTFE which can be correlated to the crystalline morphology: the lower-temperature peak may be due to the folded regions and the higher-temperature peak to the linear regions of the 'folded ribbons'. The melting of TFE–HFP copolymers has only been studied for FEP copolymers, both native [5] and isothermally crystallized [22]. Two melting endotherms have been observed only for samples crystallized at the higher temperatures.

In the present work, our previous DSC approach [8–11, 13] is extended to the room-temperature transitions and to the melting behaviour of native and melt-crystallized TFE–HFP copolymers from aqueous dispersion polymerization, with very low contents of HFP, i.e. 0.15, 0.5 and 0.8 mol%. In addition, a further investigation has been made of PTFE and the copolymer with 0.3 mol% of HFP, and the effect of the annealing at the melting temperature of the melt-crystallized polymers on the room-temperature transitions and on the melting behaviour is investigated. Conclusions are drawn concerning the morphology of the native and melt-crystallized copolymers. An interpretation of the melting peaks is given as suggested by the results for the room-temperature transitions.

EXPERIMENTAL

Materials

All the examined polymers were obtained by aqueous dispersion polymerization. The surfactant was ammonium perfluorooctanoate. The dispersion was coagulated by mechanical stirring, then washed and dried under vacuum.

Differential scanning calorimetry

Runs were performed from −20 to +50°C to investigate the room-temperature transitions, and from 200 to 400°C to study the melting behaviour. Samples of 10 ± 0.5 mg were analysed on a Perkin-Elmer DSC 7, equipped with a 1020 personal integrator, in nitrogen atmosphere using a heating rate of 10°C min^{-1}. The annealing was carried out at 329°C for PTFE, 324°C for the copolymers with 0.15, 0.3 and 0.5 mol% of HFP and at 318°C for the copolymer with 0.8 mol% of HFP, in the DSC apparatus under nitrogen atmosphere for 10 min (longer annealing times do not modify the results).

Melt-crystallized samples were obtained by heating the specimens up to 400°C with a scanning rate of 10°C $\min^{-1}$ and cooling them to −20°C at the same rate.

The apparatus was calibrated using the melting temperature of mercury (−38.9°C), indium (156.4°C), lead (327.4°C) and zinc (419.5°C) and their melting enthalpies. The transition temperatures correspond to the maxima of the peaks and their uncertainty is ±0.3°C. The enthalpy of each transition was evaluated by a computer program for integration of the partial areas; using different integration limits, the uncertainty has been evaluated as ±0.05 J g^{-1}.

RESULTS AND DISCUSSION

The DSC curves close to room temperature are reported in Fig. 1. The behaviour of the copolymer with 0.5 mol% of comonomer is quite different from that of the other copolymers and is discussed later.

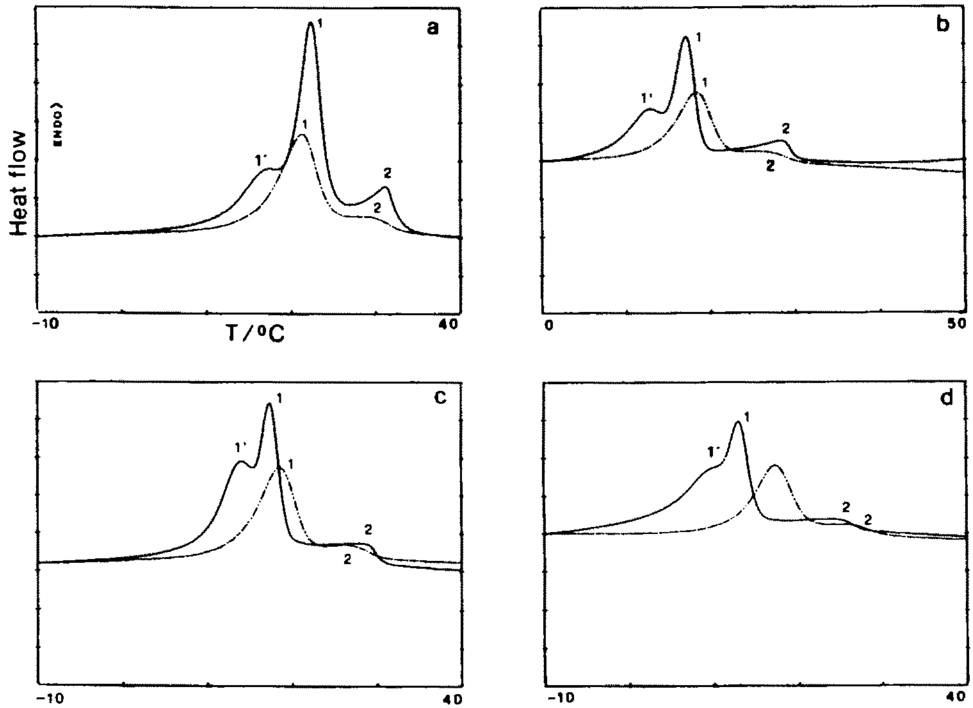

Fig. 1. DSC curves from −20 to +50°C for (a) PTFE and copolymers with (b) 0.15, (c) 0.3 and (d) 0.8 mol% of HFP: (—), native samples; (··—··), melt-crystallized samples. Transitions 1′, 1 and 2 are shown. The heat flow scale goes from 0 to 5 mW.

For melt-crystallized samples, two endothermic peaks are present in all cases, corresponding to the triclinic–hexagonal (lower temperature sharp peak 1), and the hexagonal–pseudo-hexagonal (higher temperature, broad peak 2) transitions. As has been shown for copolymers with higher comonomer contents [4], the two peaks tend to move to slightly lower temperatures and appear less resolved on increasing the comonomer content. The peak temperatures and the enthalpies of transition are reported in Table 1. The DSC curves in a range close to room temperature for the native polymers show three clear endothermic peaks (1′, 1 and 2). In all cases, the shape of the higher temperature peak, 2, (strongly asymmetric, with a plateau towards the low temperatures) may suggest that another small, broad, unresolved peak, 2′, may be present, although undetectable by our analysis. The peak temperatures and the enthalpy of the resolved transitions are reported in Table 1. There is a marked decrease in $T_{1'}$ on passing from the homopolymer to the copolymer with 0.8 mol% of HFP, while the decrease is lower for T_1 and T_2. The total heat of transition $\Delta_t H$ is very similar in all the copolymers (and lower than for the homopolymer), while the ratio $\Delta H_{1'}/\Delta H_1$ increases regularly from the homopolymer to the copolymer with 0.8 mol% of HFP. This behaviour can be explained by assuming that the native copolymers, as well as the homopolymer, are composed of two crystalline components with different morphologies giving transitions at different temperatures. (Henceforward, the two components will be defined as "low-transient" and "high-transient", respectively, in keeping with their transition temperatures (see also ref. 13).) Peaks 1′ and 2′ belong to the low-transient crystalline component and peaks 1 and 2 to the high-transient component. In particular, peaks 1′ and 1 correspond to the triclinic–hexagonal transition and peaks 2 and 2′ to the hexagonal–pseudo-hexagonal transition of the two crystalline components, respectively, according to what has been previously verified for PTFE and the copolymer with 0.3 mol% of HFP [8–11, 13]. The increase in the ratio $\Delta H_{1'}/\Delta H_1$ on passing from the homopolymer to the copolymers containing higher comonomer concentrations suggests that the content of the low-transient component is higher in the latter copolymers. Nevertheless, in all cases peak 1 is sharp, while peak 1′ becomes broader on increasing the comonomer content, confirming the ordered nature of the high-transient and the disordered nature of the low-transient components, respectively. Moreover it can be observed that, after melting the copolymers lose exactly the low-transient component (see the $\Delta_t H^{mc} - \Delta_t H^{nat}$ values in Table 1). For PTFE, however, some of the high-transient component is also lost when the polymer is melt-crystallized. This behaviour can be related to the higher melt-crystallizing abilities of the copolymers containing higher contents of comonomer, which, in turn, may be correlated to the lower macromolecular mobility of PTFE [14, 15] and to the different morphologies of PTFE and the copolymers [16–19].

TABLE 1

Temperatures and enthalpies of the room-temperature transitions for PTFE and TFE–HFP copolymers

mol% of HFP		$T_{1'}$/ °C	T_1/ °C	T_2/ °C	$\Delta H_{1'}$/ J g^{-1}	ΔH_1/ J g^{-1}	ΔH_2/ J g^{-1}	$\Delta_t H$/ J g^{-1}	$\Delta_t H^{mc}$ – $\Delta_t H^{nat}$/J g^{-1}	ΔH_1^{ann} – ΔH_1^{nat}/J g^{-1}	$\Delta H_{1'}/\Delta H_1$
0	Native	17.7	22.4	31.3	2.8	7.3	2.0	12.1	−5.5	2.5	0.38
	Annealed		21.5	29.7		9.8	1.6	11.3			
	Melt-crystallized		21.2	28.2		5.6	1.0	6.6			
0.15	Native	12.8	17.2	25.9	3.0	4.1	1.6	8.7	−2.7	4.3	0.72
	Annealed		18.4	27.0		8.5	1.6	10.1			
	Melt-crystallized		18.5	26.2		4.9	1.5	6.0			
0.3	Native	14.3	17.3	26.0	4.4	4.0	1.7	10.2	−4.3	5.6	1.1
	Annealed		18.2	26.9		9.6	1.8	11.5			
	Melt-crystallized		18.5	26.6		5.0	0.90	5.9			
0.5	Native		12.9	24.3				10.4	−2.6	1.7	
	Annealed		15.0	22.3		8.3	1.3	9.7			
	Melt-crystallized		17.8	25.3		6.6	1.2	7.8			
0.8	Native	10.0	13.0	23.1	4.8	3.8	1.8	10.4	−4.5	4.8	1.2
	Annealed		16.5	24.4		8.6	1.4	10.3			
	Melt-crystallized		17.3	26.1		4.9	0.99	5.9			

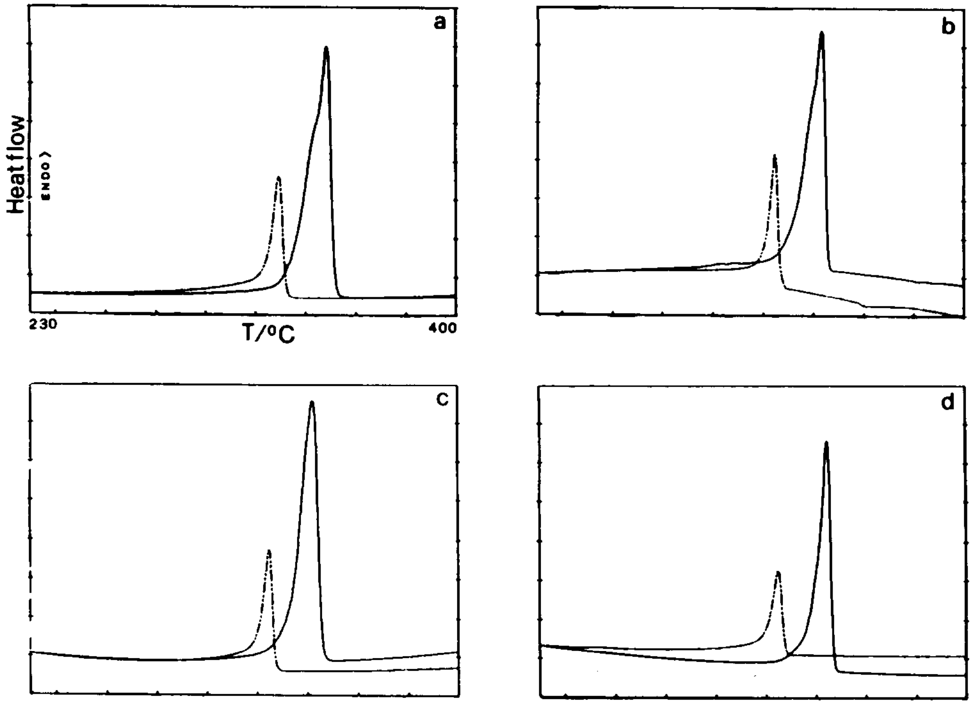

Fig. 2. DSC curves from 230 to 400°C for (a) PTFE and copolymers with (b) 0.15, (c) 0.3 and (d) 0.8 mol% of HFP: (—), native samples; (··–··), melt-crystallized samples. The heat flow scale goes from 0 to 30 mW for (a) and (c) and from 0 to 15 mW for (b) and (d).

However, in all cases, the decrease in $\Delta_t H$ on passing from native to melt-crystallized polymers is about 40%.

Figure 2 shows the DSC curves from 230 to 400°C. The lower temperature shoulder which is well known for native PTFE, is also present for the copolymer with 0.15 mol% of comonomer, whereas there is one peak with a tail towards the low temperature end for the copolymer with 0.3 mol% and a sharp peak in that with 0.8 mol%. The peak temperature decreases by about 5°C on passing from PTFE to the copolymer with 0.15 mol% of HFP; it remains about constant for the copolymer with 0.3 mol% and decreases further for the copolymer with 0.8 mol%. The $\Delta_m H$ values are roughly similar for all the polymers, except the one with 0.8 mol% comonomer where an appreciable decrease is observed (Table 2). From our previous room-temperature study of PTFE from aqueous suspension polymerization [23], and according to Suwa and co-workers [20], the presence of a shoulder in the melting peak may be correlated to the presence of the two crystalline components, i.e. the shoulder may correspond to the fusion of the low-transient and the peak to the fusion of the high-transient components, respectively. The presence of only one melting peak in the copolymers with 0.3 and 0.8 mol% of HFP may be

TABLE 2

Melting temperatures and enthalpies for PTFE and TFE–HFP copolymers.

mol% of HFP		T_m/ °C	$\Delta_m H$/ J g^{-1}
0	Native	348.2	74.4
	Annealed	347.3	74.7
	Melt-crystallized	329.3	30.0
0.15	Native	343.1	76.7
	Annealed	344.0	74.7
	Melt-crystallized	324.4	37.9
0.3	Native	344.7	77.4
	Annealed	344.8	70.4
	Melt-crystallized	324.6	38.3
0.5	Native	338.1	77.4
	Annealed	337.9	58.6
	Melt-crystallized	324.6	38.3
0.8	Native	340.5	67.0
	Annealed	343.2	67.4
	Melt-crystallized	318.6	37.1

because, on increasing the comonomer concentration, the increased chain mobility [14, 15] and the lamellar morphology allow the recrystallization of the more disordered (low-transient) component during the heating, so that the two components melt at the same temperature. In practice, the low-transient crystals would melt at lower temperatures so they would be in the state of undercooled melt; they could then recrystallize, giving more perfect crystals with higher lamellar thickness, which, in turn, would melt at higher temperatures.

The DSC curves from 230 to 400°C for melt-crystallized polymers are also reported in Fig. 2. One melting peak is present in all cases, which, as for PTFE, is at a lower temperature than for the corresponding native polymers. Also here, as for the native polymers, a decrease in the peak temperature of about 5°C occurs from PTFE to the copolymer with 0.15 mol% of HFP; it remains constant for the copolymer with 0.3 mol%, while a further decrease occurs for the copolymer with 0.8 mol%. The $\Delta_m H$ values are approximately constant for all the copolymers. The value of $\Delta_m H$ is lower for PTFE. This may be tentatively explained by the fact that molten PTFE has a higher viscosity, related to its lower macromolecular mobility with respect to the copolymers. The introduction of a defect, i.e. the comonomer unit, in the chain (at the low contents considered here) may increase the melt-crystallizing ability of the copolymers with respect to the homopolymer, according to the results for the room-temperature transitions.

According to the literature, a decrease in the heat of fusion of about 50–60% occurs for all melt-crystallized polymers with respect to the native polymers [6, 20, 21].

As mentioned above, all the polymers were subjected to thermal annealing at the melting temperature of the melt-crystallized samples. The room-temperature transtions and the melting behaviour were then further investigated. Only two transitions are present for all samples, transitions 1 and 2; transition 1′ disappears. The peak temperatures and the heat of each transition are reported in Table 1. For all polymers, ΔH_1 shows a substantial increase with respect to the native materials, while ΔH_2 is about constant. The increase in ΔH_1 corresponds to the loss of $\Delta H_{1'}$ indicating

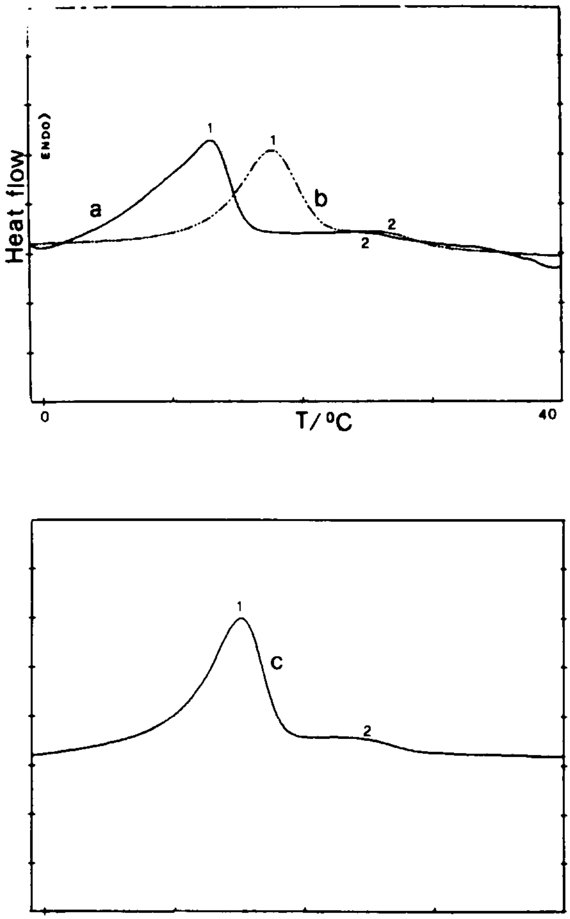

Fig. 3. DSC curves from −20 to +50°C for the copolymer with 0.5 mol% of HFP: (a) native, (b) melt-crystallized and (c) annealed at 324°C. Transitions 1 and 2 are shown. The heat flow scale goes from 0 to 5 mW.

not only that the entire low-transient component melts and recrystallizes in the high-transient component, but also that some of the high-transient improves its crystallinity, as is also confirmed by the slight increase in T_1. The DSC curves recorded from 230 to 400°C after annealing show less obvious double melting peaks than the native polymer (when present). This, together with the constancy of $\Delta_m H$ and T_m (Table 2) confirms the room-temperature observations, i.e. the almost complete recrystallization of the low-transient component.

The behaviour of the native copolymer with 0.5 mol% of HFP is very different both at room-temperature and at melting. In fact, for the native copolymer at room temperature, a broad, composite peak, strongly asymmetric towards the low temperature end, is present at 13°C (Fig. 3), indicating the collapse of transitions 1′ and 1. Transition 2 is present in a small extent. Melt-crystallized copolymer shows the two clear, well-known

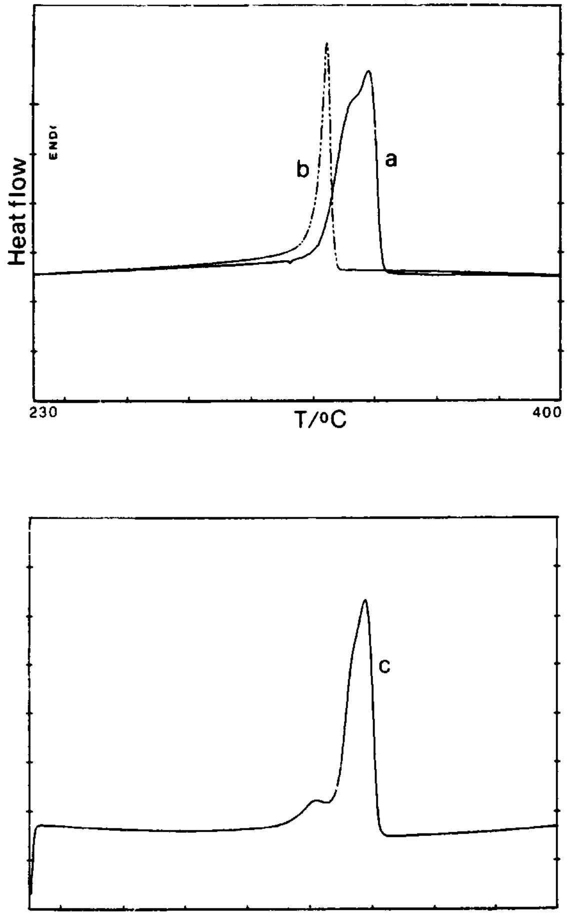

Fig. 4. DSC curves from 230 to 400°C for the copolymer with 0.5 mol% of HFP: (a) native, (b) melt-crystalized and (c) annealed at 324°C. The heat flow scale goes from 0 to 15 mW.

peaks with the temperature of the first peak increased by about 5°C (Table 1). This behaviour may be explained by the crystals of the melt-crystallized material having a lower comonomer content, the comonomer-rich regions being expelled from the crystalline phases [4]. The melting behaviour (Fig. 4) of this copolymer is also different from those of the others. For the native sample, a well-defined double peak is present with a very intense shoulder; moreover the peak temperature is at 338°C, at least 4°C below the value obtained for the other copolymers and corresponding to the value of the shoulder in PTFE. After annealing at 324°C the room-temperature DSC curve (Fig. 3) shows two well-defined transitions at 15 and 22°C. It is clear that a recrystallization has taken place, with the formation of more perfect crystals than in the native copolymer. The DSC curve of th melting behaviour after annealing (Fig. 4) shows a shoulder at 322°C corresponding to the melt-crystalized material, and a double melting peak with the shoulder that is reduced relative to that for the native copolymer, indicating that the melt-crystallized material is responsible for the shoulder at 322°C. Nevertheless the value of $\Delta_m H^{ann}$ (about $20\,J\,g^{-1}$ less than $\Delta_m H^{nat}$) indicates that there are also regions which are not able to recrystallize and which pass into the amorphous phase. This behaviour is analogous to that of the other copolymers after melting. The combined results for this copolymer suggests that an extra disorder (in addition to that introduced by the presence of the comonomer units) is present in the native material, for example, native crystals of smaller dimensions.

CONCLUSIONS

This study has elucidated the thermal properties of TFE–HFP copolymers. Together with our previous studies on the homopolymer [8–11] and the copolymer with 0.3 mol% of HFP [13], and the morphology proposed in the literature for PTFE [15, 16], our findings indicate that the native copolymers consist of two crystalline components that display transitions at different temperatures as a result of their different morphologies. The first transition peak could correspond to the triclinic–hexagonal transition of the low-transient crystals (a much smaller possible transition of the same crystals from the hexagonal to the pseudo-hexagonal phase is unquantifiable by our analysis), the second to the triclinic–hexagonal transition of the high-transient crystals, and the third to their hexagonal–pseudo-hexagonal transition.

The higher value of the ratio $\Delta H_{1'}/\Delta H_1$ on increasing the comonomer concentration suggests that the low-transient component is present to a higher extent in the copolymers with higher comonomer contents. Also, the melting behaviour confirms the presence of two crystalline components in the native copolymers, which, in agreement with Suwa and coworkers [20], may be the linear and the folded regions in the ‘folded ribbons’.

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