Extreme Thermal Behaviors of Polytetrafluoroethylene and Random Tetrafluoroethylene Fluorinated Copolymers

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ABSTRACT: By differential scanning calorimetry (DSC), the thermal behavior of polytetrafluoroethylene (PTFE) and random fluorinated copolymers of tetrafluoroethylene-containing hexafluoropropylene (FEP copolymers) or perfluoroalkylvinylether (PFA copolymers) as comonomers was investigated. Rapid-melt crystallization was employed to provide new data about the problem of inclusion/exclusion of co-units from the homopolymer crystal lattice. Equilibrium melting points were determined and tested in light of random copolymer predictions. Both nonequilibrium and equilibrium behaviors seem to point to the inclusion of —CF_3 side groups and the exclusion of larger ones. Finally, a new value of the equilibrium melting point of PTFE is given, in good agreement with those present in the literature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 919–925, 1999

Key words: polytetrafluoroethylene; tetrafluoroethylene copolymers; inclusion/exclusion of counits; equilibrium melting temperature

INTRODUCTION

The thermal properties of polytetrafluoroethylene (PTFE) have been extensively studied.[1–5] Melt-crystallized PTFE shows a lower melting temperature than the native polymer, with a lower heat of fusion, likely because of the smaller and more defective crystallites obtained in these conditions with respect to those of the native polymer. Close to room-temperature, melt-crystallized PTFE shows two crystal–crystal transitions corresponding to the triclinic–hexagonal and hexagonal–pseudohexagonal transitions, respectively.[6,7]

Random fluorinated copolymers of tetrafluoroethylene are very interesting for both their technological applications, being much more easily processable than PTFE, and their structural features. The most diffuse are those with hexafluoro-

propylene (FEP) or perfluoroalkylvinylethers (PFA) as comonomers. The former present room-temperature transitions shifted to lower temperatures when the comonomer content is increased merging to only one transition at higher co-unit concentrations.[8] In a previous article,[9] the thermal properties of PFA copolymers with —OCF_3, —OCF_2CF_3, and —$OCF_2CF_2CF_3$ side groups were studied. Only one crystal–crystal transition is present, up to 4 mol % of comonomer, at a much lower temperature than those of the homopolymer, decreasing in temperature and extent on increasing the comonomer content. The independence of the low temperature and the melting behavior on the different size of co-units has been shown.

FEP and PFA copolymers were reported to behave differently from a structural viewpoint as far as the inclusion or exclusion of co-units in the PTFE crystal lattice are concerned. In particular, most authors report, essentially on the basis of X-ray diffraction and calorimetric studies, that —CF_3 groups of FEP copolymers are included in the crystallites.[10–13] Nonetheless, some authors, on the basis of the determination of structural cell

parameters,[14] have proposed that —CF_3 groups are excluded from PTFE crystals.

In previous articles, by calorimetric investigations, —OR_F side groups (where R_F = —CF_3, —CF_2CF_3, —$CF_2CF_2CF_3$) were reported to likely be excluded from the homopolymer crystal lattice.[9,15,16] Our results have been substantiated by subsequent molecular mechanics[17] and by wide- and small-angle X-ray spectroscopy (WAXS and SAXS, respectively) investigations.[14,18]

In this article, to provide a further insight on the inclusion or exclusion of —CF_3 and —OR_F side groups, we studied the thermal behavior of FEP and PFA copolymers in extreme conditions, (a) very far from equilibrium and (b) at equilibrium.

For the first condition, we adopted the method suggested by Mandelkern for ethylene copolymers[19,20] and used previously for some PFA copolymers,[9] [i.e., the study of the thermal behavior after very fast cooling from the molten state (quenching), which was demonstrated to be very effective in comparing copolymers containing differently sized side groups]. We examined both the low-temperature transitions (crystal–crystal transitions) and the melting behavior.

With regard to the equilibrium conditions, we evaluated for the same copolymers the equilibrium melting temperature, which for macromolecules is a very important macroscopic quantity. A number of methods have been developed for its determination,[21] among which was that proposed by Hoffman and Weeks.[22] Although their method raised some criticism since being proposed, it allows the determination of the equilibrium melting temperature by avoiding the problems arising from its direct determination and by giving reasonable values for either homo- or copolymers.[23] Therefore, we also used a similar method in our determination, taking into account that it had also been used for some PFA copolymers with —OCF_3 side groups [tetrafluoroethylene–perfluoromethylvinylether (PFMVE) copolymers][16] and by Centore et al. for some FEP copolymers.[24]

Finally, a special method for PTFE was developed for its equilibrium melting temperature determination[3] because of its difficulty in being isothermally melt crystallized. In fact, it was reported that for PTFE, crystallization is so rapid that the sample crystallizes during the cooling from the melt to the selected crystallization temperature.[25] Nevertheless, in an article in press,[26] we have shown that it is possible, by carefully controlling the experimental conditions, to perform isothermal melt-crystallization experiments

Table I   Samples Analyzed Throughout the Work

Polymer	Comonomer	Comonomer Content (mol %)
PTFE	—	0.0
FEP01	CF_2=CF—CF_3	0.15
FEP03	CF_2=CF—CF_3	0.3
FEP05	CF_2=CF—CF_3	0.5
FEP08	CF_2=CF—CF_3	0.8
FEP1	CF_2=CF—CF_3	1.0
FEP8	CF_2=CF—CF_3	8.0
PFMVE05	CF_2=CF—OCF_3	0.5
PFMVE1	CF_2=CF—OCF_3	1.0
PFMVE2	CF_2=CF—OCF_3	2.0
PFMVE4	CF_2=CF—OCF_3	4.0
PFMVE6	CF_2=CF—OCF_3	6.0
PFMVE10	CF_2=CF—OCF_3	10.0
PFEVE	CF_2=CF—OCF_2CF_3	2.0
PFPVE	CF_2=CF—$OCF_2CF_2CF_3$	2.0

even for this polymer. Moreover, in the past, the equilibrium melting temperature of PTFE was determined from data of melting temperature as a function of the lamellar thickness,[27] a method strictly related to that used by Hoffmann and Weeks.[22] Therefore, in this article we are concerned also in the evaluation of the equilibrium melting temperature of PTFE through the determination of the melting temperature as a function of the crystallization temperature and in the comparison of the obtained value with those evaluated by the above-mentioned different techniques.[3,27]

EXPERIMENTAL

Materials

Powder samples of polymers examined throughout this work are reported in Table I. They were obtained by conventional aqueous dispersion polymerization. The comonomer concentration ranging from 0.15 to 10 mol % was determined by the infrared analytical method.[28]

Thermal Analysis

Thermal analysis was performed by a differential scanning calorimeter (DSC 7, Perkin Elmer). The software Pyris, running under Windows NT 4.0, on a Pentium Compaq Prolinea 5133 personal computer, was used to analyze the data.

All runs were performed on 10 ± 0.5 mg samples in a nitrogen atmosphere. The apparatus was calibrated by using the melting temperatures of mercury (−38.9°C), tin (231.8°C), and lead (327.4°C) and their heats of fusion. Before each run, the baseline was optimized in the range of interest and subtracted from the corresponding calorimetric curve. Transition and melting temperatures are given as the maxima of the peaks.

The isothermal crystallizations were performed in the DSC apparatus in a nitrogen atmosphere and the subsequent runs were carried out at 10°C/min.
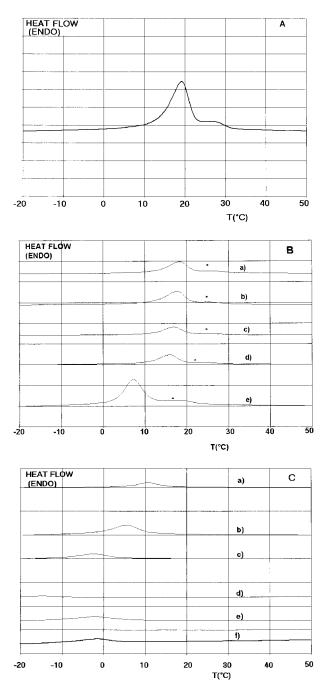
The quenching (rapid crystallization procedure) was carried out in the DSC in a nitrogen atmosphere by taking the sample from the melt to −35°C at the maximum rate allowed by the instrument. The subsequent runs were performed at 20°C/min. This procedure was shown by Alamo and Mandelkern[20] to be very effective in comparing differently sized group copolymers and was previously adopted by us for fluorinated tetrafluoroethylene random copolymers.[15]
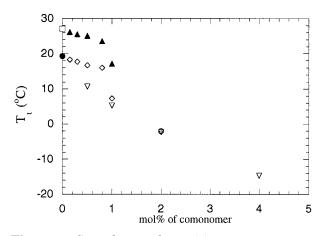
RESULTS AND DISCUSSION

Nonequilibrium Behavior

In Figure 1, we report the calorimetric curves recorded at low temperatures (from −30 to +50°C) for copolymers and, for the sake of comparison, also for PTFE, after quenching from the molten state. FEP copolymer with 8 mol % of comonomer shows no low-temperature transition in these conditions, as well as PFMVE copolymers starting from 6 mol %. The behavior of FEP copolymers appears to be very similar to that of the homopolymer; in fact, two crystal–crystal transitions are always observed for our samples, whereas for PFMVE, already for 0.5 mol %, only one transition is observed. Moreover, as can be observed in Figure 2 where the crystal–crystal transition temperatures are reported as a function of the comonomer content, those of PFMVE (and those of PFA with larger side groups, which are practically equal to those of PFMVE at the same comonomer concentration) are always lower than those of both FEP copolymers, with the corresponding comonomer content (i.e., 0.5 and 1.0 mol %).

This behavior can be interpreted by assuming that, in the case of PFA, the side groups are likely to be rejected from the crystal lattice. In fact, in this assumption, even at low comonomer concen-

Figure 1 DSC scans at low temperature after quenching the following samples: (A) PTFE; (B) FEP copolymers with (a) 0.15, (b) 0.3, (c) 0.5, (d) 0.8, and (e) 1 mol % of comonomer. The location of the higher temperature transition is indicated by an asterisk; (C) PFA copolymers with (a) 0.5, (b) 1, (c) 2, and (d) 4 mol % of perfluoromethylvinylether, (e) 2 mol % of perfluoroethylvinylether, and (f) perfluoro-*n*-propylvinylether. The scanning rate is 20°C/min.

tration, only one broad crystal–crystal transition is present, shifted toward much lower temperatures than both transitions in PTFE. This can be

Figure 2 Crystal–crystal transition temperatures as a function of the comonomer content of: (●) lower transition temperature of PTFE; (□) higher transition temperature of PTFE; (◇) lower transition temperature of FEP copolymers; (▲) higher transition temperature of FEP copolymers; (▽) transition temperature of PFMVE copolymers; (+) transition temperature of PFEVE copolymer; (○) transition temperature of PFPVE copolymer.

justified by taking into account that the length of the sequences that are able to crystallize is limited by the excluded co-units. This phenomenon becomes more and more pronounced as the concentration of randomly introduced co-units is increased.

In contrast for FEP copolymers, —CF$_3$ groups are likely to be included in the homopolymer crystal lattice; in fact, even for copolymers at the same composition as PFMVE (i.e., 0.5 and 1 mol % of comonomer), two crystal–crystal transitions are present as in PTFE, but with a slight lowering in the transition temperature, clearly because of the larger disorder of the crystal structure of copolymers with respect to that of homopolymer.

In Figure 3, we report the melting curves obtained for all samples after quenching, and in Figure 4, the melting temperatures as a function of the comonomer content. The general trend is that the FEP melting temperatures are higher than those of PFMVE (and also of larger sized co-unit PFA, that in this case are nearly equal to those of PFMVE of the same composition); this difference is more pronounced for the higher comonomer concentrations. A similar trend observed for ethylene copolymers by Alamo et al.[19,20] was considered as proof of the inclusion of methyl groups and exclusion of the larger ones from the homopolymer crystal lattice. Finally, in Figure 5(A) we report the relative crystallinity at low temperatures and in Fig. 5(B) the relative crystallinity at melting point evaluated as $\Delta H_t/\Delta H_t^h$ and $\Delta H_m/\Delta H_m^h$, respectively. ΔH_t and ΔH_m
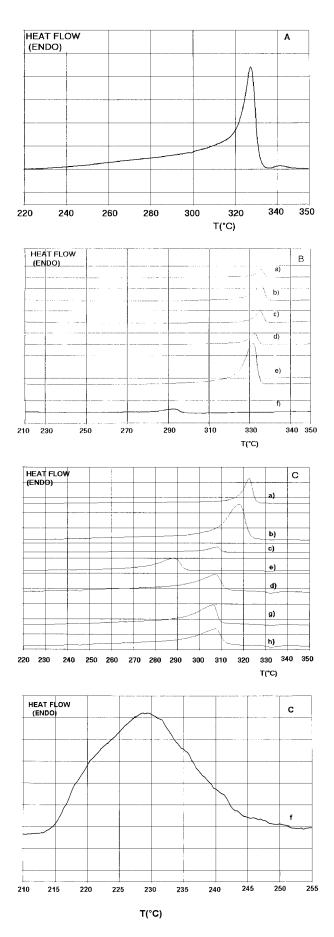
are the total heats of transition and fusion, respectively, of the examined sample; ΔH_t^h and ΔH_m^h are the total heats of transition and fusion, respectively, of rapidly crystallized PTFE. First, it is worth noting that at variance with all other series homopolymer/copolymers, as shown in a previous paper,[29] the heats of transition and fusion of copolymers containing small comonomer contents can be higher than those of the homopolymer. This behavior has been related to the very high melt viscosity of PTFE. The introduction of a defect (e.g., the comonomer unit in the chain, at least at very low concentrations) reduces the melt viscosity, increasing the melt-crystallizing ability of the copolymers with respect to the homopolymer. Coming back to Figure 5(A) and (B), we observe for PFMVE copolymers (the values for PFA with longer side groups are practically coincident with those of PFMVE at the same comonomer concentration), a fast decrease of the relative crystallinity as a function of the comonomer content either at low temperature or at melting. This observation may reflect that in these cases the side groups are excluded from the crystal lattice; in fact, in this hypothesis, upon increasing the co-unit content, the concentration of crystallizable sequences becomes lower and lower.
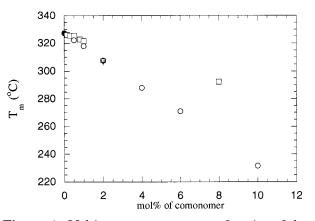
By contrast, the decrease in relative crystallinity of FEP copolymers is much less severe, which could indicate again that they do not behave as random copolymers with co-units excluded from the crystal lattice.

Finally, we note the sharper and more intense endotherms and the higher values of relative crystallinities of FEP1. This is a clear exemplum of the reported statement about the higher melt-crystallizing ability of copolymers with respect to the homopolymer.[29]

Equilibrium Behavior

To derive the equilibrium melting temperatures T_m^0 for each polymer reported in Table I, the method by Hoffman and Weeks was used.[22] The experimental melting temperature T_m values for each sample as a function of the crystallization temperature T_c were determined as follows. The sample was first molten at a heating rate of 10°C/min, cooled to the selected crystallization temperature at the maximum rate allowed by the instrument to avoid crystallization on cooling, and then taken at that temperature for a determined time. T_m was determined by heating the sample at a rate of 10°C/min. Plotting the observed T_m versus

Figure 4 Melting temperatures as a function of the comonomer content of: (●) PTFE; (□) FEP copolymers; (○) PFMVE copolymers; (▽) PFEVE copolymer; (+) PFPVE copolymer.

T_c, one goes from less perfect crystals grown at a higher supercooling to crystals of higher perfection grown at a lower supercooling. The value $T_m = T_c$ yields the extrapolated equilibrium melting temperature for each sample.

In Figure 6 the plots of T_m versus T_c are reported, together with the extrapolation on the line $T_m = T_c$. For PTFE, a value $T_m^0 \approx 336°C$ is obtained. This result is in very good agreement with that of Bassett and Davitt,[27] through extrapolation of data of melting temperature as a function of lamellar thickness. A reasonable agreement is also reached with the value obtained by Lau et al.[3] by using a different method.
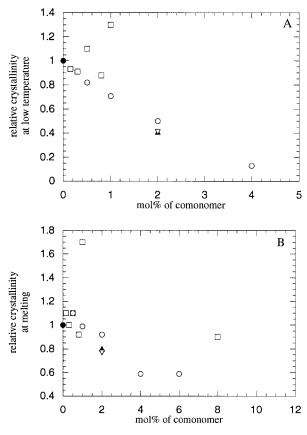
In Figure 7, we plotted the preceding equilibrium melting temperatures as a function of the comonomer content. From the inspection of Figure 7, FEP copolymers are apparent to display equilibrium melting temperatures significantly higher than those with —OCF_3 side groups of corresponding composition. This behavior is reminiscent of that of ethylene copolymers; in fact, it was shown that ethylene copolymers containing directly bonded methyl groups have significantly higher temperatures than those with longer alkyl-type side groups.[19,20] This behavior was interpreted by admitting that the methyl groups enter

Figure 3 Melting curves after quenching the following samples: (A) PTFE; (B) FEP copolymers with (a) 0.15, (b) 0.3, (c) 0.5, (d) 0.8, (e) 1, (f) 8 mol % of comonomer; (C) PFA copolymers with (a) 0.5, (b) 1, (c) 2, (d) 4, (e) 6, (f) 10 mol % of perfluoromethylvinylether, (g) 2 mol % of perfluoroethylvinylether, and (h) perfluoro-*n*-propylvinylether. The scanning rate is 20°C/min.
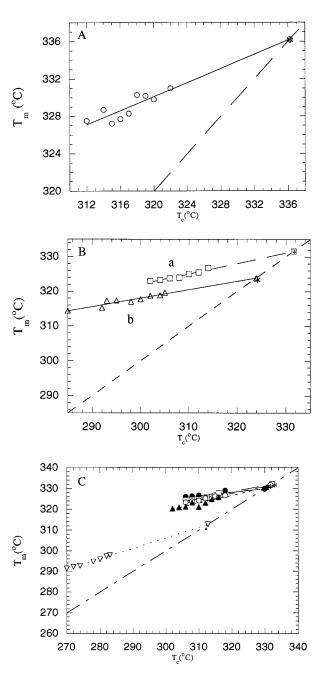
the lattice on an equilibrium basis, although the inclusion may be only partial if the comonomer concentration becomes rather high. Therefore, our results also constitute a further indication that, under equilibrium requirements, —CF_3 groups enter the lattice, whereas larger side groups are likely to be rejected.

CONCLUSIONS

In this article, we studied the thermal behavior of random fluorinated copolymers of tetrafluoroethylene in two extreme conditions (i.e., very far from and at equilibrium). All our observations point to the inclusion of —CF_3 groups in the homopolymer crystal lattice and the exclusion of larger side groups, for instance: (1) the shape of the calorimetric curves and the values of the crystal–crystal transition temperatures of rapidly crystallized samples; (2) the trend of the melting temperatures of rapidly crystallized samples; and (3) the
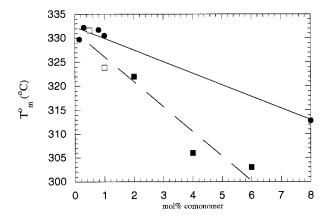

Figure 5 Relative crystallinity at low temperature (A) and at melting (B) of: (●) PTFE; (□) FEP copolymers; (○) PFMVE copolymers; (▽) PFEVE copolymer; (▲) PFPVE copolymer.

Figure 6 Peak positions of the melting endotherms T_m taken from the DSC scans recorded at 10°C/min versus the crystallization temperature T_c for the following polymers: (A) PTFE; (B) (a) PFMVE05 and (b) PFMVE1; (C) (a) FEP01, (b) FEP03, (c), (d) FEP08, (e) FEP1, and (f) FEP8. The star indicates the extrapolated values on the line $T_m = T_c$.

trend of the equilibrium melting temperatures. These conclusions are in agreement with our previous experimental work on PFA,[9,15,16] with literature data on PFA,[3,18] with most literature works on FEP,[10–13] and with the data concerning ethyl-

Figure 7 Equilibrium melting temperatures versus the comonomer content: (○) FEP copolymers; (□) PFMVE copolymers; (■) PFMVE copolymers taken from ref. 16.

ene copolymers.[19,20,30] Finally, another result of this article was a further determination of the equilibrium melting temperature of PTFE to be added to the data present in the literature.[3,27]

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