NOTE

Equilibrium Melting Temperatures of Tetrafluoroethylene–Perfluoroalkylvinylether Copolymers

RACHELE PUCCIARIELLO

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro, 85, 85100, Potenza, Italy

INTRODUCTION

Fluorinated copolymers of tetrafluoroethylene possess very favorable mechanical and chemical properties and require easier processing conditions than the homopolymer in that they can be processed by usual melting extrusion or injection molding technology. Therefore, the study of the thermal behavior is particularly important as it plays a key role in their processing and use conditions.

In previous articles,[1,2] we have studied by differential scanning calorimetry (DSC) the thermal properties of tetrafluoroethylene–perfluoroalkylvinylether (PFA) copolymers. The melting and the low-temperature (crystal–crystal transitions) of PFA containing different comonomers at various concentrations have been investigated.[1] The presence of a reasonable crystal–crystal transition at a much lower temperature than room temperature has been demonstrated for concentrations up to 4 mol % of comonomer. The independence of the thermal behavior of the nature of the side groups suggested at least a partial exclusion of them from the crystal lattice. As far as the melting behavior is concerned, the endothermic peaks broaden, and the melting temperatures and the heats of fusion increase on increasing the comonomer content. We have also studied[2] the effect of the thermal history on the melting and on the crystal–crystal transitions of the same PFA copolymers. Upon thermal annealing, they show the presence of two melting peaks, whose value and extent strongly depend on annealing temperature and/or time. On increasing the annealing temperature, the crystal–crystal transition shows a shoulder at lower temperatures that can be attributed to more defective crystals, those responsible for the lower-temperature

endotherm in the melting curve. The crystal–crystal transition temperature increases as a function of the annealing temperature, confirming the rejection of the side groups from the crystal lattice.

In the present article, the determination of the equilibrium melting temperatures of PFA copolymers containing different contents of perfluoromethylvinylether as a comonomer are reported, and the obtained data tested in light of random copolymer predictions about the counits inclusion in, or the exclusion from, the crystal lattice.

EXPERIMENTAL

Materials

Powder samples of copolymers of tetrafluoroethylene with 2, 4, 6, and 10 mol % of perfluoromethylvinylether as a comonomer have been used. They have been obtained by conventional aqueous dispersion polymerization, coagulated with mechanical stirring, then washed and dried in an air circulating oven.

Thermal Analysis

Thermal analysis was performed by a differential scanning calorimeter (DSC 7, Perkin–Elmer) equipped with a 1020 Personal Integrator. All runs were performed on 10 ± 0.5 mg samples in a nitrogen atmosphere. Melting temperatures are given as the maxima of the peaks. They were checked using the melting temperatures of tin (231.8°C) and lead (327.4°C) and are reproducible to ±0.3°C. The isothermal crystallizations were performed in the DSC apparatus in a nitrogen atmosphere.
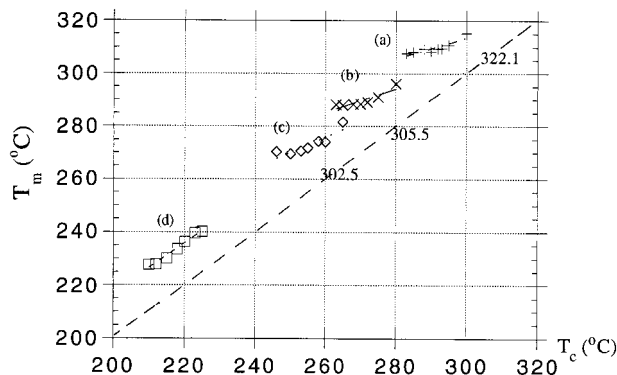
Figure 1 Peak positions of the melting endotherms T_m taken from the DSC scans recorded at 10°C/min versus the crystallization temperatures T_c for the copolymers containing (a) 2, (b) 4, (c) 6, and (d) 10 mol % of comonomer. The extrapolated values on the line $T_m = T_c$ (dashed line) are reported for (a), (b), and (c). The equations of the interpolating lines fitting the points T_m versus T_c are $T_m = 196.41 + 0.390\ T_c$, $T_m = 168.93 + 0.447\ T_c$, and $T_m = 116.80 + 0.614\ T_c$ and the correlation coefficients 0.888, 0.883, and 0.918 for (a), (b), and (c), respectively.

RESULTS AND DISCUSSION

To derive the equilibrium melting temperatures $T_m^o(X)$, where X is the mole fraction of comonomer for each copolymer, the method by Hoffman and Weeks[3] was used. 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 taken to 350°C at a heating rate of 10°C/min, then cooled to the selected crystallization temperature at the maximum rate allowed by the instrument in order to avoid crystallization on cooling, then taken at that temperature for a determined time. T_m was determined by heating up the sample to 350°C at a rate of 10°C/min. Plotting the observed T_m versus T_c, one goes from less perfect crystals grown at higher supercooling to crystals of higher perfection grown at lower supercooling. The value $T_m = T_c$ yields the extrapolated equilibrium melting temperature $T_m^o(X)$ for each sample.

In Figure 1, the plots of T_m versus T_c are reported together with the values of $T_m^o(X)$. For the copolymer with 10 mol %, the comonomer content is likely to be too high to reach a reasonable level of crystallization so that the extrapolation to a possible equilibrium temperature of equal T_m and T_c is too long, giving an absurd value for $T_m^o(10)$. The obtained data are examined in the light of the theories for the melting of copolymers, i.e., the exclusion of counits from,[4] and the uniform inclusion in,[5] the crystal lattice. According to both models, a depression in the equilibrium melting temperature of the homopolymer is expected on passing to a random copolymer with a molar fraction X of comonomer, following the equations
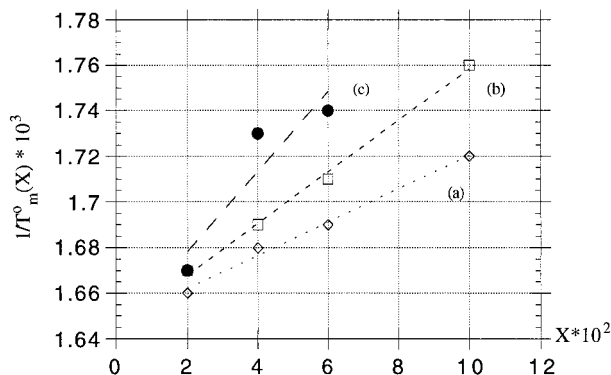

Figure 2 Inverse of the extrapolated equilibrium melting temperatures versus the mole fraction of comonomer: (a) the uniform inclusion model, (b) calculated by the exclusion model, and (c) experimental data (see text).

$$1/T_m^o(X)$$
$$= 1/T_m^o - R/\Delta H^o \ln(1 - X)\ (\text{exclusion}) \quad (1)$$

$$1/T_m^o(X)$$
$$= 1/T_m^o + \epsilon X/\Delta H^o T_m^o(X)\ (\text{uniform inclusion}) \quad (2)$$

where T_m^o and ΔH^o are the equilibrium melting temperature and the enthalpy of fusion of the corresponding homopolymer (in our case 333°C and 4.10 kJ/mol[6]), and ϵ is the excess free energy of the defect created by incorporating a counit in the crystalline lattice of the homopolymer.

In Figure 2, the experimental values of $1/T_m^o(X)$ and those calculated according to eqs. (1) and (2) are reported versus the comonomer fraction. For the calculation using eq. (2), the value of $\epsilon = 0.04$ eV obtained for —CF_3 group[5] has been used, the value of ϵ for —OCF_3 group being unknown, in the poor approximation that the disturbance induced by the two groups in PTFE
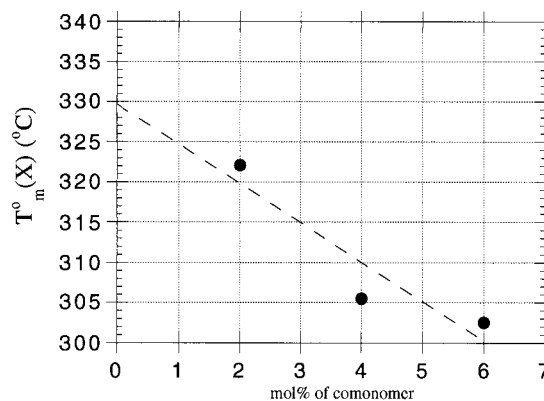
Figure 3 Experimental equilibrium melting temperatures versus the comonomer content.

crystal lattice is similar. The comparison of the experimental points with those calculated does not allow to univocally decide which of two theories holds in our case, especially taking into account the assumption made on ϵ and the small number of available experimental data. Nevertheless, we would suggest that the trend of $1/T_m^o(X)$ versus X appears to be closer to that derived from the exclusion model, the lower values of $T_m^o(X)$ with respect to those predictable by the theory being possibly attributable to the difficulty in actually achieving the required equilibrium condition and on a possible random inclusion of a particular counit in the crystal lattice.

Our hypothesis is, on the other hand, supported by our previous results about PFA copolymers[1,2] and by the monotonic decrease of the extrapolated equilibrium temperatures with increasing the comonomer content. This trend is clearly substantiated by the result shown in Figure 3 where the values of $T_m^o(X)$ are reported as a function of the concentration of the comonomer. The extrapolated value for $X = 0$ gives 329.6°C, a value which is not far from that obtained for PTFE with a different technique.[6] Although not unequivocal, this outcome is consistent with a phase diagram in which the crystalline phase remains pure, as observed in the past for ethylene copolymers.[7]

REFERENCES

1. R. Pucciariello, *J. Polym. Sci. Part B: Polym. Phys.,* **32,** 1771 (1994).
2. R. Pucciariello, *J. Polym. Sci. Part B: Polym. Phys.,* **34,** 1751 (1996).
3. J. D. Hoffman and J. J. Weeks, *J. Res. Natl. Bur. Stand.,* **66A,** 13 (1962).
4. P. J. Flory, *J. Chem. Phys.,* **17,** 223 (1949).
5. I. C. Sanchez and R. K. Eby, *Macromolecules,* **8,** 639 (1975).
6. S. F. Lau, H. Suzuki, and B. Wunderlich, *J. Polym. Sci. Part B: Polym. Phys.,* **22,** 379 (1984).
7. C. H. Baker and L. Mandelkern, *Polymer,* **7,** 71 (1966).