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MELTING AND CRYSTALLIZATION OF TETRAFLUOROETHYLENE-ETHYLENE COPOLYMERS

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Abstract

The melting and crystallization of copolymers of tetrafluoroethylene with ethylene, synthesized in bulk and in suspension by semi-flow method, were studied by DSC.

X-ray diffractions and infrared spectra of the copolymers were measured and new crystalline reflections, different from those of the homopolymers were observed.

The melting temperature of the copolymers synthesized in bulk depends strongly on the composition and exhibits several maxima. A certain small decrease in the melting temperature within the range of the alternating composition is observed.

For alternating copolymers synthesized in suspension, the peaks are monomodal indicating a higher structural and chemical homogeneity of the copolymer.

The nonisothermal crystallization kinetics in the temperature interval from 260 to 255°C of the alternating copolymer prepared in suspension can be described by a modified Avrami equation. The mechanism of nucleation and nuclei growth during the nonisothermal crystallization of the tetrafluoroethylene-ethylene copolymer is close to that of polyethylene.

Keywords: crystallization, melting, nonisothermal crystallization, phase transitions, tetrafluoroethylene-ethylene copolymers

Introduction

Copolymers of tetrafluoroethylene (TFE) with ethylene (E) are well known for their high thermal, radiation and chemical resistance, good dielectric and mechanical properties and good processibility [1].

Alternating TFE-E copolymers are crystalline. The primary cell is orthorhombic with unit cell dimension parameters $a = 8.57$ Å, $b = 11.20$ Å, $c = 5.04$ Å. The chain packing in the primary cell is similar to that of the orthorhombic polyethylene (PE) [2].

Both the melting and the maximum operating temperatures of the copolymer are 50–70°C lower than those of polytetrafluoroethylene (PTFE). The melting temperature depends on the composition and the distribution of the TFE and E

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monomer units in the copolymer. The observed melting temperature of the alternating copolymer ranges from 305 to 315°C whereas that of the random copolymer varies between 275 and 285°C [3]. Yamabe *et al.* [4] have found a non-linear correlation between the melting temperature and the copolymer composition.

The crystallization of TFE-E copolymers occurs so rapidly that isothermal crystallization cannot be observed, because it happens during the period of cooling of the sample to the desired constant temperature [5]. These processes associated with the mode of cooling should be observed in order to evaluate the crystallization behaviour. On the other hand, in some actual processes as fabrication and melt spinning of crystalline polymers, crystallization takes place nonisothermally, so that nonisothermal observation of crystallization has also an actual significance.

In previous works some general aspects of peroxide initiated bulk and suspension copolymerization of TFE and E were discussed [6, 7]. In the present paper the phase transitions on heating and cooling and the kinetics of nonisothermal crystallization of TFE-E copolymers are investigated by differential scanning calorimetry.

Experimental

TFE-E copolymers of different compositions were used, including alternating copolymers, obtained in bulk or suspension by the technique described earlier [6, 7].

Calorimetric studies were carried out by a differential scanning calorimeter DSC-111 (SETARAM, France) using heating and cooling rates of 1, 5 and 10 $\mathrm{deg \cdot min^{-1}}$, respectively.

The nonisothermal crystallization kinetics was studied applying the modified Avrami equation [5] for experimental DSC curves obtained by cooling at a constant rate:

$$\lg[-\ln(1-C)] = \lg X_c(T) - n\lg\Phi$$

C is the crystallized fraction at temperature T and cooling rate Φ; $X_c(T)$ - the crystallization cooling function and n - the Avrami exponent which varies from 1 to 4 depending on the type of the nucleation and the growth dimension [5].

The X-ray studies were carried out on a TURM-61 apparatus (Carl Zeiss, Germany) equipped with a HGZ-3 diffractometer using $\mathrm{CuK_\alpha}$ radiation. Refraction of powdery copolymer samples has been employed.

Results and discussion

Structure and structural transitions in TFE-E copolymers

The characteristic DSC melting and crystallization curves of TFE-E copolymers of different compositions obtained in bulk are shown in Figs 1a and 1b. Within the range of random structures of the copolymer, two monomodal endothermic melting peaks are observed on the DSC curves recorded on heating (1–5). To elucidate the nature of the low-temperature peak ($T_{m_1}^{max}$) in the range of 82–93°C (Fig. la, curves 1–5), homopolymerization of E was carried out under conditions similar to those employed for the TFE-E copolymerization and ca.1% PE yield was obtained. Besides, by decalin extraction of the samples at 190°C, about 10% of low molecular fractions of copolymers of high ethylene content were extracted. Therefore, the endothermal peak at about 90°C can be attributed to the melting of the low molecular PE fraction and/or copolymer fraction with high E content.

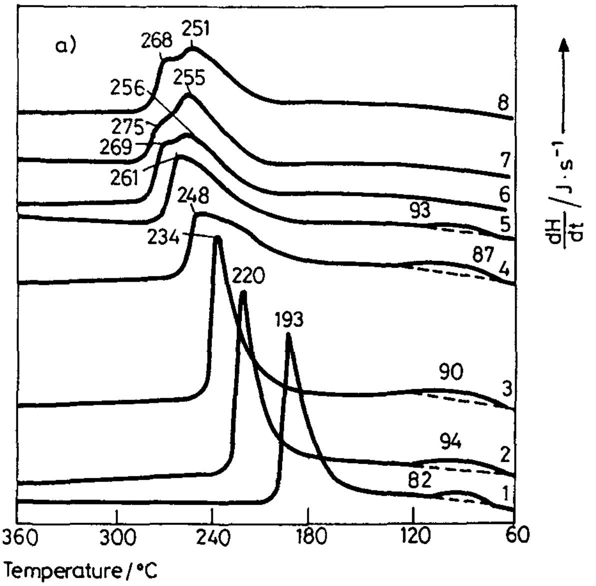

Fig. 1a Typical DSC heating curves of TFE-E copolymers. TFE content (mol%) of the copolymer: 1 - 29.4; 2 - 33.3; 3 - 37.1; 4 - 42.2; 5 - 43.9; 6 - 49.2; 7 - 48.5; 8 - 49.5

The temperature of the second endothermic peak, which indicates the melting of the TFE-E copolymer, increases with the increase of the TFE content from 193°C (29 mol% TFE) to 261°C (44 mol% TFE). Within the range of

48–50 mol% TFE in the copolymer, on the corresponding DSC curves no low-temperature endothermic peak characteristic of the PE fractions was observed. At the same time, the higher temperature endothermic peak of the melting of the TFE-E copolymer was found to be bimodal. The corresponding lower temperature maximum of this bimodal endothermic peak was about 255°C, whereas the higher temperature maximum was observed between 268 and 274°C.

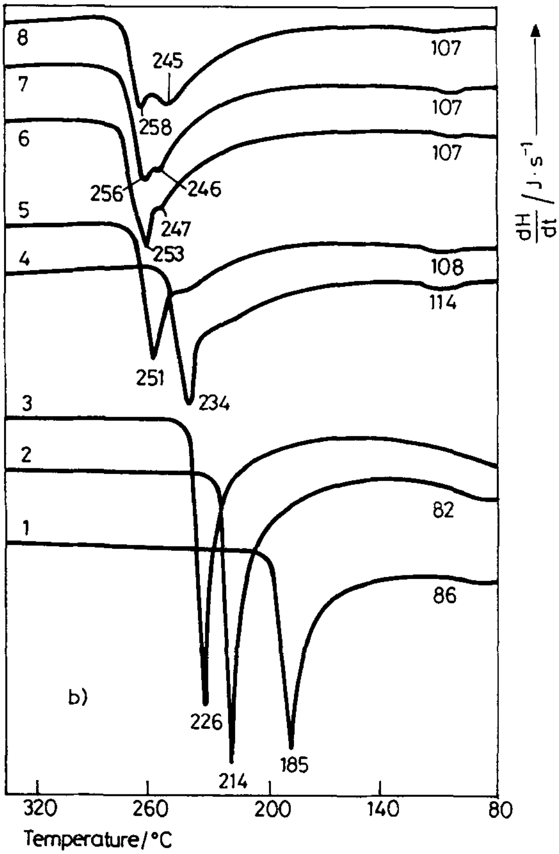

Fig. 1b Typical DSC cooling curves of TFE-E copolymers. TFE content (mol%) of the copolymer: 1 - 29.4; 2 - 33.3; 3 - 37.1; 4 - 42.2; 5 - 43.9; 6 - 49.2; 7 - 48.5; 8 - 49.5

The DSC crystallization curves shown in Fig. 1b were similar. For TFE content from 29.4 to 37.1 mol%, the high temperature exothermic peak of the copolymer crystallization was monomodal, whereas for higher TFE contents it was found to be bimodal. Within the entire range of the compositions studied, a low temperature exothermic peak was also observed at 86–107°C. The latter has been attributed to the crystallization of PE fractions and/or to fractions of copolymer with high E content.

In general, both the melting and crystallization temperatures of the TFE-E copolymer increase nonlinearly with the increase of the content of TFE in the copolymer (Figs 2, 3; curves 1, 2), the corresponding curves showing maxima.

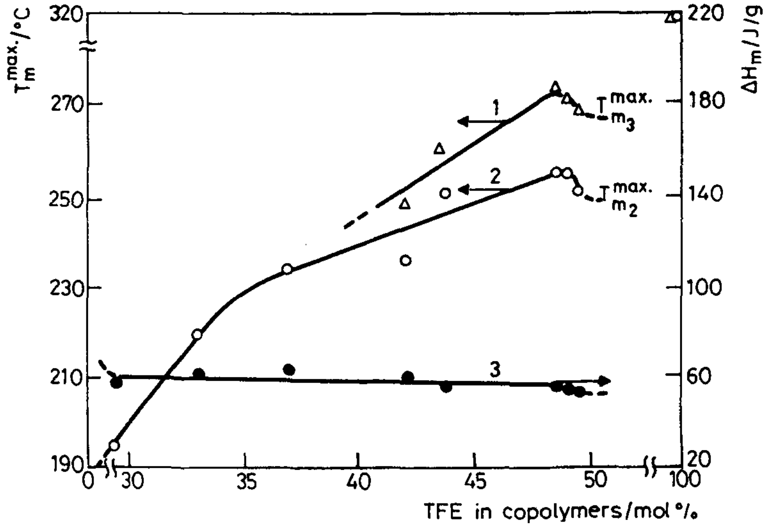

Fig. 2 Dependence of the melting temperatures, $T_{m_2}^{max}$ and $T_{m_3}^{max}$ (curves 1, 2) and of the melting enthalpy, ΔH_m (curve 3) of TFE-E copolymers obtained in bulk on the TFE content (mol%) of the copolymer

On the curves representing the dependence of both the melting and the crystallization temperatures of the copolymer on the TFE content, a maximum at about 48 mol% TFE monomer units is observed, as well as a small but measurable minimum, corresponding to the alternating composition. These results correlate with those of other authors [3, 4].

The bimodal endothermal peaks of melting and crystallization may be explained by the corresponding bimodal distribution of the chemical composition of the copolymers which means a different sequence distribution of the copolymer units [3]. It is connected with the heterogeneity of the process of copolymerization of TFE with E. The appearance of TFE-E copolymer blocks of different average distributions of copolymer chains determines the microstructure and the character of the melting and crystallization curves of the polymer studied.

The composition dependence of the enthalpies of melting (ΔH_m) and crystallization (ΔH_c) of TFE-E copolymers is shown in Figs 2 and 3, curve 3. Obviously, ΔH_m (and ΔH_c) is nearly constant in the range from 30 to 50 mol%, they decrease slightly with increasing TFE content of the copolymer.

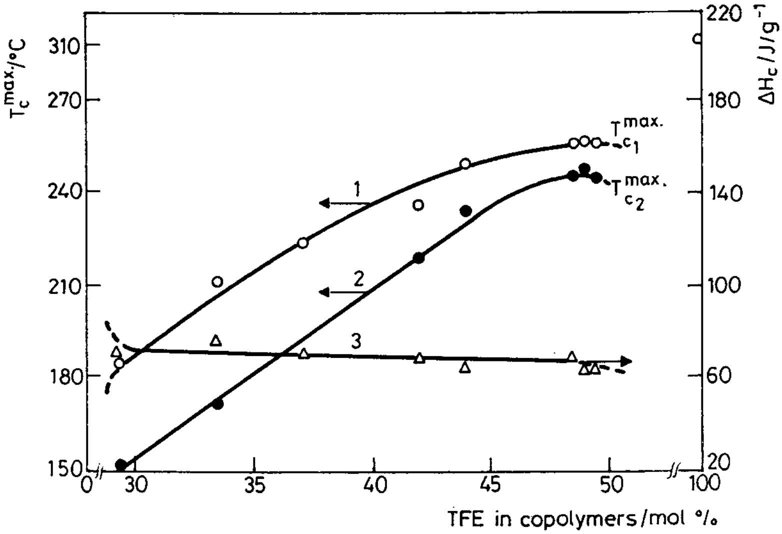

Fig. 3 Dependence of the crystallization temperatures, $T_{c_1}^{max}$ and $T_{c_2}^{max}$ (curves 1, 2) and of the crystallization enthalpy, ΔH_c (curve 3) of TFE-E copolymers obtained in bulk on the TFE content (mol%) of the copolymer

The wide-angle X-ray diffraction (WAXD) curves of powdery copolymer samples are shown in Fig. 4. For the alternating TFE-E copolymers obtained in bulk (copolymer 1) a strong crystalline reflection is observed at $2\theta = 19.2°$ and a weaker one at $2\theta = 21.4°$. They are characteristic of the alternating copolymer crystal phase having orthorombic unit cell [4] and do not coincide with the known crystalline reflections of either PE or PTFE homopolymers.

The DSC curves of melting and crystallization of TFE-E copolymers obtained by semi-flow suspension technique, maintaining thus a constant copolymer composition, are shown in Fig. 5. The observed monomodal peaks prove the higher structural (and/or chemical) homogeneity of the copolymer as compared to those obtained in bulk. The X-ray pattern of the copolymer obtained in suspension is also shown in Fig. 4 (copolymer 2). It is a typical WAXD pattern of an alternating copolymer crystal phase.

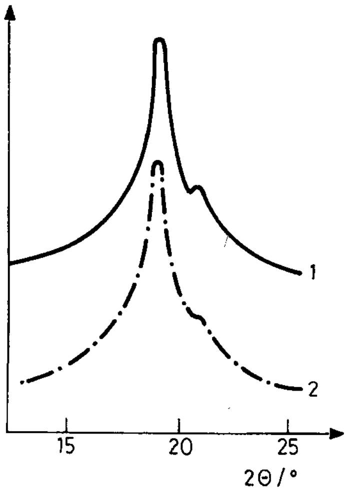

Fig. 4 Equatorial WAXD intensity curves of the TFE-E copolymer (50 mol% TFE) at room temperature; copolymer 1 was obtained in bulk (curve 1) and copolymer 2 - in suspension (curve 2)

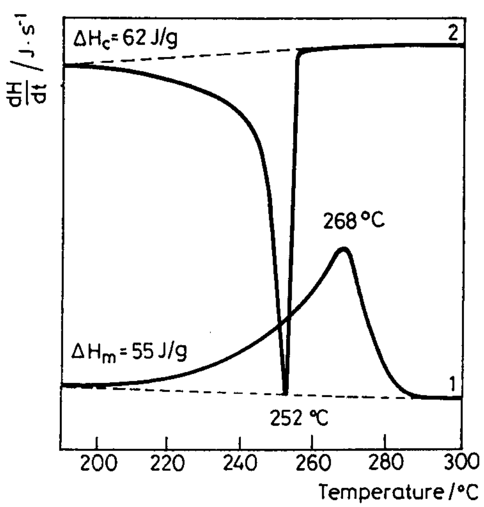

Fig. 5 Heating - (1) and cooling - (2) DSC curves of the TFE-E copolymer obtained in suspension

Kinetics of nonisothermal crystallization of TFE-E copolymer

The kinetics of the nonisothermal crystallization of the TFE-E copolymer of equimolar content of TFE and E monomer units prepared in suspension was studied by calorimetry. The modified Avrami kinetic equation [5] was found to be applicable in the narrow temperature range of 266 to 255°C.

The dependence of the proportion of crystalline fraction C at different temperatures on the cooling rate Φ is shown in Fig. 6 using the Avrami coordinates lg[–ln (1 – *C*)] *vs.* lgΦ.

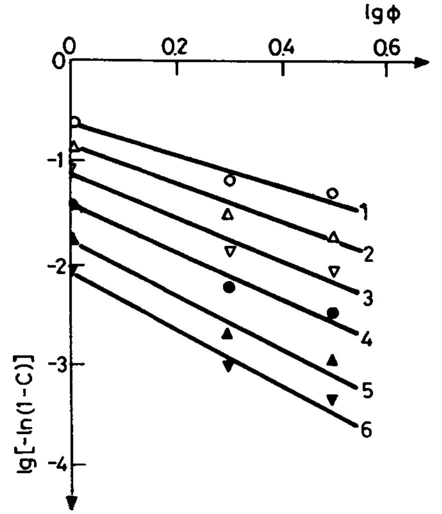

Fig. 6 Graphical solution of the Avrami equation for the nonisothermal crystallization of the TFE-E alternating copolymer (50 mol% TFE, 50 mol% E) obtained in suspension at different temperatures: 1 - 255°C; 2 - 256°C; 3 - 257°C; 4 - 258°C; 5 - 259°C; 6 - 260°C

The graphs representing these dependences are straight lines with slightly changing slope in the temperature range studied. Avrami exponents, *n*, calculated from the slope of these lines, have values between 1.5 and 2.7. Therefore, the crystalline nuclei in TFE-E copolymers grow mainly two-dimensionally, probably by heterogeneous nucleation, since homogeneous nucleation should be excluded under the applied crystallization conditions. At high temperatures of nonisothermal crystallization two-dimensional and one-dimensional growth of the crystal nuclei was found to occur for the PE and PTFE, respectively. Hence, the crystallization mechanism of TFE-E alternating copolymers is closer to the PE homopolymer crystallization mechanism.

At the initial temperatures of nonisothermal crystallization the cooling function (X_c) of the TFE-E copolymer (Table 1) was found to be visibly lower than that of the PTFE homopolymer. It is comparable to the cooling function of the PE nonisothermal crystallization at 126–122°C.

Table 1 Temperature depedence of the Avrami exponent (*n*) and crystallization function X_c for the TFE–E alternating copolymer

T/°C	n	$-\lg X_c/T$
260	2.7	2.1
259	2.6	1.8
258	2.3	1.5
257	2.0	1.2
256	1.7	0.9
255	1.5	0.7
	av. 2.1	
PE (126–122)	av. 2.0	ca. 1.6–2.0
PTFE (317–306)	av. 1.0	ca. (+1)–(–1)

The crystallization cooling function X_c is an exponential function of temperature. It is illustrated in Fig. 7 by the linearity of the corresponding dependence in semilogarithmic co-ordinates.

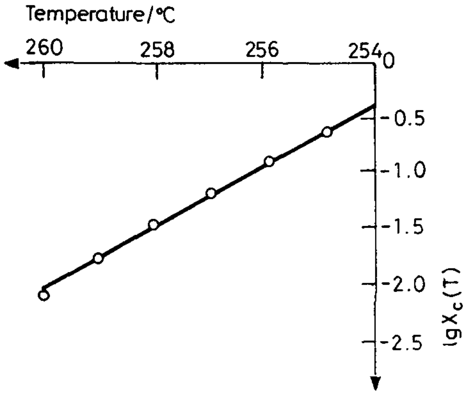

Fig. 7 Dependence of the crystallization cooling function (X_c) on the crystallization temperature T_c

Conclusions

The DSC curves of TFE-E copolymers, synthesized in bulk with a composition up to alternating, show two monomodal melting (respectively crystallization) peaks. The lower temperature maximum is due to phase transitions in the copolymer containing low molecular fractions, extremely rich in E monomer units. The high-temperature peak is associated with the melting of the crystalline phases built up from chains with higher content of TFE monomer units.

The melting (respectively crystallization) temperatures of the copolymers show a maximum in the range of the alternating composition (48–50 mol% TFE). This maximum is bimodal and it is probably due to a bimodal distribution of the monomer units within the copolymer chain.

A monomodal DSC curve is observed for the copolymer of constant alternating composition prepared in suspension.

The alternating copolymer possesses a significant crystallinity which can be explained by a new crystalline structure determined by the repeating sequence ($-CF_2-CF_2-CH_2-CH_2-$).

The kinetics of the nonisothermal crystallization of alternating TFE-E copolymers can be described in terms of a modified Avrami equation. The Avrami exponent (ca. 2) indicates heterogeneous nucleation and a two-dimensional growth mechanism close to that of the PE homopolymer.

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Zusammenfassung — Mittels DSC wurde das Schmelzen und die Kristallisation von Kopolymeren, die mittels der Semi-Flow-Methode in Masse und in Suspension aus Tetrafluorethylen und Ethylen hergestellt wurden, untersucht.

Es wurden Röntgendiffraktionen und Infrarotspektren der Kopolymere aufgezeichnet sowie neue Kristallreflexionen, die von denen der Homopolymere abweichen.

Die Schmelztemperatur des in Masse synthetisierten Kopolymeres hängt stark von der Zusammensetzung ab und zeigt verschiedene Maxima. Innerhalb der Reihe der alternierender Zusammensetzung wurde ein gewisses Absinken der Schmelztemperatur beobachtet.

Bei alternierenden Kopolymeren, die in Suspension hergestellt wurden, handelt es sich um monomodale Peaks, was eine größere strukturelle und chemische Homogenität des Kopolymers anzeigt.

Die Kinetik der nichtisothermen Kristallisation des in Suspension hergestellten alternierenden Kopolymers im Temperaturbereich von 260 bis 255°C kann durch eine modifizierte Avrami'sche Gleichung beschrieben werden. Der Mechanismus von Kristallkernbildung und -wachstum bei der nichtisothermen Kristallisation von Tetrafluorethylen-Ethylen-Kopolymer ähnelt dem von Polyethylen.