

# On Melt-Crystallization of Polytetrafluoroethylene and of Random Fluorinated Copolymers of Tetrafluoroethylene

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**ABSTRACT:** Through differential scanning calorimetry, isothermal crystallization from the melt of polytetrafluoroethylene (PTFE) has been investigated. PTFE was regarded as one of the polymers for which crystallization is so rapid that the samples crystallize during the cooling from the melt to the selected crystallization temperature. By contrast, we now report that a stochastic behavior is observed for isothermal melt-crystallization of PTFE. In fact, on cooling very quickly the samples from the molten state to the selected crystallization temperature, crystallization during the cooling is randomly observed. Therefore, repeating the experiments until crystallization on cooling was absent, it was possible to investigate isothermal melt-crystallization of PTFE. However, crystallization is very fast; in fact, crystallization kinetics can be followed just for very low undercoolings, while as the undercooling becomes as large as about 15°C, only secondary crystallization is observed. In both cases, the data have been examined through the well-known Avrami analysis, taking into account the different physical meaning of the obtained parameters. For the first cases (actual crystallization kinetics) very low, noninteger Avrami exponents have been obtained. They have been related to the fractal dimension of the crystallites and their values to the morphological observations on PTFE. For the second cases, the typical low values of Avrami exponents of secondary crystallization are obtained. Moreover, isothermal melt-crystallization of random fluorinated copolymers of tetrafluoroethylene with either hexafluoropropylene or perfluoromethylvinylether as comonomers has been studied and compared with that of PTFE. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1607–1613, 1999

**Key words:** melt-crystallization; PTFE; TFE

## INTRODUCTION

The kinetics of melt-crystallization of polymers have been studied extensively. The major part of the work concerns the isothermal crystallization as this process is easily accessible through the experimental determination of the macroscopic crystallinity as a function of time, e.g., through calorimetric measurements.<sup>1</sup> For polytetrafluoroethylene (PTFE), it has been reported that crys-

tallization is so rapid that isothermal experiments are not possible; the polymer crystallizes in the period during which the sample is cooled to the selected crystallization temperature.<sup>2</sup> The study of crystallization kinetics of PTFE has been tried, however in a more general study of *condis* (conformationally *disordered*) crystal formation from the melt.<sup>3</sup> Herein, the results of this work will be compared with the present ones.

The knowledge of the crystallization kinetics of PTFE should be of increasing interest either for its technological importance or for the aim of providing new insights to the special properties of this macromolecule. Therefore, through differential scanning calorimetry (DSC), we tried to carry

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out isothermal crystallizations from the molten state by taking the sample to the crystallization temperature at the maximum rate allowed by the instrument. We found a stochastic behavior, in that sometimes the sample crystallized during the cooling to the selected crystallization temperature, sometimes it did not. Therefore, we repeated each experiment until no crystallization on cooling was observed. The outcome was analyzed by the well-known Avrami equation,<sup>4-6</sup> largely used to investigate the crystallization kinetics of polymers.<sup>1,7</sup>

On the other hand, we have examined the isothermal melt-crystallization of random fluorinated copolymers of tetrafluoroethylene (TFE), in particular those with hexafluoropropylene or perfluoromethylvinylether as comonomers (FEP and PFMVE copolymers, respectively). These copolymers are particularly interesting either for their technological applications or for their structural features. In fact, they retain most of the outstanding properties of PTFE, such as excellent thermal and chemical stability, high insulating activity, low refractive index and dielectric constant, insolubility in most solvents, and high crystallinity, but their lower melt viscosity allows fabrication by the usual melting extrusion or injection molding technologies.<sup>8</sup> In contrast, it is well known that the homopolymer, because of its high melting temperature and melt viscosity, requires unconventional processing techniques, such as powder sintering and paste extrusion. In regard to their structure, FEP and PFMVE differ as far as the incorporation of counits in the homopolymer crystal lattice is concerned. In fact, most authors agree that  $-\text{CF}_3$  is included<sup>9-12</sup> while  $-\text{OCF}_3$  is rejected<sup>13,15</sup> from PTFE crystals.

In this work, we report also the study by DSC of the isothermal melt-crystallization of these copolymers, for which it has been shown that crystallization on cooling from the melt to the crystallization temperature is not observed.<sup>13-16</sup> Also in this case the Avrami analysis of the data was carried out. The obtained data are also analyzed to study the effect of two differently behaving structural counits on crystallization kinetics of PTFE and, possibly, to gain a better understanding of the exclusion<sup>17,18</sup> or inclusion<sup>19</sup> of the side groups in the crystals.

## EXPERIMENTAL

### Materials

Powder samples of PTFE and of copolymers of TFE with 1 mol % of PFMVE or FEP as comono-

mers have been used throughout this work. They were obtained by conventional aqueous dispersion polymerization.

### Thermal Analysis

Thermal analysis was performed by a DSC 7 (Perkin Elmer) and the data analyzed by the Pyris software.

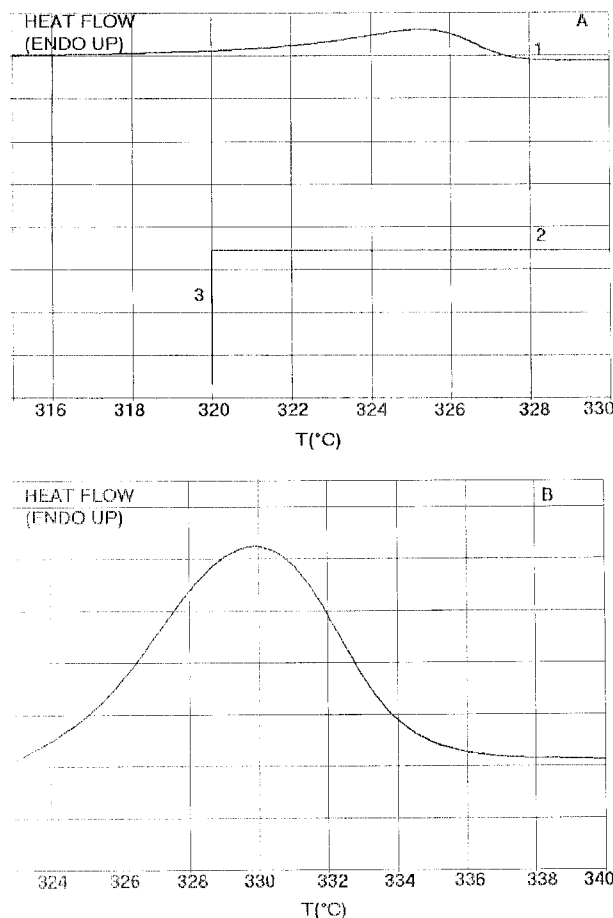
Runs were performed on  $10 \pm 0.5$  mg samples in a nitrogen atmosphere. Before each run the baseline was recorded and optimized in the temperature range of interest, then subtracted from the corresponding DSC curve. The heats of fusion were calculated from the peak areas and their uncertainty is  $\pm 0.3$  J/g.

Isothermal crystallizations were performed in the DSC apparatus in a nitrogen atmosphere for times ranging from 0.1 to 300 min. Each sample was taken to 400°C at 10°C/min, held at this temperature for 5 min (a procedure that was reported to produce negligible thermal degradation<sup>20</sup>) to be assured of its complete melting, then cooled to the selected crystallization temperature  $T_c$  at the maximum velocity allowed by the instrument and taken at  $T_c$  for a predetermined time  $t_c$ . As mentioned previously, each experiment was repeated until no crystallization during the fast cooling occurred. Then the sample was reheated at 10°C/min to 400°C. The area under the resulting melting peak is taken as a measure of the crystalline polymer fraction obtained at the selected  $T_c$  in the time  $t_c$ .

This procedure, although more tedious than the usually adopted one, reduces the errors in the determination of crystallinity originating from the small DSC signals corresponding to isotherms, and allows the evaluation of crystallinity using a very reliable reference value, i.e., the enthalpy of fusion of a perfect crystal of PTFE. It is worthy noting that this procedure has often been used for the study of crystallization kinetics of liquid crystalline polymers<sup>21-23</sup> and also in the previously cited work on PTFE itself.<sup>3</sup>

## RESULTS AND DISCUSSION

In Figure 1(A) we report, for example, a thermal treatment performed on a sample of PTFE, before the final analysis. Curve 1 represents the melting of the as-polymerized sample recorded from 200 to 400°C at 10°C/min; curve 2 the very fast cooling at the maximum rate allowed by the instrument



**Figure 1** DSC curves of the thermal treatments performed on PTFE before the analysis: (A), 1. melting of the native sample at 10°C/min; 2. cooling the sample from the melt to the selected crystallization temperature  $T_c$  at the maximum rate allowed by the instrument; and 3. isothermal crystallization at  $T_c$  for a predetermined time  $t_c$ . (B): melting at 10°C/min of a sample of PTFE after a thermal treatment as that reported in Figure 1(A).

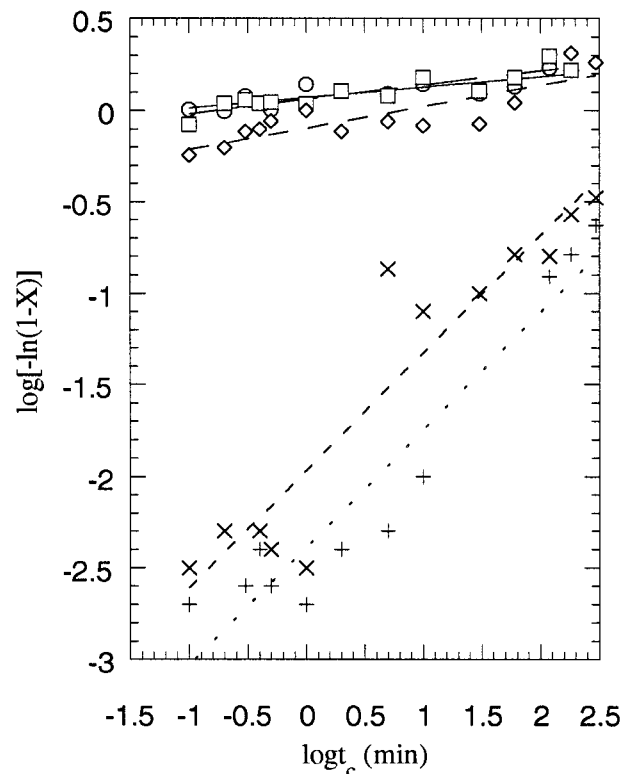
from the melt to the selected crystallization temperature, from which it is apparent that no crystallization occurs on cooling. Curve 3 corresponds to the crystallization at  $T_c$  during a predetermined time  $t_c$ . It is noteworthy that for  $T_c < 319^\circ\text{C}$ , crystallization is complete even for the lowest  $t_c$  allowed by the instrument (0.1 min); in such cases, just the kinetics of secondary crystallization or crystal perfection can be observed, i.e., the early stages of crystallization are lost. The heats of fusion determined from the scans from  $T_c$  to 400°C at 10°C/min, like that of Figure 1(B), were converted to degrees of crystallinity  $X$  using the enthalpy of fusion of a perfect PTFE crystal (4.10 kJ/mol taken from Lau et al.<sup>24</sup>).

It is well known that the overall isothermal crystallization rate, as the development of crystallinity vs. time, can be described by the Avrami equation<sup>4-6</sup> which, in its logarithmic form, reads as:

$$\log[-\ln(1 - X)] = \log k + n \log t \quad (1)$$

where  $X$  is the crystallinity degree developed at time  $t$ ,  $k$  contains the rate constants of nucleation and crystal growth and  $n$  reflects the type of nucleation and the habit of the growing nuclei.

In Figure 2 we report the data of  $\log[-\ln(1 - X)]$  vs.  $\log t_c$  for some of the investigated crystallization temperatures. As mentioned previously, the curves corresponding to  $T_c = 280, 285,$  and  $318^\circ\text{C}$ , respectively, concern secondary crystallizations, while the curves corresponding to  $T_c = 319$  and  $320^\circ\text{C}$ , are relative to actual crystallization kinetics. Let us begin the discussion from these last ones. A linear trend of the data is observed without the usual breakdown of crystallinity vs. time. The Avrami parameters, namely  $n_1$



**Figure 2** Development of crystallinity as  $\log[-\ln(1 - X)]$  vs.  $\log t_c$  for isothermal crystallizations from the melt of PTFE:  $T_c = 319$  (x) and  $320^\circ\text{C}$  (+). Secondary crystallizations:  $T_c = 280$  (o),  $285$  (□), and  $318^\circ\text{C}$  (◇).

**Table I Avrami Constants for Isothermal Crystallization ( $n_1$  and  $k_1$ ) and Secondary Crystallization ( $n_2$  and  $k_2$ ) Calculated for PTFE as a Function of the Crystallization Temperature  $T_c$**

$T_c$ (°C)	$n_1$	$k_1$ (min <sup>-n<sub>1</sub>)</sup>	$n_2$	$k_2$ (min <sup>-n<sub>2</sub>)</sup>
280 <sup>a</sup>			0.057	0.99
285 <sup>a</sup>			0.078	0.99
318 <sup>a</sup>			0.12	0.97
319 <sup>b</sup>	0.62	16.4		
320 <sup>b</sup>	0.58	20.5		

<sup>a</sup> Secondary crystallizations: only the second stage can be detected.

<sup>b</sup> Actual crystallizations: only the first stage observed at the used crystallization times.

and  $k_1$  as referring to the primary crystallization stage, are reported in Table I.

The values of  $n_1$  are similar to those obtained for liquid crystalline polymers, according to the rod-like and stiff chain character of their molecules.<sup>21-23</sup> It must be kept in mind that the mesophase character of PTFE in its high temperature phase (polymorph I),<sup>25</sup> is recognized as a *condis* crystal.<sup>26</sup>

Moreover, morphological studies on melt-crystallized PTFE have shown that its microstructure is constituted of extended chain lamellae, where very long polymer chains may still be folded at the lamellar surface.<sup>27</sup> Following another point of view,<sup>20</sup> melt-crystallized PTFE can be regarded as a chain-folded polymer whose lamellar thickness is much greater than nearly all other crystalline polymers.

However, it should be noted that the obtained values of  $n$  are not integer, as often observed for most polymers. This has been considered in the past as a proof that the  $n$  parameter in Avrami equation does not have a physical meaning.<sup>1</sup> By contrast, as some of us have proposed,<sup>28</sup> the non-integer values of  $n$  may be viewed as the *fractal dimension*<sup>29</sup> of the crystallites, taken also into account that the functional form of the Avrami equation is the same as that defining the dimensionality of an object.<sup>29</sup> In the framework of Mandelbrot fractal theory,<sup>29</sup> we hypothesize that the Avrami exponents, which characterize the power law of the crystal growth, are related to the *fractal dimension*  $D$  of the crystallites as  $n = D - 1$ . In such a way we estimate  $D \sim 1.6$ . PTFE extended chain crystals, due to their extraordinary length, will have an unstable shape, accord-

ing to their *condis* character. In such a way a self-avoiding walk takes place in agreement with the estimated fractal dimension and with the folded-ribbons crystal model proposed by Suwa<sup>30</sup> for as-polymerized PTFE.

At this point let us to come back to the curves of Figure 2, corresponding just to a secondary crystallization process, i.e., to the second stage of the transformation, since the first stage at these crystallization temperatures cannot be detected; in fact, even for the lowest crystallization time allowed by the instrument (i.e., 0.1 min), crystallization appears to be complete. The slight increase in crystallinity observed as a function of time may be only due to secondary crystallization and crystal perfection. The Avrami parameters,  $n_2$  and  $k_2$  calculated for this stage, are reported in Table I. The very low values obtained for  $n_2$  are those expected for this process.

Now we wish to briefly compare our results with those of Grebowicz et al.<sup>3</sup> For the actual crystallization kinetics, we obtained  $n$  ( $n_1$ ) values similar to those reported for the lowest undercoolings in Grebowicz et al.<sup>3</sup> For the other crystallization temperatures in the work of Grebowicz et al.,<sup>3</sup> it is not taken into account that the primary crystallization is lost (note that the authors start from  $t_c = 32$  sec, whereas we start from  $t_c = 6$  sec). In Table II, we report the Avrami parameters that one could calculate if a two-stage crystallization had been hypothesized, as in Grebowicz et al.<sup>3</sup> even for the higher undercoolings. Qualitatively similar values of  $n_1$  and  $n_2$  would be obtained; nevertheless, as we have shown previously, such an analysis of the data and the comparison of secondary crystallization with crystallization kinetics appears to be misleading.

Finally the different values of  $k$  ( $k_1$ ) obtained by us also for the actual crystallization kinetics may be due to the different experimental conditions; in fact, as previously said, we consider just those cases in which no crystallization occurs on cooling the sample from the melt to  $T_c$  [see segment 2 in Fig. 1(A)]. Nothing is said about this point in Grebowicz et al.<sup>3</sup>

For random copolymers, the study of the crystallization kinetics becomes more difficult taking into account that the comonomer unit can be included in the homopolymer crystal lattice as a point defect<sup>19</sup> or rejected from it,<sup>17,18</sup> thereby interrupting or terminating the crystal growth.<sup>7</sup> Therefore, the trend of the isotherms is even more complex and difficult to understand than for homopolymers. In this work, we have analyzed FEP

**Table II Avrami Parameters Calculated for PTFE Secondary Crystallizations Hypothesizing a Two-Stage Process**

$T_c$ (°C)	$n_1$	$n_2$	$k_1$ (min <sup>-n<sub>1</sub></sup> )	$k_2$ (min <sup>-n<sub>2</sub></sup> )	Time at Break (min)
280	0.23	0.065	1.62	0.99	0.4
285	0.20	0.081	1.41	0.99	0.4
290 <sup>a</sup>	0.21		0.92		
315 <sup>a</sup>	0.14		1.24		
317 <sup>a</sup>	0.36		1.82		
318	0.27	0.19	1.04	1.11	0.5

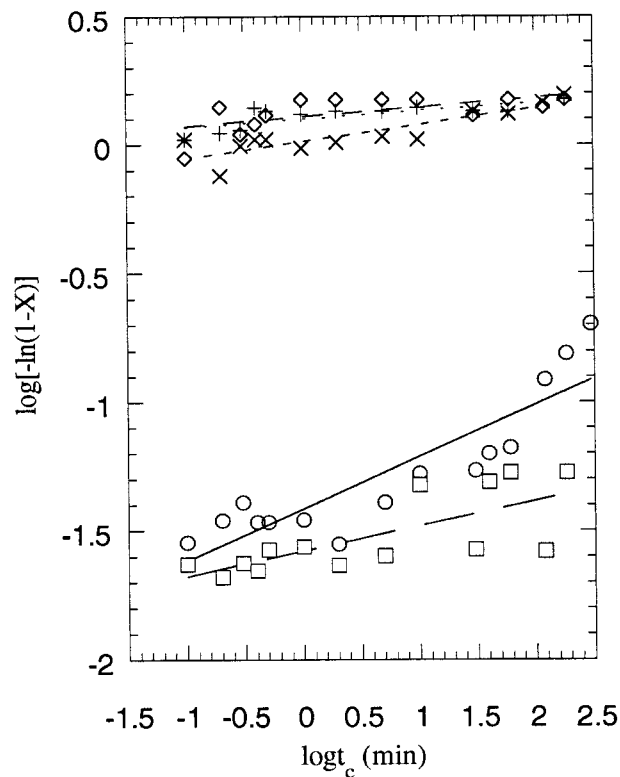
<sup>a</sup> Only times corresponding to the first stage investigated.

and PFMVE copolymers with 1 mol % of comonomer. The enthalpies of fusion determined from the DSC thermograms were converted to degrees of crystallinity  $X$  using the enthalpy of fusion of a perfect PTFE crystal<sup>24</sup> at the equilibrium melting point of the copolymer.<sup>7</sup> For FEP it was determined by us as 330°C<sup>31</sup> through the method by Hoffman and Weeks,<sup>32</sup> while that of PFMVE was determined as 325°C by interpolation of the data of Centore et al.<sup>16</sup>

In Figures 3 and 4 the calorimetric crystallinity as  $\log[-\ln(1 - X)]$  vs. time is reported for FEP and PFMVE, respectively. In Figure 3, the curves corresponding to  $T_c = 270, 272,$  and  $274^\circ\text{C}$  concern secondary crystallizations, while those corresponding to  $T_c = 312$  and  $315^\circ\text{C}$  to actual crystallizations. Similarly, in Figure 4, the curve at  $T_c = 285^\circ\text{C}$  concerns secondary crystallization, while those at  $T_c = 310$  and  $315^\circ\text{C}$  actual crystallizations. Secondary crystallizations show the expected trend, previously observed for PTFE, therefore they will not be further discussed. As far as actual crystallizations are concerned, we can note for both copolymers (but especially for PFMVE) a retardation at long times with respect to the homopolymers. This behavior is expected particularly at low undercoolings (as those considered by us) and has been attributed mainly to the attenuation in the nucleation rate on passing from the homopolymer to copolymers.<sup>1,7</sup> In Table III, we report the kinetic parameters evaluated for FEP and PFMVE.

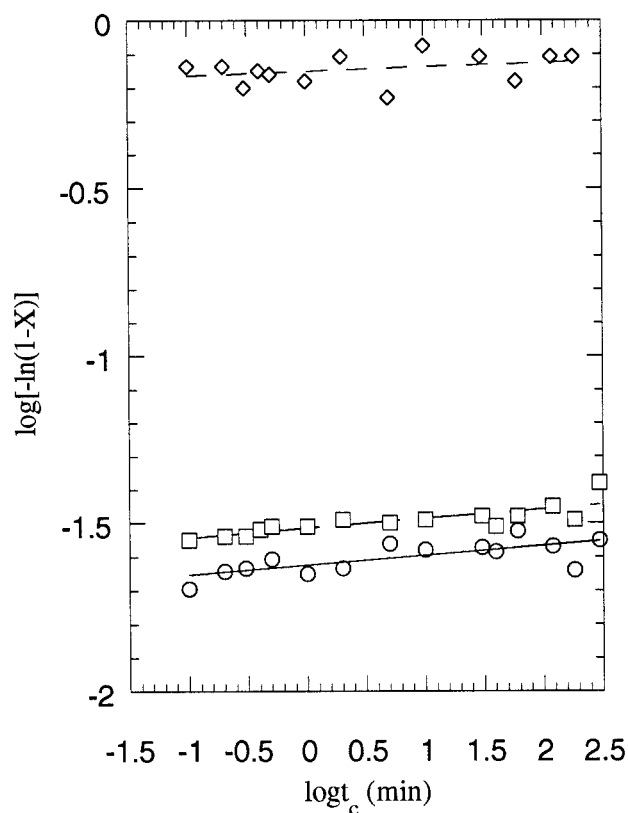
The curves reported in Figures 2, 3, and 4 may be also considered to give an insight to the problem of counits inclusion in—or exclusion from—the homopolymer crystals. It is well known that for copolymers, a change in the nature of crystallization occurs with respect to the homopolymer.<sup>6</sup> In particular, if the counits are rejected from the homopolymer crystal lattice, the copolymer iso-

therms show deviations from those of the homopolymer, essentially because of the changing composition of the melt, caused, in turn by the rejection of the counits from the crystalline phase as the transformation proceeds. By contrast, if the counits entered the crystal lattice, the melt would not continuously change its composition, so the copolymer isotherms should resemble more closely those of the homopolymer. From the com-



**Figure 3** Development of crystallinity as  $\log[-\ln(1 - X)]$  vs.  $\log t_c$  for isothermal crystallizations from the melt of FEP:  $T_c = 312$  (○), and  $315^\circ\text{C}$  (□). Secondary crystallizations:  $T_c = 270$  (◇),  $272$  (+), and  $274^\circ\text{C}$  (×).

parison of Figures 2, 3, and 4, we are not allowed to univocally discriminate these two cases. Nevertheless the retardation at long times is more pronounced for PFMVE, as well as the Avrami parameters are much more different with respect to those of PTFE, although the comonomer concentration (1 mol %) is the same for both copolymers. The fractal dimensions show significantly lower values for the copolymers,  $D \sim 1.2$  for FEP and  $D \sim 1.0$  for PFMVE, with respect to PTFE. This indicates more linear crystals, according to lower lamellar thickness and greater shape stability. These effects are particularly important for PFMVE. These observations are in agreement with a more pronounced disturb on the homopolymer crystallization induced by random  $-\text{OCF}_3$  side groups than by  $-\text{CF}_3$  ones. Therefore, even if indirectly, our results may suggest the exclusion of the first ones and a probable inclusion of the second, according to the literature.<sup>9-12,13-15</sup>



**Figure 4** Development of crystallinity as  $\log[-\ln(1-X)]$  vs.  $\log t_c$  for isothermal crystallizations from the melt of PFMVE:  $T_c = 310$  ( $\square$ ) and  $315^\circ\text{C}$  ( $\circ$ ). Secondary crystallization:  $T_c = 285^\circ\text{C}$  ( $\diamond$ ).

**Table III** Avrami Constants for Isothermal Crystallizations ( $n_1$  and  $k_1$ ) and Secondary Crystallizations ( $n_2$  and  $k_2$ ) Calculated for (A) FEP and (B) PFMVE Copolymers as a Function of the Crystallization Temperature  $T_c$

$T_c$ ( $^\circ\text{C}$ )	$n_1$	$k_1$ ( $\text{min}^{-n_1}$ )	$n_2$	$k_2$ ( $\text{min}^{-n_2}$ )
(A)				
270 <sup>a</sup>			0.043	0.99
272 <sup>a</sup>			0.075	1.00
274 <sup>a</sup>			0.032	0.99
312 <sup>b</sup>	0.20	1.92		
315 <sup>b</sup>	0.14	1.64		
(B)				
285 <sup>a</sup>			0.0086	1.00
310 <sup>b</sup>	0.028	1.10		
315 <sup>b</sup>	0.037	1.15		

<sup>a</sup> Secondary crystallizations: only the second stage can be detected.

<sup>b</sup> Actual crystallizations: only the first stage observed at the used crystallization times.

## CONCLUSIONS

Isothermal melt-crystallization of PTFE has been investigated and kinetic parameters calculated. The calculated Avrami coefficients  $n$  have been related to the fractal dimension  $D$  of the crystallites as  $D = n + 1$ . The obtained values of  $D$  are in agreement with the morphologies proposed for PTFE.

The trend of the isotherms corresponding to the melt-crystallization of the random TFE copolymers, compared with those of the homopolymer, seems to confirm the exclusion of  $-\text{OCF}_3$  side groups and the inclusion of  $-\text{CF}_3$  ones from PTFE crystals.

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