

# The Crystallization of a Copoly(chlorotrifluorethylene-vinylidene Fluoride) from the Amorphous Rubbery State

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## Synopsis

A random copoly(chlorotrifluorethylene-vinylidene fluoride) in the ratio of 3 : 1 was annealed at the temperature range of  $T_g < T < T_m$ . The copolymer slowly crystallizes, attaining a rather low ultimate degree of crystallinity, depending on the annealing temperature, in the form of randomly distributed ribbonlike lamellae. The crystallites' melting temperatures are much lower than those of the corresponding homopolymers, increasing with annealing temperature and time. The crystallization kinetics, analyzed using the Avrami equation, indicates the formation of small, low-ordered crystallites. The crystallization process results in a dramatic increase in the elastic modulus at  $T > T_g$ . Annealing of stretched samples results in oriented crystallization at much higher rates than in the unstretched material, without markedly affecting the ultimate degree of crystallinity. The oriented crystallites, distributed in an isotropic amorphous matrix, exhibit lower thermal stability than the corresponding unoriented crystals. Their melting temperatures increase with annealing time; however, they decrease with the extent of stretching, suggesting a strong kinetic effect on the crystallites' degree of order.

## INTRODUCTION

The random copolymer of chlorotrifluorethylene (CTFE) and vinylidene fluoride (VDF) in a 3 : 1 ratio is used as an elastomer binder for plastic-bonded explosives and propellants for its chemical resistance and low permeability to moisture. Since its glass transition is at ambient temperature (20–40°C), both physical aging and annealing effects can occur during its end use. The ability of such random copolymers to crystallize depends mainly on their composition. Although rather small amounts of CTFE reduce the crystallinity of PVDF, more than 30% VDF can be incorporated into the helical structure of PCTFE before the crystallinity and structure are appreciably affected.<sup>1</sup> However, Leshchenko et al.<sup>2</sup> have reported complete loss of crystallinity after introduction of 20% VDF units in PCTFE.

Since the copoly(CTFE-VDF) exhibits changes in its mechanical behavior upon storage at room temperature or just above it, a study was undertaken to evaluate the copolymer crystallization rate and extent and its thermal and mechanical behavior following annealing at temperatures between the glass transition and melting. The above was also studied for annealed samples while under strain.

## EXPERIMENTAL

A copolymer consisting of 72–77 mol% CTFE and 23–28 mol% VDF, Kel-F800 ( $M_w = 75 \times 10^3$ ,  $M_n = 29 \times 10^3$ ), supplied by the 3M Company (USA) in the form of translucent granules was used throughout this study. The granules were compression-molded into  $10 \times 300 \times 3$  cm rectangles at a temperature of  $140^\circ\text{C}$  (about  $30^\circ\text{C}$  above melting) and a pressure of 1.5 MPa followed by quenching to ambient temperature. These samples were amorphous, as determined by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The material was annealed at various temperatures in the range between the glass transition temperature ( $T_g$ ) and the melting temperature ( $T_m$ ) for the desired period of time, using a constant temperature oil bath. To eliminate direct polymer–oil contact, the samples were placed in a glass-covered Erlenmeyer flask.

The effect of annealing on the copolymer structure was studied using a DSC (Mettler TA 3000) at a heating rate of  $10^\circ\text{C}/\text{min}$  and a wide-angle X-ray diffractometer (Philips-PW 1050/25), counting every  $0.1^\circ$  for 5 s. The degree of crystallinity was evaluated from the DSC thermograms using  $42 \text{ J/g}^3$  for the heat of fusion of totally crystalline polymer and from the WAXD scans (uncorrected), according to the area separation method. The crystallographic orientation in stretched specimens was obtained using a texture goniometer (Philips PW 1078/24) at  $2\theta = 16.5^\circ$  (an angle at which a maximum intensity was observed). The specimens were rotated at  $1^\circ/\text{s}$ .

The tensile mechanical properties were obtained using an Instron 1195 at a stretching rate of 20 cm/min (nominal initial length of 40 mm). Since the copolymer's  $T_g$  is at ambient temperature, all tensile tests were carried out in an air-circulated oven at  $45^\circ\text{C}$ .

Thin films of the copolymer for transmission electron microscopy (TEM) were cast from a 2% solution in 1 : 4 mixture of acetone and methylisobutylketone. The films were mounted on TEM grids followed by annealing and Pd/Au shadowing prior to their observation (Jeol 100CX).

## RESULTS

### Crystallization of Unstrained Polymer

The effect of annealing temperature ( $T_g < T < T_m$ ) and duration (0–36 days) was first studied by thermal analysis. A characteristic set of thermograms, obtained from samples annealed at  $55^\circ\text{C}$  for up to 32 days, is presented in Figure 1. The amorphous nature of the as-molded polymer is clearly seen in the respective thermogram; no melting endotherm is observed. Upon annealing, the glass transition temperature is not significantly altered ( $27$ – $30^\circ\text{C}$ ) while a single broad melting endotherm appears at about  $90^\circ\text{C}$ . Upon further annealing, the endotherm area increases and the peak melting temperature is simultaneously shifted to higher values. The degree of crystallinity, calculated from the DSC endotherms area, is shown as a function of annealing time in Figure 2. These isotherms describe a rather slow crystallization process. No crystallinity could be detected even after a day of annealing at  $40^\circ\text{C}$  (just above  $T_g$ ) and  $70^\circ\text{C}$  (just below  $T_m$ ). The maximum crystallization rate and degree of crystallinity were attained, among the studied crystallization tem-

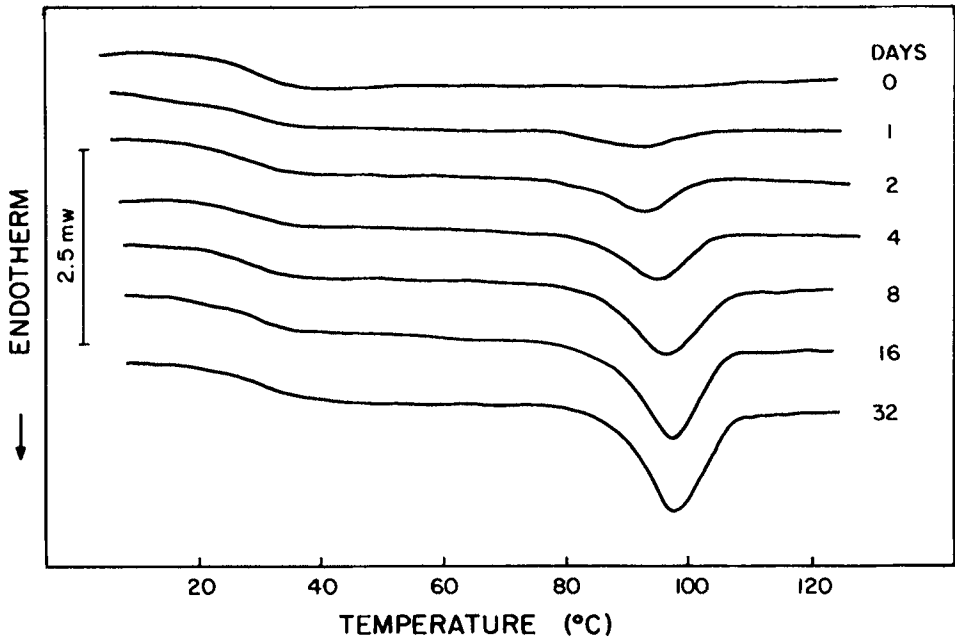


Fig. 1. DSC thermograms of a copoly(CTFE-VDF) annealed at 55°C for different periods of time.

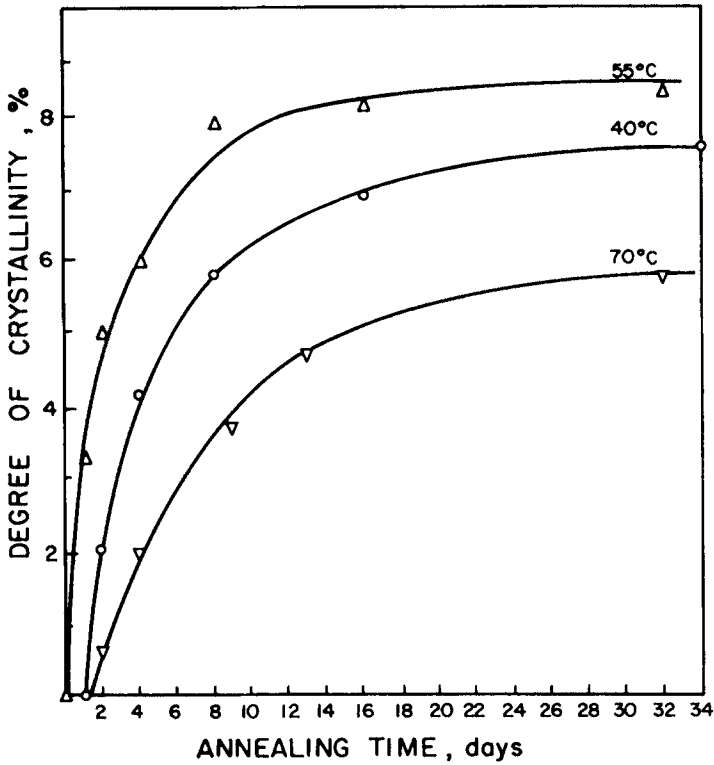


Fig. 2. Crystallization isotherms of a copoly(CTFE-VDF) for different crystallization temperatures [40 (O), 55 (Δ), 70 (▽) °C].

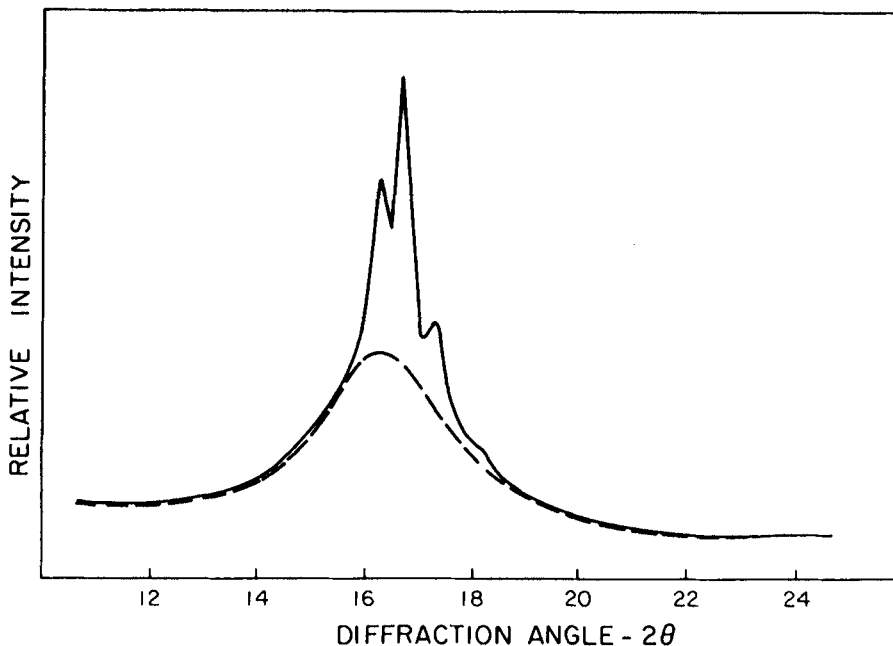


Fig. 3. Wide-angle X-ray diffraction pattern of copoly(CTFE-VDF): (-----) as molded, (—) annealed at 40°C for 16 days.

peratures, at 55°C; both rather low (3.3%/day and 8.3%, respectively). The single melting temperature observed was found to increase (81–104°C) with both annealing temperature and time. These copolymer melting temperatures are much lower than those of the corresponding homopolymers (PCTFE: 214–216°C, PVDF: 150–180°C).<sup>4</sup> It should also be noted that the melting range of the copolymer was not affected by the crystallization conditions. The effect of annealing on the structure of poly(CTFE-VDF) was also studied by WAXD. Typical diffractograms of as-molded and annealed materials are shown in Figure 3. The diffraction pattern of the as-molded copolymer consists of a halo, while that of the annealed sample exhibits three quite sharp intensity peaks. The degree of crystallinity, as evaluated from such WAXD scans, changes with annealing time and temperature similarly to that obtained by DSC. However, the calculated values are higher by a factor of 3–4 than those obtained by DSC.

The tensile mechanical properties of the copoly(CTFE-VDF) at ambient temperature were scattered due to the proximity of the measuring temperature to the polymer glass transition temperature. Therefore, the copolymer mechanical behavior was studied at an elevated temperature, just above  $T_g$ . While at room temperature the rubbery copolymer deforms inhomogeneously, through neck formation and propagation, at 45°C the samples undergo uniform deformation through their whole length. The zero strain elastic moduli measured at 45°C, of the copolymer samples that have been annealed at various temperatures for different lengths of time, are presented in Figure 4. The elastic modulus versus annealing time curves obtained for specimens annealed at 40 and 55°C are similar in shape to the crystallization isotherms

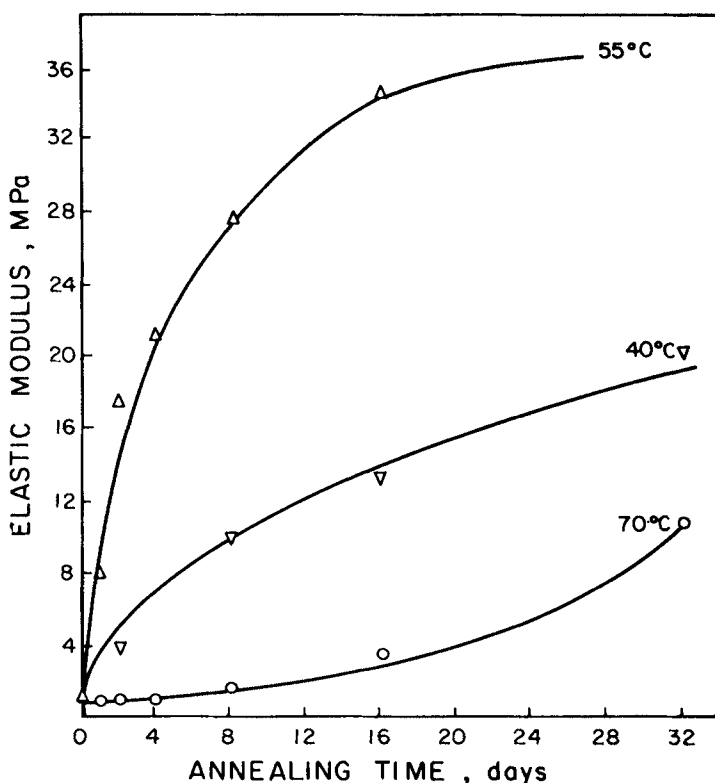


Fig. 4. Elastic modulus, at 45°C, of copoly(CTFE-VDF) as a function of crystallization time and temperature.  $\Delta$  = 55°C,  $\nabla$  = 40°C;  $\circ$  = 70°C.

(Fig. 2). However, the moduli continue to increase with annealing time while the degree of crystallinity has already attained its ultimate level after about 14 annealing days. Different behavior is exhibited by samples crystallized at the highest studied temperature, 70°C. The elastic modulus changes first gradually with annealing time, insignificantly during the first eight days of annealing (the degree of crystallinity has simultaneously changed at the highest measured rate). However, the modulus of the material changes at a much faster rate upon further annealing while the crystallinity has already leveled off.

The morphological developments during the crystallization of copoly(CTFE-VDF) were followed in cast thin films using transmission electron microscopy (TEM). The observed morphologies were found to depend on the annealing temperature and time. These parameters affect the rate and extent of crystallization, as mainly judged by the number of crystallites per unit film area. A series of electron micrographs (Fig. 5) shows for example the morphological changes as a result of annealing at 40°C. The first lamellar crystallites were only observed after 4 annealing days (crystallinity was already detected after two days). Their number and length increase with time; their thickness, however, seems to be time independent, staying constant at about 10 nm. Annealing at 55°C resulted in a larger number of crystallites, while after

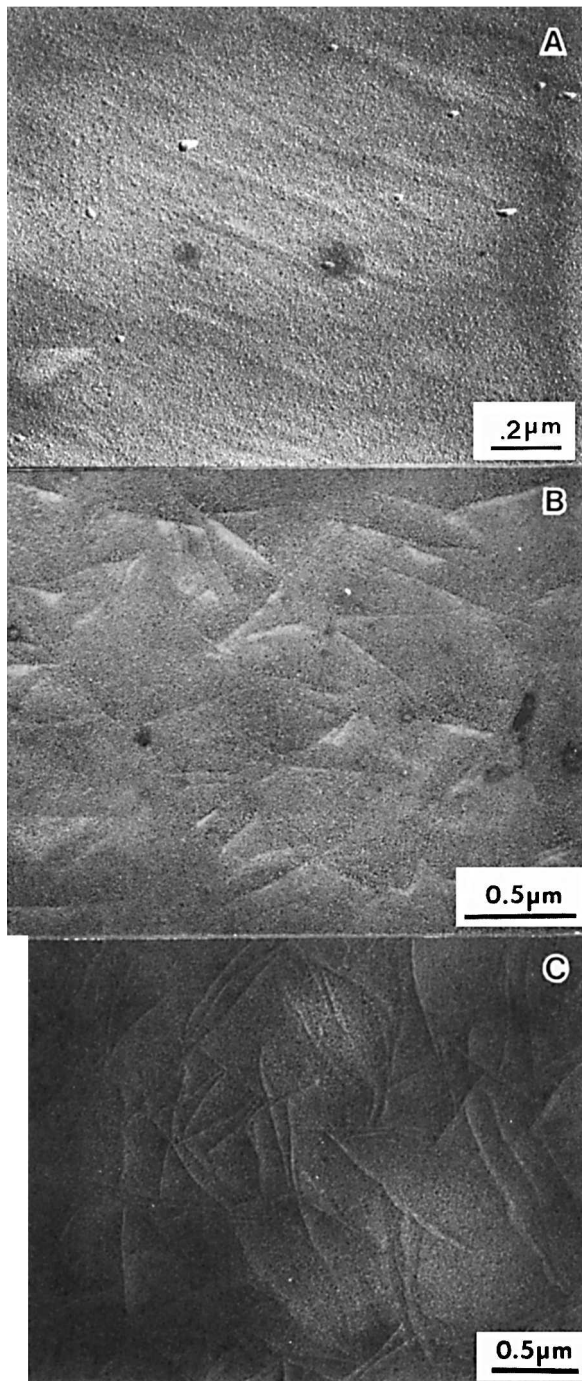


Fig. 5. Electron micrographs of thin copoly(CTFE-VDF) films annealed at 40°C for (A) 0, (B) 4, (C) 6, (D) 9, and (E) 20 days.

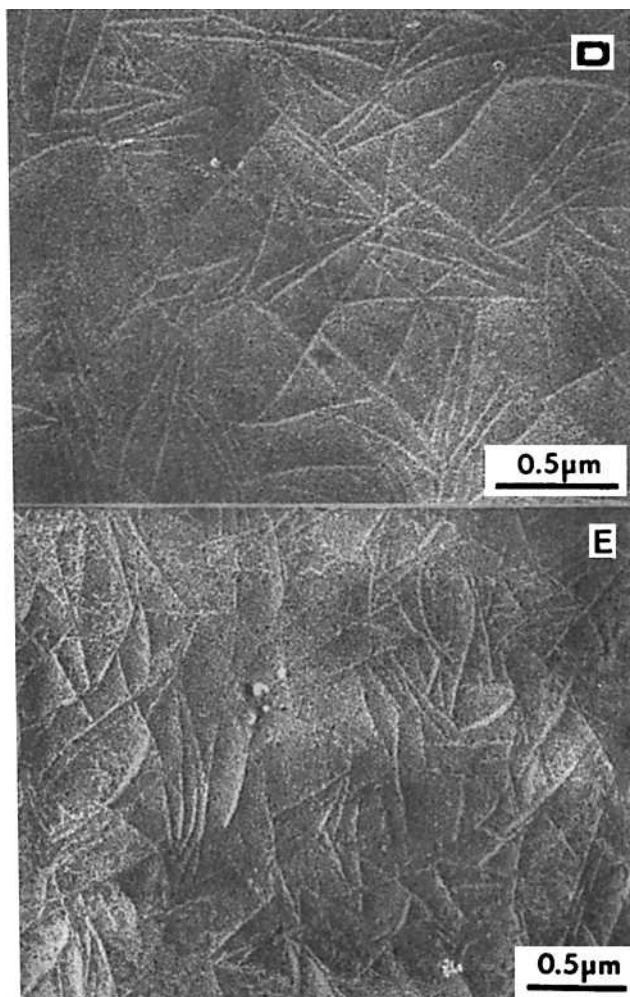


Fig. 5. (Continued from the previous page.)

annealing at 70°C the number of crystallites was the lowest, which is in agreement with the crystallinity measurements. Interestingly, the thickness of the lamellae crystallized at the different temperatures, covering almost the entire range between  $T_g$  and  $T_m$ , remained constant. Another interesting morphological observation is the lack of any complex structures such as spherulites. The lamellae seem to have been individually nucleated at the carbon substrate interface and then grown at an oblique angle with respect to the film plane.

#### Crystallization of Strained Polymer

The crystallization of the copoly(CTFE-VDF) under various extents of strain (50, 150, 250%) at different temperatures was also investigated. The samples were annealed under the desired strain and, when later released, did

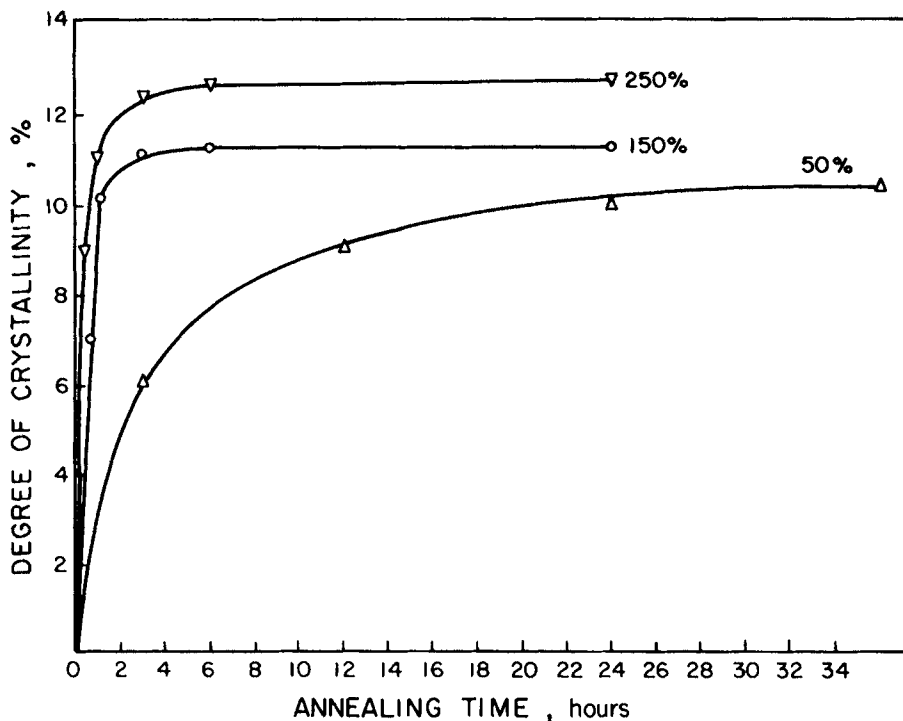


Fig. 6. Crystallization isotherms at 40°C of strained copoly(CTFE-VDF).  $\nabla$  250%;  $\circ$  150%;  $\triangle$  50%.

not contract. The DSC thermograms of these samples (not shown) exhibit a glass transition at a temperature identical to that observed for the unstrained polymer. However, the melting endotherms of the strained samples are much sharper and larger in their area compared with those of the unstrained material. Crystallization isotherms, based on DSC crystallinity measurements, for the strained copolymer annealed at 40°C are shown in Figure 6. The main effect of straining is on the crystallization rate while its effect on the attainable degree of crystallinity is only secondary. Both the rate and degree of crystallization increase with the extent of strain. Upon increasing the crystallization (annealing) temperature from 40 to 55°C the crystallization rate slightly increases; however, the effect of the extent of straining decreases. Further elevation of the annealing temperature to 65°C results in much lower crystallization rates as well as lower crystallinity. Interestingly, the melting temperature of the copolymer is strongly affected by straining. As can be seen in Figure 7, the melting temperature markedly decreases with increasing strain for all studied crystallization temperatures. (The depicted values are of samples annealed for 3 h; the melting temperature was found to change only slightly with annealing time.)

The effect of annealing temperature on the chain orientation was studied in samples that were crystallized (3 h annealing) while stretched to 250%, using wide-angle X-ray diffraction. The highest orientation was found in samples crystallized at 55°C and the lowest in samples crystallized at 65°C. These



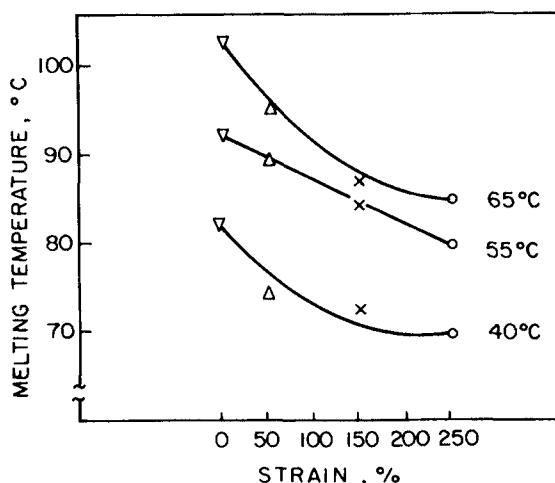


Fig. 7. Melting temperature of a copoly(CTFE-VDF) crystallized for 3 h under various extents of strain at different temperatures.

temperatures also, respectively, correspond to the crystallization conditions at which the highest and lowest degrees of crystallinity were measured.

## DISCUSSION

The presently studied copoly(CTFE-VDF), when rapidly cooled from the molten state to ambient temperature, is a glassy amorphous material, as determined by DSC and X-ray diffraction. The amorphous polymer crystallizes upon annealing at temperatures in the range of  $T_g < T < T_m$  at quite low rates, depending on the crystallization temperature, attaining rather low degrees of crystallinity. Comparison of the X-ray diffraction patterns presently obtained with those presented by Moggi et al.<sup>1</sup> suggests that the VDF units are incorporated in the PCTFE crystal structure, the spacings of which are maintained virtually unvaried. According to Moggi et al.,<sup>1</sup> the structure is appreciably affected in CTFE-VDF copolymers that consist of more than 30% VDF, however, their degree of crystallinity is already lower when 15% VDF is incorporated (due to structural irregularities), which is in agreement with the presently obtained data. It is interesting to note at this point that in spite of the similar X-ray patterns obtained for the copolymer and for PCTFE,<sup>1</sup> the melting temperatures of the former, 70–110°C (depending on the crystallization temperatures), are much lower than that of PCTFE, 211–216°C. Such large differences suggest the formation of "small" copolymer crystals exhibiting a low degree of order. Moreover, since the interchain distance in the copolymer is not significantly affected by the presence of VDF, being approximately the same as in PCTFE, the copolymer crystals are under internal stresses, which also contribute to the melting temperature depression. These arguments should also be taken into consideration when the large differences in the degree of crystallinity as determined by DSC and X-ray are questioned. These differences are partially due to the uncertain value of the copolymer

heat of fusion<sup>3</sup> used for the DSC crystallinity calculations. It should, however, be pointed out that although the absolute crystallinity values are different, the crystallization isotherms based on DSC and X-ray diffraction are similar in shape and identical with respect to their time axis. The crystallization kinetics was evaluated using the Avrami equation.<sup>5,6</sup> Each of the Avrami plots for the three crystallization temperatures exhibits two regions having distinctly different slopes, all being lower than one. Such a change in the slope is usually due to either changes in the nucleation rate<sup>7</sup> or in the growth mechanism.<sup>8</sup> The low slopes of the Avrami plots indicate either a system consisting of an irregular structure<sup>9</sup> and thus a low crystallizable fraction,<sup>10</sup> which is in agreement with the present crystallinity measurements, or the formation of ribbonlike crystallites,<sup>10</sup> which is in agreement with the presently observed morphology.

The glass transition was found to be quite constant, independent of the annealing temperature and time. This behavior should have been expected since the annealing always took place at temperatures above  $T_g$  without allowing for any physical aging to occur. Secondly, the degree of crystallinity attained during annealing was always too low to justify any significant restricting effects of crystallites on the mobility of the amorphous segments.<sup>11</sup> The unexpected low melting temperatures exhibited by the copoly(CTFE-VDF) crystallites relative to those of the corresponding homopolymers were discussed previously. The increasing melting temperature of the copolymer, from 70°C up to 110°C, with the crystallization temperature is expected.<sup>10</sup> However, it is interesting to observe the increasing melting temperature with annealing time. This temperature rise is probably due to increasing crystalline order during the very long crystallization process. It should be noted, however, that the high melting crystals were formed at a temperature in which the lowest crystallization rate and lowest degree of crystallinity were observed. Hence, the crystals formed at that high temperature and low rate are of relatively high order and thus thermally more stable.

The above-described structural changes during the annealing of copoly(CTFE-VDF) are clearly reflected in its mechanical behavior. The elastic modulus dramatically increases with annealing time at all temperatures, which is expected for a polymer with increasing degrees of crystallinity.<sup>12</sup> However, the moduli continue to increase after the crystallinity has leveled off. This is due to the continuing increase in the crystals' order, which also is reflected by the continuous increase in their melting temperature. The different shape of the modulus versus annealing time curve for samples crystallized at 70°C is unexplainable at present.

The most pronounced effect of stretching the amorphous elastomer prior to its annealing is on the isothermal crystallization rate, as also reported for various homopolymers (e.g., Refs. 13–15). The time required to attain the pseudoequilibrium degree of crystallinity is, as expected (e.g., Refs 16–18), markedly reduced in the stretched material compared with that in the unstretched one. Surprisingly, stretching prior to annealing does not have a large effect on the ultimate degree of crystallinity, which probably is because of the restrictions imposed by the copolymer random structure. The "quality" of the crystals formed in the oriented systems is reflected in their melting temperatures. They increase with the crystallization temperature, as in the

case of unstretched copolymer, however, they are always significantly lower than those of the isotropic samples, annealed at identical temperatures. Furthermore, the melting temperature was found to decrease with increasing extent of stretching. These results seem to contradict the predictions<sup>19,20</sup> and observations<sup>21,22</sup> reported for homopolymers, which were crystallized under strain. It is suggested that, in the presently studied material (a copolymer, the composition of which imposes the formation of low-ordered crystallites), the dominant factor is the crystallization rate. Samples that crystallized at similar rates (stretched to 150 and 250%) exhibit quite the same melting temperatures. Hence, higher crystallization rates result in the formation of relatively low-ordered crystallites that exhibit lower irreversible melting temperatures than the unstretched material.

The glass transition temperature was not affected by the stretching, indicating that the amorphous phase has relaxed during the annealing process. However, the crystalline phase was found oriented in the stretching direction. The extent of crystallographic anisotropy depends on the crystallization rate and extent and on the simultaneously occurring relaxation process, which becomes more effective at the higher annealing temperatures.

In conclusion, annealing ( $T_g < T < T_m$ ) of a random 3:1 copoly(CTFE-VDF) results in a slow crystallization process attaining a rather low crystallinity, the degree of which depends on the annealing temperature. The randomly distributed ribbonlike lamellae, formed during annealing, exhibit melting temperatures much lower than those of the corresponding homopolymers, due to their rather low level of order. The crystallization kinetics analysis also suggest the formation of small, low-ordered crystallites. This should be expected when a copolymer of the present structure and composition crystallizes with both comonomers in the same crystal structure. Stretching prior to annealing results in much higher crystallization rates, which depend on the extent of stretching and annealing temperature, and no large effect on the ultimate crystallinity. The oriented crystals, distributed in an isotropic amorphous matrix exhibit a lower thermal stability than the unoriented ones. The crystals formed from an oriented rubbery copolymer exhibit melting temperatures that decrease with increasing the extent of stretching due to the even lower levels of order in crystals obtained at higher rates. The behavior of the copoly(CTFE-VDF), as observed during the present work, is predominated by its random structure, its composition, and the low-order structures it forms.

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