Crystallinity Studies of Polychlorotrifluoroethylene by the Infrared Method. II. Kinetics of the Crystallization

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The isothermal rate of spherulitic growth of polychlorotrifluoroethylene (PCTFE) was studied by Price[1] by direct microscopic observation. He observed, however, that there was an ordering process, detectable by X-rays, which developed much more rapidly than did the spherulites. Allen[2] also suggested that there would be no necessary simple connection between the rate of growth of a spherulite and the rate of change of density. On the other hand, Morgan[3] and Flory[4] demonstrated that spherulitic growth was a true measure of the crystallization rate in the cases of polyethylene terephthalate and polydecamethylene sebacate, respectively.

In the preceding paper[5] it was shown that the infrared method was available for reliable estimates of crystallinity in PCTFE, completely independent of other methods. Furthermore, this method is responsive to crystallinity changes taking place rapidly. The investigation reported in the present paper was undertaken with the objective of measuring the isothermal rate of crystallization and to understand the crystallization kinetics of PCTFE by employing this technique. These results were discussed, comparing them with those obtained by other methods.

Experimental

The crystalline band at 440 cm^{-1} of the infrared spectrum was used to follow the production of crystalline material as the crystallization proceeded.

To determine the isothermal rate of crystallization, a procedure was used similar to that used by Reding and Brown[6] to measure the rate of crystallization of polyethylene. Two ovens, one directly over the other, were mounted on a Perkin-Elmer Model 112 infrared spectrometer with potassium bromide optics. The ovens were separately controlled; the upper oven was heated to 230°C of melting temperature and the lower one was heated to any desired growth temperature between 190 and 170°C by circulating a rapid stream of air through an insulated duct from the heaters. A calibrated thermocouple inserted in the lower oven very close to the sample led to a recorder-controller. The controller served to keep the growth temperature within the accuracy of ±0.5°C.

A thin film (0.03~0.06 mm. thick) of commercial PCTFE (NST 270) was clamped in a thin metal holder and placed in the upper oven. After five minutes at 230°C the sample holder was dropped into the lower oven so that it was in the path of the infrared radiation. The melt sample was estimated to reach the desired growth temperature in less than ten seconds. Since the spectrometer was responsive to changes taking place in three seconds or more, this technique proved adequate to follow the crystallization at high rates.

Results

The crystallized fraction of the sample was calculated from the experimental curves. Measurements of the rate of crystallization were carried out at temperatures between 174 and 190°C. Fig. 1 is

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[1] F. P. Price, *J. Am. Chem. Soc.*, **74**, 311 (1952).

[2] P. W. Allen, *Trans. Faraday Soc.*, **48**, 1178 (1952).

[3] L. B. Morgan, *Phil. Trans.* (*London*), **A247**, 23 (1954).

[4] P. J. Flory and A. D. McIntyre, *J. Polymer Sci.*, **18**, 592 (1955).

[5] H. Matsuo, ibid., **25**, 234 (1957); This Bulletin, **30**, 593 (1957).

[6] F. P. Reding and A. Brown, *J. Appl. Phys.*, **25**, 848 (1954).

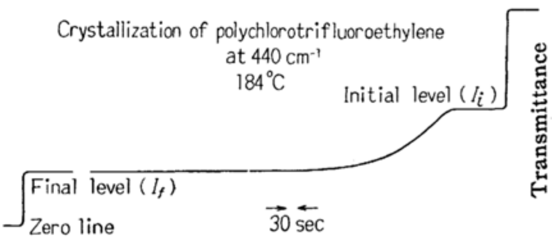


Fig. 1. Typical experimental record.

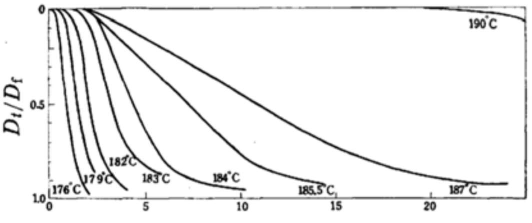
a typical experimental record obtained in this manner at 184°C. The optical density at time t is defined as

$$D_t \log = (I_i/I_t)$$

Similarly, obtical densities at final and initial states of the crystallization process are obtained by

$$D_f = \log(I_i/I_f), \quad \text{and} \quad D_i = 0$$

The continuously determined data for one curve at each growth temperature were plotted to form Fig. 2. The sigmoid-shaped curves seem to indicate that the crystallization process consists of an induction period, an intermediate period of accelerating rate of crystallization, and a final period to approach an equilibrium state. The degree of crystallinity of the sample, which completed the crystallization process, was measured by the infrared method5) at room temperature. It is shown in Fig. 3.



Time, min.

Fig. 2. Ratio of optical density at time t to that at completion of the process, plotted against t at various growth temperatures.

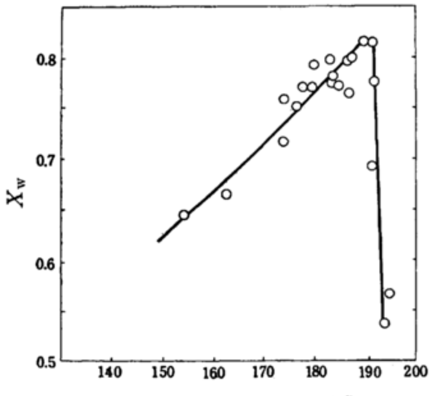


Fig. 3. Degree of crystallinity at completion of crystallization vs. growth temperature.

Discussion

In general, it is found7) that

$$\ln(V_f - V_t)/(V_f - V_i) = (-1/X_w)kt^n \qquad (1)$$

where V_t, V_f and V_i denote the specific volumes at time t, final and initial states of the crystallization process, respectively. X_w is the degree of crystallinity at the completion of the process, and k is the crystallization rate constant. Since the proportionality between the optical density of 440 cm^{-1} and the specific volume for the crystallization process of the polymer is known5), Eq. 1 becomes

$$\ln(D_f - D_t)/D_f = (-1/X_w)kt^n \qquad (2)$$

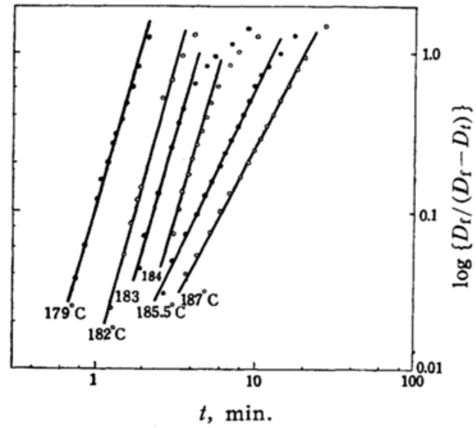


Fig. 4. Plot of log log $[D_f/D_f - D_t)$ vs. $\log t$.

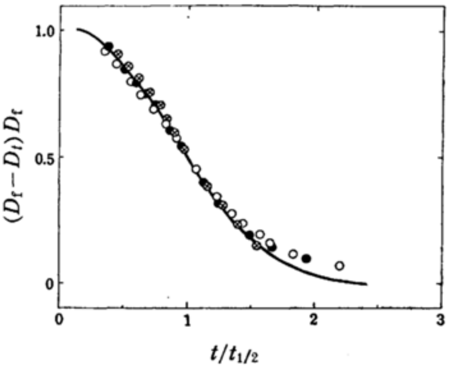


Fig. 5a. Superposition of isotherms at 188°C (⊗); 187°C (○); 185.5°C (●) to Eq. 2 for $n = 2.2$.

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7) L. Mandelkern, ibid., **26**, 443 (1955); *Chem. Revs.*, **56**, 903 (1956).

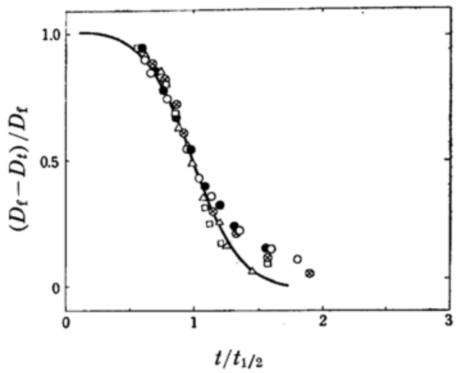

Fig. 5b. Superposition of isotherms at 184°C (●); 183°C (○); 182°C (⊗); 179°C (△); 178°C (□) to Eq. 2 for $n=3.4$.

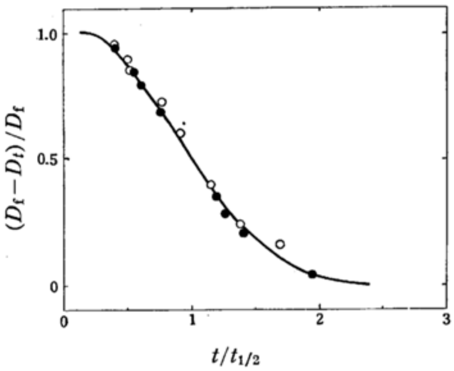

Fig. 5c. Superposition of isotherms at 176°C (●); 174°C (○) to Eq. 2 for $n=2.2$.

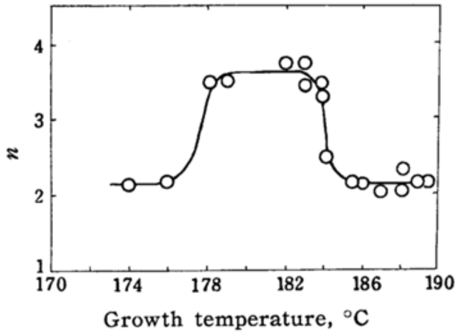

Fig. 6. Values of n at various growth temperatures.

By plotting $\ln \ln(D_f-D_t)/D_f$ against $\ln t$, the value of n can be obtained from the slope of the resultant straight line in Fig. 4. In Fig. 5 typical isotherms are plotted according to Eq. 2, where the half time $t_{1/2}$ indicates that the time at $D_t=1/2\,D_f$. The solid lines represent the theoretical isotherms. Good agreement can be obtained for the early stages of the process, but as the crystallization proceeds, the calculated amount of crystallinity is systematically greater than the observed.

The experimental values of n at various growth temperatures are plotted in Fig. 6. The value of n in Avrami's analysis[8] is dependent upon the type of crystallites in nucleation and growth as Table I shows.

TABLE I

Type of growth	Type of nucleation	n
spherical	homogeneous	4
disk	homogeneous	3
spherical	heterogeneous	3
disk	heterogeneous	2

It is, therefore, conceivable that at the growth temperature between 190 and 185°C the nucleation process will be promoted by any heterogeneities which are present in the melt. A fixed number of stable nuclei are present and subsequent transformation is a consequence only of the disk-type lineal growth of these centers. At the growth temperature between 184 and 178°C the nucleation process will be mainly governed by homogeneous nucleation. Price[1] observed by the microscopic method that at temperatures between 190 and 175°C the spherulites are heterogeneously nucleated, and at 170°C and below they are both heterogeneously and homogeneously nucleated. The difference in the results obtained by Price and the present method will be mainly due to the differences in molecular weight, thickness, form of the sample, and in the melting temperature and time, just as has been pointed out in the case of polyethylene terephthalate[3]. In this experiment samples could not be preserved physically as films at higher melting temperatures for a long time prior to the initiation of the crystallization process. Therefore, it will be difficult to say whether the variation of the exponent n with growth temperature is an inherent property of the polymer or not. Very recently, Hoffman[9] indicated that crystallization of the polymer is a results of one-dimensional growth of primary nuclei that are born at later and later dates, and that no obvious relation exists between the growth of primary nuclei and that of spherulites. Furthermore, he pointed out that the polymer has to be heated to the vicinity of 305°C prior to crystallization so as to destroy virtually all of the embryos in the crevices of the heterogeneities.

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[8] M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).

Next, the temperature coefficient of the crystallization rate was examined. In the vicinity of $T_m(\Delta T=25-30°C)$ the growth rate of crystallites shows a great negative temperature coefficient, in contradiction to the concept of growth controlled by diffusion. The fact leads to the concept of growth governed by secondary nucleation at the spherulite surface[4]. Accurate measurement of the rate of crystallization in the lower growth temperature range was prevented by the rapid onset of crystallization as the material was cooled from the melt through the temperature region of the maximum rate of crystallization, however short the time spent there. It will be, however, expected by Fig. 7 that the maximum rate of crystallization of the polymer locates at a lower temperature near 170°C[9].

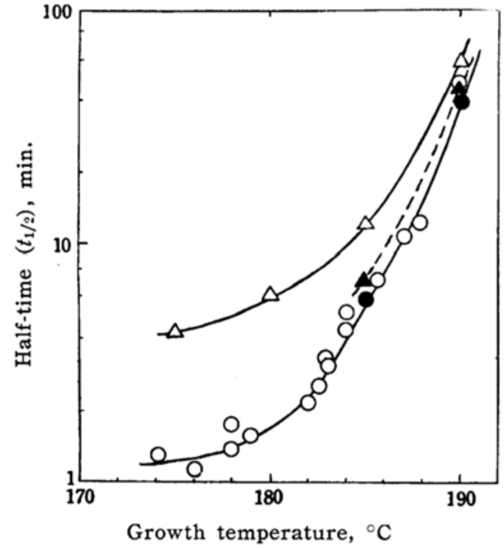

Fig. 7. Half-time vs. growth temperature.
(○) obtained by the infrared method (NST 270);
(●) obtained by the density method (NST 270);
(▲ and △) obtained by the microscopic method (NST 240 and 300).

Considering the formation of disk nuclei of fixed thickness which possess only lateral surface energy, the free energy, ΔF_d, can be expressed as

$$\Delta F = 2\pi r l\sigma - \pi r^2 l\Delta f_0 \qquad (3)$$

where σ is the interfacial free energy per unit area for the cylindrical surface, and Δf_0 is the bulk free energy of fusion per unit volume. Maximizing Eq. 3 with respect to r and equating Δf_0 to $(\Delta T/T_m)\Delta h_u$, where Δh_u is the heat of fusion per unit volume of repeating unit, there is obtained

$$\Delta F^* = (\pi l\sigma^2/\Delta h_u)(T_m/\Delta T) \qquad (4)$$

The rate of nucleation in condensed systems may be expressed by

$$A = A_0 \exp(-E/kT - \Delta F^*/kT) \qquad (5)$$

Furthermore, assuming the growth to be mainly diffusion controlled, then

$$G = G_0 \exp(-E/kT) \qquad (6)$$

Therefore, the rate constant may be expressed[10]

$$k = k_0 \exp\{-3E/kT - (\pi l\sigma^2/H_u)T_m/\Delta T\cdot kT\} \qquad (7)$$

Over the small temperature range of the present experiments the pre-exponential factor may be considered to remain constant, then

$$\log k = A - B(T_m/\Delta T\cdot T) \qquad (8)$$

The plot of $\log k$ against $T_m/T\cdot T$ is shown in Fig. 8. Here the melting point of the polymer is taken as 215°C and the values of k in the microscopic method[1] are calculated by

$$k = \frac{4}{3}NS^3$$

where N is the number density and S is the growth rate of spherulites. In this

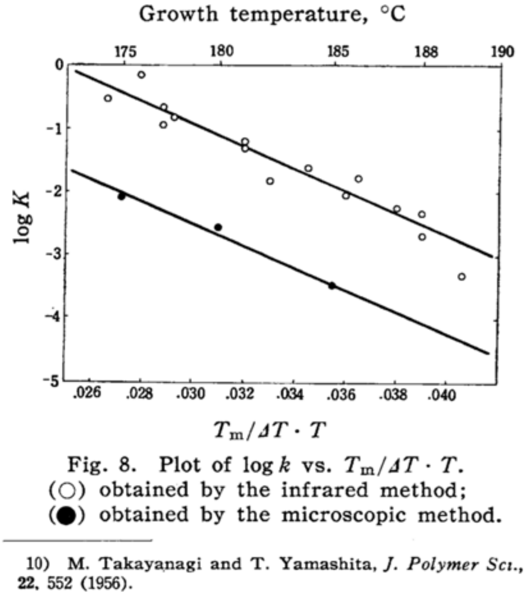

Fig. 8. Plot of $\log k$ vs. $T_m/\Delta T\cdot T$.
(○) obtained by the infrared method;
(●) obtained by the microscopic method.

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[9] J. D. Hoffman of the National Bureau of Standards, private communications.

[10] M. Takayanagi and T. Yamashita, *J. Polymer Sci.*, **22**, 552 (1956).

figure the results obtained by both the microscopic and the infrared methods can be approximated by straight lines which indicate the same negative temperature coefficient.

Finally, the effect of melting temperature on the rate of crystallization of the polymer was examined by the present method. After samples had been maintained at different melting temperatures (273~210°C) for five minutes, the half-times of crystallization at 188, 187 and 183°C were measured. They are shown in Fig. 9. The increase in the rate of crystallization with an increase of the melting temperature was indicated contrary to the cases of Nylon 66²⁾ and polyethylene terephthalate³⁾. The fact had been explained by Price¹⁾ as due to degradation of the polymer at a higher melting temperature. Recently, thin films of the polymer of NST 300 and 290 were supplied. The average molecular weight of the polymers were estimated to be approximately 81,000 and 78,000, respectively. Using these samples the half-time of crystallization at 183°C and the degree of crystallinity at the completion of the crystallization process were measured. The half-times were 4.6 and 7.4 min., respectively; the degree of crystallinity at the completion of the crystallization process were 74 and 64%, respectively. It will be expected that both the rate of crystallization and the degree of crystallinity at the completion of the crystallization process increase as the molecular weight of the polymer decreases.

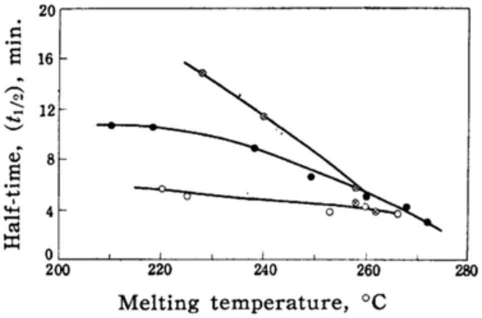

Fig. 9. Half-times as a function of melting temperature for crystallizations at 188°C (⊗), 187°C (●), and 183°C (○).

Summary

The isothermal rate of crystallization in polychlorotrifluoroethylene was measured at temperatures ranging from 172 to 190°C below the melting point by following the change of observed absorbance of crystalline band at 440 cm^{-1}. The isothermal rate of crystallization and apparent induction time are dependent on temperature. The data on the kinetics of the crystallization are compared with the result of Avrami's analysis. At temperatures between 190 and 185°C the nucleation process will be promoted by heterogeneities which exist in the melt. Between 184 and 178°C it will be mainly governed by homogeneous nucleation.

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