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Nonisothermal Crystallization of Poly(tetrafluoroethylene)

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Crystallization of poly(tetrafluoroethylene) was observed by differential scanning calorimetry at constant cooling rates. A method for kinetic analysis of thermoanalytical data of nonisothermal crystallization was applied to analyze the data, and it was elucidated that poly(tetrafluoroethylene) crystallizes one-dimensionally from preexisting nuclei, which are presumably impurities. These results are in accordance with electron-microscopic observation of the crystalline morphology of poly(tetrafluoroethylene), which consists of band-like or star-like crystallites. The kinetic parameters, especially the temperature dependence of the linear growth rate, were estimated.

Isothermal crystallization of various polymers has been extensively observed mainly by differential scanning calorimetry (DSC). However, for some polymers such as poly(tetrafluoroethylene) (PTFE), the crystallization is so rapid that one can not observe isothermal crystallization, because it crystallizes in the period during which the sample is cooling to a desired constant temperature. To observe these crystallization behavior, we should observe the process in cooling mode. The present author published a method for analyzing thermoanalytical data of crystallization, and the method was applied to nonisothermal crystallization of poly(ethylene terephthalate) proceeding at constant cooling rates.[1] For more simple crystallization mechanism, *i.e.*, crystallization from preexisting nuclei, another method was devised by the author.[2]

On the other hand, in some actual processes such as fabrication and melt spinning of crystalline polymers, crystallization proceeds nonisothermally, so that nonisothermal observation of crystallization has also actual meaning. Moreover, thermoanalytical observation of crystallization behavior was recently extensively investigated especially for amorphous materials such as amorphous magnetic materials by differential thermal analysis and DSC.

PTFE dealt with in this paper has some unusual features, one of which is its crystalline morphology; the spherulite has not been observed. Bunn *et al.*[3] reported striated band-like structures on fractured surfaces of PTFE. On the other hand, Symons observed dendrites and star-like crystals in the solution-grown crystals[4] and he also observed both the plate-like single crystals of clear hexagonal habit and the striated broad needles.[5] Afterword, Rahl *et al.*[6] observed emulsion-grade PTFE and found ribbon-like and rod-like crystallites; they postulated that these crystallites consist of single crystals of extended chain packing. Thus, it is interesting to know the crystallization kinetics of the polymer, especially the mechanism of the crystal growth. The nonisothermal crystallization was observed with a DSC, and the data were analyzed by the above-mentioned methods. These results are reported in this paper, and the applicability of the method for kinetic analysis of nonisothermal crystallization is illustrated in this report.

Experimental

Teflon No. 5 (E. I. du Pont de Nemours & Co. Inc., bulk polymerized PTFE), Teflon No. 6J (Mitsui Fluorochemicals Co., Ltd., emulsion polymerized PTFE), and Polyflon F-101 (Daikin Co., Ltd., emulsion polymerized PTFE) were used as received. Teflón No. 5 gamma-irradiated by 1 Mrad to decrease the molecular weight was also investigated. A DSC made by Rigaku Denki Co., Ltd. was used; the sample of 10—20 mg was heated in the flow of dry nitrogen up to 350—360 °C and then cooled immediately at a programmed cooling rate of 1, 3 or 5 K/min. Because the temperature of the sample is measured in this apparatus with a thermocouple, a junction of which is located on the bottom of the sample holder, the temperature can be measured precisely even in the cooling mode.

Results and Discussion

As is well known, for isothermal crystallization Avrami's equation holds;

$$-\ln(1-C) = Zt^n, \tag{1}$$

where C, t, Z, and n are the crystallized fraction, the time, a constant and an integer related to the nucleation and the growth dimension, respectively. As was elucidated in the previous paper, the following nonisothermal equation was derived instead of the above Avrami's equation.

$$-\ln(1-C) = \chi_c(T)/\phi^n, \tag{2}$$

or

$$\log(-\ln(1-C)) = \log\chi_c(T) - n\log\phi, \tag{3}$$

where T, ϕ, and $\chi_c(T)$ are respectively the temperature, the cooling rate, and the cooling crystallization function, which is the function characteristic of the sample; this function is dependent on the temperature but independent on the cooling rate. Therefore, the straight line should be obtained by plotting $\log(-\ln(1-C))$ against the logarithms of the cooling rates.

In order to observe this relation, the DSC curves of crystallization were converted to integral type curves of C versus t as is shown in Fig. 1, where C is estimated as follows;

$$C = \int_0^t (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \Big/ \int_0^\infty (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t, \tag{4}$$

where $\mathrm{d}H/\mathrm{d}t$ is the rate of heat evolution due to the exothermic crystallization observed by DSC.

Typical plots of $\log(-\ln(1-C))$ against $\log\phi$ are shown in Fig. 2, where the straight lines of the slope of unity are drawn. As is clearly seen, the crystallization follows Eq. 3 with $n=1$. The values of n obtained by

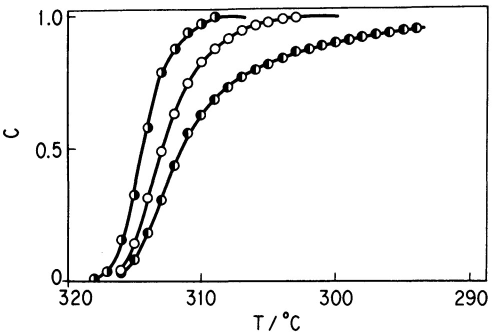

Fig. 1. Relations of crystallized fraction versus temperature obtained at different cooling rates for Teflon No. 5: ◐; 4.5°C/min, ○; 2.9°C/min, and ◑; 0.9°C/min.

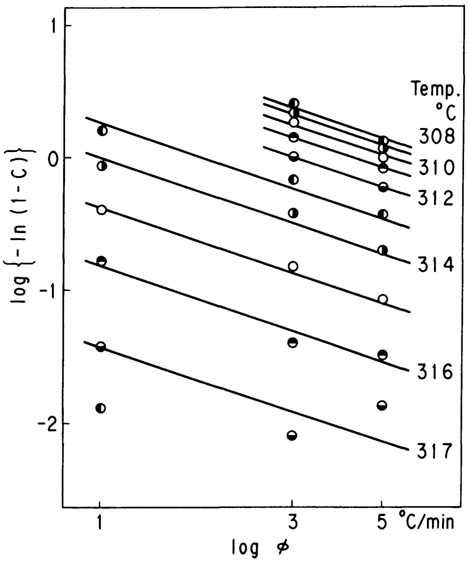

Fig. 2. Plots of $\log(-\ln(1-C))$ *versus* $\log \phi$ at given temperatures for Teflon No. 5. Slopes of straight lines shown are all unity.

the similar plots for the other samples are tabulated in Table 1. Although the data are somewhat scattered in a few cases, the values of n are estimated to be approximately unity for all samples by the method of the least square. It can be concluded from these facts that the crystals grow one-dimensionally from preexisting nuclei. However, the origin of the nuclei is not elucidated in this investigation.

This mechanism of one-dimensional growth is in accordance with the above-mentioned report of Bunn *et al.*[3] who observed the fractured surface of the sintered Teflon No. 5 with an electron-microscope and found band-like crystals. The one-dimensional growth is also in accordance with the formation of dendrites and star-shaped crystals in the solution-grown crystallization observed by Symons[4] and with needle-like structure found in sintered deposits by Symons.[5] From the electron-microscopy, the electron-diffraction and the optical observation, Symons proposed a model of a stack of single crystal plate or lamella of hexagonal habit, in which molecular chains are folded and perpendicular to the basal plane.[5] The one-dimensional growth mechanism is also in accordance with the observation of Rahl *et al.*[6] who found ribbon-like and rod-like crystals, and they postulated extended chain structure. According to Symons' models, the value of n obtained in this investigation corresponds to the mechanism of whole process of crystallization and not to the growth of single crystals of hexagonal habit postulated by Symons.[5]

TABLE 1. ESTIMATED VALUES OF n

Temerature °C	Teflon No. 5	Teflon No. 5 γ-irradiated	Teflon No. 6J	Polyflon F-101
317	1.0	—	—	—
316	1.0	—	—	—
315	1.0	—	—	—
314	0.9	—	0.8	1.8
313	1.0	0.9	1.1	1.4
312	0.9	1.3	0.8	1.5
311	0.9	1.2	0.7	1.4
310	1.0	1.1	0.7	1.2
309	—	0.9	0.7	1.5
308	—	0.8	0.7	1.1
307	—	—	0.7	0.8
306	—	—	0.7	—
Average	1.0	1.0	0.8	1.3

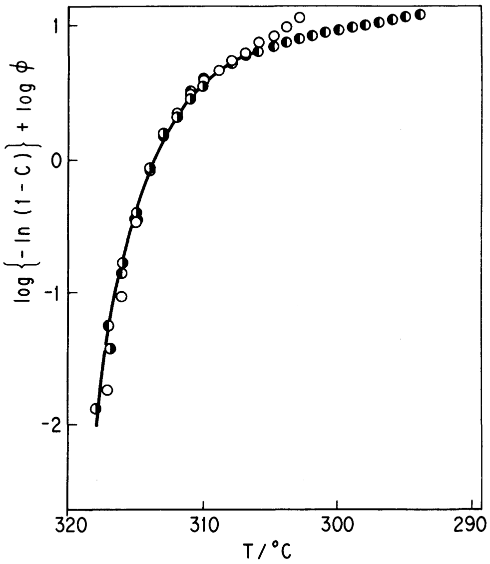

Fig. 3. Experimental master curve reduced to ϕ=1 K/min for Teflon No. 5. The cooling rates are 4.5°C/min (◐), 2.9°C/min (○) and 0.9°C/min (◑).

From Eq. 3, another plot can be derived; if one plots $\log(-\ln(1-C))$ against the temperature, the curves of different cooling rates can be superposed on each other by longitudinal shift and an experimental master curve can be obtained. The superposition could not be made, if the slow "secondary" (post-Avrami) crystallization occurs. A typical experimental master curve drawn in this way is shown in Fig. 3. Except the latter part, the curves can be superposed on each other very well, and the discrepancy in the latter part seems to indicate the existence of the secondary crystallization. After the completion of the process, *i.e.*, $C=1$, the heat of crystallization of the gamma-irradiated sample is measured to be about 50% of the heat of the fusion of the sample by using the peak areas of DSC curves, and that of the Teflon No. 5 is about 30% of the heat of the fusion of the sample. These facts also suggest the existence of the secondary crystallization, since the crystallinity of the sample sintered ordinarily is higher than those observed in cooling crystallization, and the effect of the secondary crystallization is smaller in the cooling crystallization than in the isothermal run, because the sample is cooled rapidly through the temperature range of the secondary crystallization.

The intercepts of the plots as shown in Fig. 2 give the cooling crystallization function, $\chi_c(T)$. Namely for the crystal growth from preexisting nuclei,[1]

$$\chi_c(T) = gN\int_{T_m}^{T} \{R_c(T) - R_c(\theta)\}^m v(\theta)\,\mathrm{d}\theta, \tag{5}$$

where g, N, T_m, θ, $(m+1)$ and $v(\theta)$ are the geometrical factor, the density of the nuclei, the melting temperature, a variable, the growth dimension and the linear growth rate, respectively, and

$$R_c(T) = \int_{T_m}^{T} v(\theta)\,\mathrm{d}\theta. \tag{6}$$

For the one-dimensional growth in which m is equal to zero,

$$\chi_c(T) = gN\int_{T_m}^{T} v(\theta)\,\mathrm{d}\theta. \tag{7}$$

The values of the function obtained for the samples are plotted in Fig. 4. It is interesting to note that $\chi_c(T)$ for the Teflon No. 5 locates in higher temperature range than the gamma-irradiated Teflon No. 5, though the latter seems to have large tendency to crystallize due to the low molecular weight caused by gamma-irradiation. Since $\chi_c(T)$ represents the nature of crystallization of the sample, it is very interesting to compare $\chi_c(T)$ for Teflon No. 6J with that for polyflon F-101; both samples are polymerized by emulsion-polymerization and used in paste extrusion, and the two curves resemble to each other.

For the one-dimensional growth from the preexisting nuclei, another following simple relation holds from Eq. 2, because $n=1$.

$$\frac{1}{1-C}\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\mathrm{d}\chi_c(T)}{\mathrm{d}T} \tag{8}$$

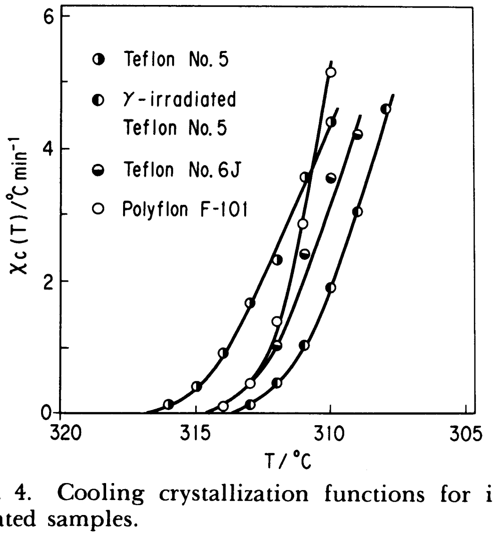

Fig. 4. Cooling crystallization functions for indicated samples.

Because $\mathrm{d}\chi_c(T)/\mathrm{d}T$ is equal to $gNv(T)$, which is equal to Z in Eq. 1,[2] we can estimate Z directly from the DSC curves by using Eq. 8. The values of Z thus estimated are plotted in Figs. 5 and 6 for Teflon No. 5 and gamma-irradiated Teflon No. 5. As is seen in these figures, the values obtained from the DSC curves at different cooling rates are on the same curve. From these facts the crystallization of Teflon No. 5 and gamma-irradiated Teflon No. 5 is ascertained to follow Avrami's model of the one-dimensional growth from preexisting nuclei. It is interesting that Z of gamma-irradiated Teflon No. 5 is in the lower temperature range, but its maximum is larger than Teflon No. 5. This tendency is in accordance with that of $\chi_c(T)$. On the other hand, the values of Z thus estimated for the other PTFE's are not on the same curve and large scattering of the values is observed. For these

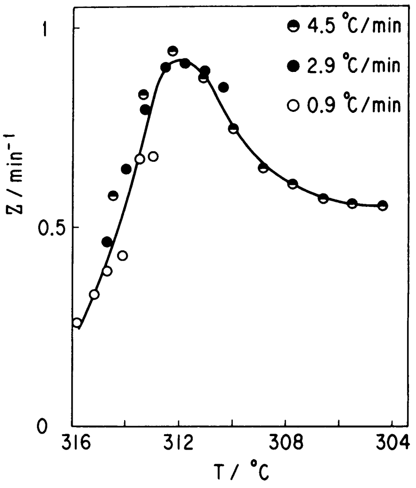

Fig. 5. Temperature dependence of kinetic parameter, Z, for Teflon No. 5. The cooling rates are 4.5 °C/min (◓), 2.9 °C/min (●), and 0.9 °C/min (○).

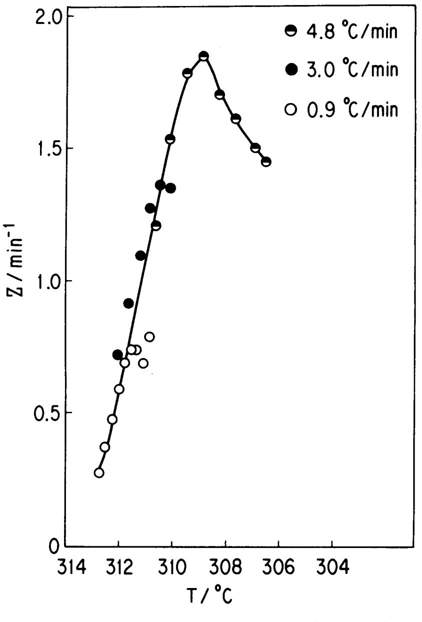

Fig. 6. Temperature dependence of kinetic parameter, Z, for gamma-irradiated Teflon No. 5. The cooling rates are 4.8 °C/min (◓), 3.0 °C/min (●), and 0.9 °C/min (○).

emulsion-polymerized PTFE's, the values of n are also scattered and somewhat different from unity, so that other processes, such as the secondary crystallization, seem to have large effect for these PTFE's.

For poly(vinylidene difluoride), Nakamura *et al.*[7] observed nonisothermal crystallization by DSC and found that $\log(-\ln(1-C))$ is in a linear relation with $\log\phi$ and that the slope is four, which indicates homogeneous random nucleation and three-dimensional growth mechanism. They also observed the crystallization isothermally and elucidated the same mechanism by applying the above-mentioned Avrami's equation. In three examples of nonisothermal crystallization of polymers, *i.e.*, poly(ethylene terephthalate),[1] poly(vinylidene difluoride),[7] and poly(tetrafluoroethylene), the applicability of the present author's theory and method of nonisothermal crystallization is illustrated, and the theory and method are clearly shown to be applicable to other substances, such as amorphous materials and so on.

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