Poly(ethylene Terephthalate).   I. Study of Crystallization Kinetics

K. G. MAYHAN, W. J. JAMES, WOUTER BOSCH, *Departments of Chemical Engineering and Chemistry, University of Missouri, Rolla, Missouri*

Synopsis

Cast amorphous one mil films of poly(ethylene terephthalate) were allowed to crystallize isothermally in silicone oil over the temperature range 25–240°C. The crystallization paths were followed by recording the percent of transmission of 4000 A. light through the films as a function of time at specific temperatures. At temperatures between 70 and 90°C. the transmission increased to a value higher than the initial transmission and did not decrease with time. From about 95 to 125°C. the curves showed a similar increase, followed by a decrease to a minimum and then an increase to a new maximum before leveling off. The shapes of these curves were interpreted in terms of the sizes of the growing spherulites. The first detectable signs of crystallization were observed at 96.5°C., as evidenced by density and densitometer measurements. It is shown that the polymer passed through a temperature range beginning at the glass transition point (66°C.) and extending to about 95°C., where molecular and chain rearrangements occurred without crystallization. Half lives and rate constants were found to increase exponentially over the range 96.5–119.5°C. Above approximately 125°C., the crystallization process took place at such a rapid rate that accurate data were impossible to obtain. Activation energies were calculated from the rate constants and from an estimation of induction times from the light transmission–time curves. These values were found to be 37 and 30 kcal./mole, respectively. The density–time data were also fitted to the Avrami relationship. Evaluation of the constants indicated that the initial crystallization growth was lineal.

Poly(ethylene terephthalate) (PET) has been studied from below its glass transition temperature by several investigators.[1-7]

The most complete study of the crystallization kinetics of PET, to date, has been published by Cobbs and Burton.[7] They followed the crystallization of 1-mil films of amorphous PET by observing changes in the infrared spectra at 972 cm.[-1]. These samples did not have a previous melt history. The changes in absorption were correlated with density changes to provide a measure of crystallinity. Samples were crystallized over the range 120–240°C. Induction times were observed up to 170°C. Half-times for crystallization were found to decrease to a minimum as the processing temperature was increased from 120 to about 210°C. and then decreased again over the range of 220–240°C. These findings were consistent with theory. An activation energy of 20 kcal./mole, based on induction times, was reported. The kinetic data were fitted to the Avrami equation and the results interpreted as an indication of platelike growth of crystallites.

The preceding work suggested an investigation of the crystallization kinetics of PET from the glass transition temperature to 240°C. As far as the authors are aware, kinetic data for the initial stages of crystallization have not been made for PET. The purpose of this investigation was to ascertain the effects of temperature and time upon the isothermal crystallization kinetics of PET and to explain, if possible, the mechanism by which crystallization proceeded. This entailed the determination of the degree of light transmission of a selected wavelength through polymer films as they were allowed to crystallize in silicone oil and the subsequent testing and analysis of the semicrystalline polymers to obtain kinetic data.

Experimental

The polymer used* was furnished as cast 1-mil films which had an inherent viscosity of 0.55–0.56 and a number-average molecular weight of 14,500.   The diethylene glycol content was between 2.5 and 3.5 mole % and the melting range was 245–264°C. Density measurements and x-ray diffraction patterns indicated that the samples were amorphous. The samples used did not have a previous melt history.

A General Electric recording spectrophotometer was modified to record transmission as a function of time so that the wavelength of the light could be specified. The isothermal crystallization of the films was followed by recording the transmission of 4000 A. light with time. This wavelength was selected since it gave a maximum intensity change for a given change in crystallinity of the polymer. In order to operate isothermally, a circulating system using silicone oil was constructed around a Pyrex crystallizing cell. At thermal equilibrium the temperature of the oil in the crystallization cell proper did not vary from one point to any other by more than 0.2°C. A sample holder of low heat capacity was used to keep the samples essentially flat and free of distortion during processing. The mass of the holder was low compared to the volume of oil in the cell and the holder was of sufficient size so that the temperature in the area of the light beam was not affected by the holder. Temperatures were measured by using copper–constantan hot junctions having time constants less than 0.1 sec. in conjunction with an L & N precision potentiometer capable of detecting 0.001 mv. All samples were dried for a period of 16 hr. at 60°C. prior to processing. Samples were introduced into the crystallizing cell by means of a sliding section in the cell housing. This operation was practically instantaneous.

Before making a run the samples were checked for uniformity by using an ARL densitometer.

To obtain transmission–time curves the spectrophotometer was standardized against a blank cell. (The transmission of the silicone oil did not change over the range 24–190°C.) Samples were allowed to crystallize until the per cent transmission became constant with time at a particular

temperature.   At this point the sample was assumed to have crystallized to a maximum consistent with the particular temperature.   A series of samples was then crystallized at the same temperature at predetermined time intervals.

Results

At least three samples were crystallized at each of the temperatures reported in the range 25–240°C.   Figures 1 and 2 show the effects of crystallization on light transmission.   Samples which were allowed to crystallize for periods as long as 16 hr. gave no further indication of change after the initial leveling-off.   At temperatures below 130°C. it was possible to quench samples at small crystallization intervals up to the leveling-off point, thereby obtaining a series of samples over the entire period.   Above
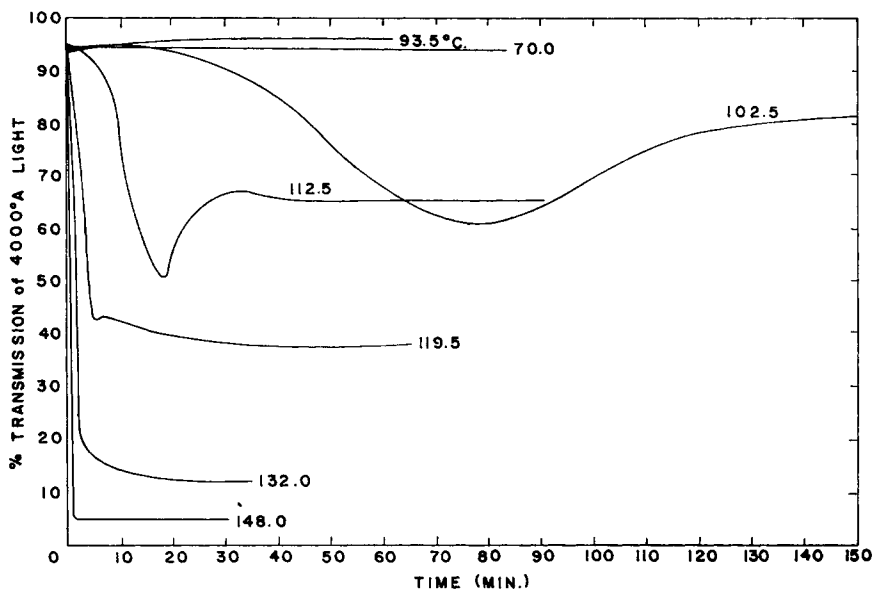

Fig. 1. Time–transmission plots for PET.

130°C. the crystallization proceeded too rapidly to permit the process to be followed for any finite increment of time.   Although equipment limitations precluded measurements above 190°C., samples were crystallized at 200, 220, and 240 ± 2°C. in silicone oil in a forced convection oven.

A close inspection of the curves revealed no changes in transmission for samples annealed below 90°C.   At 90°C., approximately 20°C. above the glass transition temperature, a slight but reproducible increase was noted. This increase was taken as an indication of an initial molecular rearrangement prior to crystallization.   Other investigators have surmised that there is some molecular mobility or relaxation just above the glass transition temperature; however, this is not of sufficient magnitude to form stable
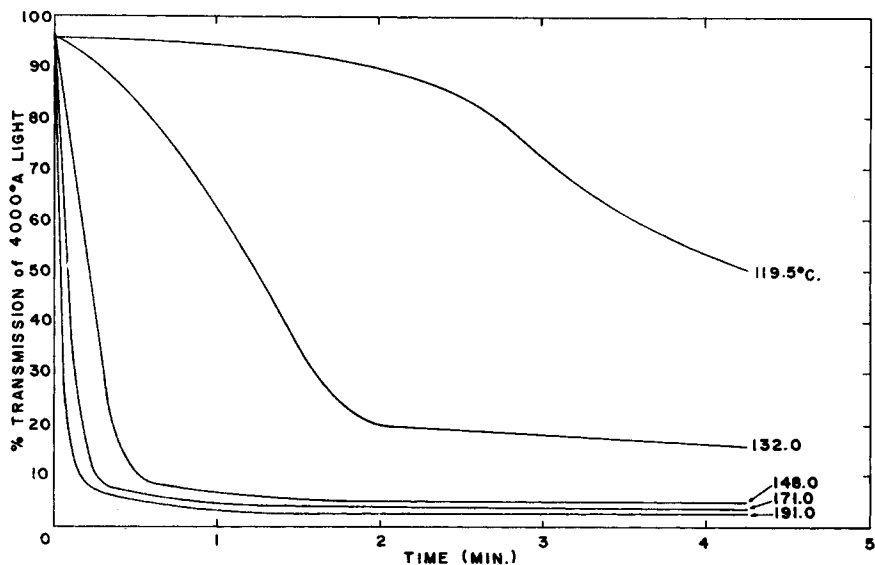
Fig. 2. Time–transmission plots for PET.

crystal nuclei.[2,8] Detectable crystallization did not occur until the glass transition temperature was exceeded by about 30°C.

It can be seen from the curves that at temperatures of 102.5, 112.5, and 119.5°C., the transmission first increased slightly above the ambient value, then decreased, going through a minimum, and then increased again going through a maximum before leveling off. The curves representing the crystallization processes above approximately 125°C. did not pass through any minima but instead decreased rapidly and leveled off. As expected, the time to reach the final transmission was found to decrease with increasing temperature. The transmission–time curves can be adequately explained if the crystallization process is considered in a broader scope. If the initial nuclei have dimensions less than the wavelength of the light being transmitted, then a great deal of scattering would not be expected. However, as the crystallites continue to grow, they acquire dimensions approaching the wavelength of the light. At this point a difference in the refractive indices of the amorphous and crystalline phases would be expected. The indices of the amorphous material and a sample crystallized at 240°C. were measured by using the Becke line technique and found to be 1.57–1.58 and 1.64–1.65, respectively. Some of the light would therefore be scattered, and a noticeable decrease in transmission would be observed. The transmission then decreases and levels off, due to the formation of more crystalline phase, to a final value consistent with the crystallization temperature. After an appreciable volume of the polymer has crystallized, the refractive index remains essentially constant. At temperatures exceeding about 125°C. these changes occurred so rapidly that their detection was not within the limitations of the spectrophotometer.

Several investigators have studied the crystallization of polyethylene from the melt by light transmission.[9–11]   Curves having the same general shape as those found in this study were obtained, except that the peaks became sharper as the temperature was decreased from the melting point. The decrease and subsequent recovery was attributed to the random growth of crystallites which were formed prior to spherulitic growth followed by the partial orientation of the crystallites into spherulites.   Alternatively, the possibility exists that in the early stages of crystallization isolated spherulites are dispersed in the polymer and the boundary between the spherulites and amorphous background results in light scattering which increases with crystallization time.   As the crystallites become more developed, they impinge upon each other, thus decreasing the scattering ability of the polymer.   This ability is expected to be greater at the amorphous-crystalline boundary than at the area between impinged spherulites.   The latter postulation appears to be consistent with the findings of this work.

Changes in volume due to partial crystallization of the polymer films were not detectable by measuring dimensional changes or changes in thickness.   Since it was important to know if these small changes were occurring uniformly throughout the polymer, it was necessary to devise a means of checking polymer uniformity.   This was accomplished by recording the average transmission of white light through the films over 40–50 small areas of each sample, by using an ARL comparator densitometer. This method of detecting changes in uniformity proved to be very sensitive to imperfections which result from small changes in film thickness or turbidity.   Although the original intent was to use the densitometer only as a measure of uniformity, the overall results were of additional interest. Figure 3 gives evidence that the polymer passes through a relaxation (trans-
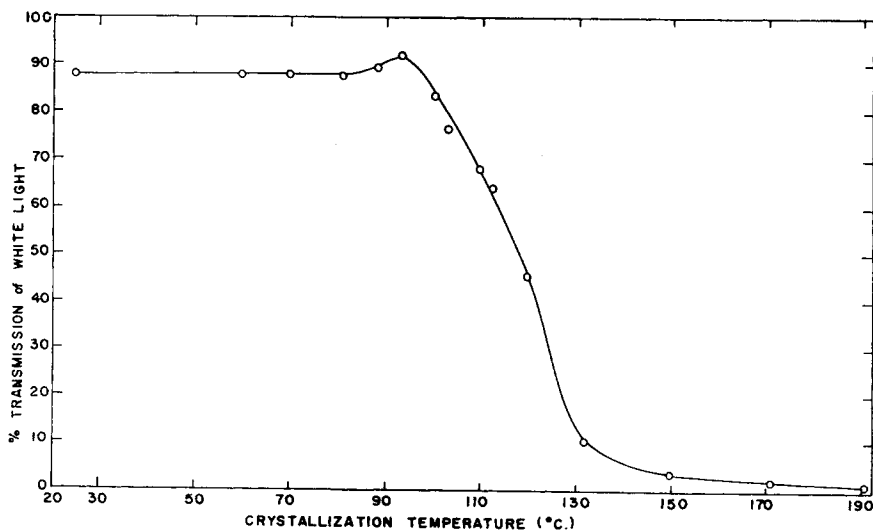

Fig. 3. Transmission of white light as a function of crystallization temperature for PET.
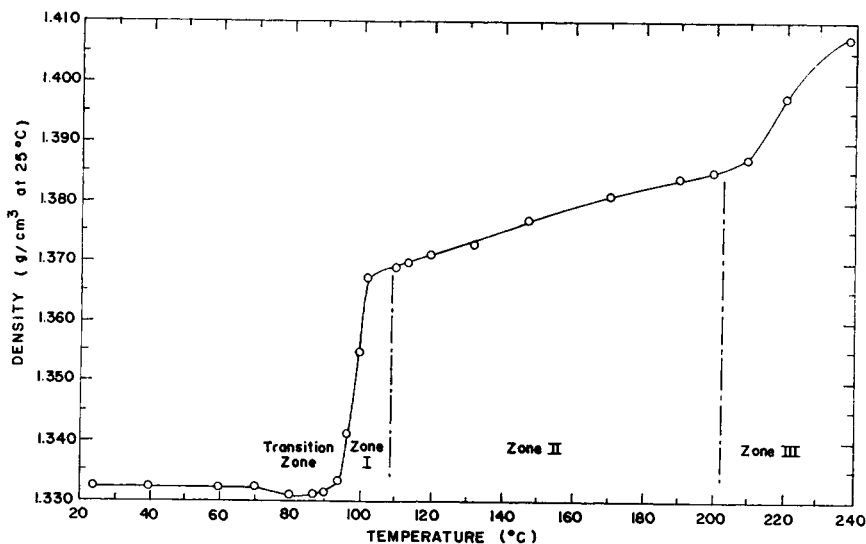
Fig. 4. Density–temperature plot for PET.

ition) zone which is most pronounced between 70 and 95°C. and that the changes that take place are permanent.

Because of the arbitrariness involved in measuring the degree of crystallinity and because it is difficult to draw a line between which part of the polymer is crystalline and which part is not, it is necessary to state exactly what is being measured and what assumptions are being made in the calculations. In this study, the degree of crystallinity of PET was calculated from density measurements. The degree of crystallinity can be directly related to density if a knowledge of the densities of the amorphous and the 100% crystalline polymer are known. The density of the amorphous polymer was measured directly by the gradient method and found to be 1.333 g./cm.³ at 25°C. and that of the completely crystalline polymer was obtained from x-ray diffraction data as 1.455 g./cm.³ at 25°C.[1] Densities were determined for all samples processed and in most cases a sufficient number of determinations was made to permit the data to be treated statistically. The statistical analysis indicated that densities could be reported to ±0.001 g./cm.³. Figure 4 shows the limiting densities that were obtained at different crystallization temperatures. This limiting value is considered to be the maximum density that can be obtained at a particular temperature. Figure 5 shows the change of density with time at different temperatures. There was no evidence of crystallization within the transition zone. Apparently, molecular rearrangements do occur between the glass transition temperature and 95°C. but evidently take place without a detectable amount of crystallization. It appears reasonable to assume that there is sufficient thermal motion of the polymer chains to cause some amount of concurrent alignment of small segments to form primary nucleation sites. Or, some nucleation sites could form during the initial quench-
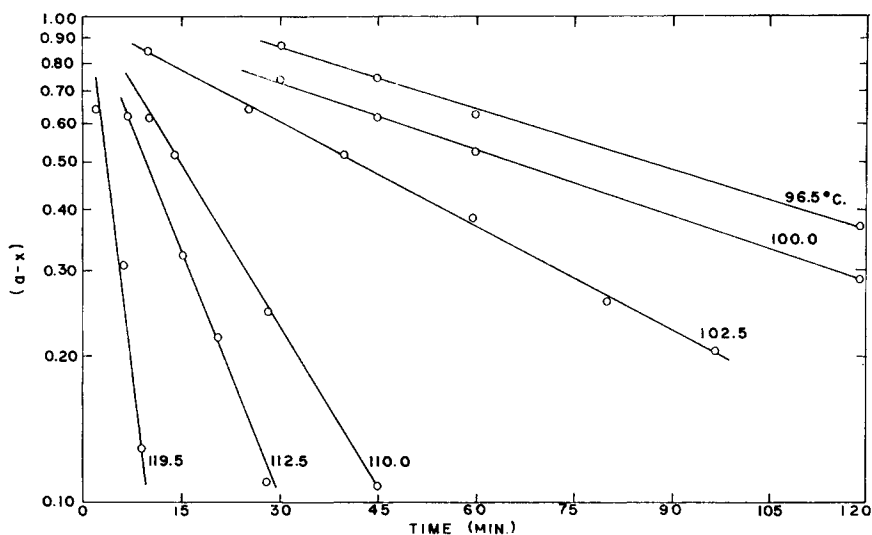
Fig. 5. Change in crystallinity of PET with time.

ing of the polymer which remain dormant until a suitable temperature is reached where nucleation and subsequent crystallization can occur. The temperature dependence of the nucleation process would be expected to be different than that for the crystals growing from these nuclei. Then if the free energy of the crystalline phase were lower than that of the amorphous phase, under proper conditions crystallization would occur. This criterion appears to be well satisfied. Figure 4 indicates a transition zone extending in the range of 70–95°C. where the density of the polymer decreases slightly, followed by three crystallization zones.

Zone I can be reasonably described as one in which a primarily crystallization process occurs as a result of initial nucleation. A reasonable explanation of zone II and III is, however, considerably more speculative. There appear to be several possible alternatives. Since the increase in crystallinity in zone II is much less than that in the primary zone, there is a possibility that existing crystallites obtain increased order by further growth. Concurrently, it is also likely that during the initial stages of crystallization (zone I), low molecular weight or impurity-rich fractions of the polymer melt are selectively pushed aside by the growing spherulites. As the crystallization process progresses, the impurity-rich melt accumulates in random pockets between the initial crystalline products, and spherulitic growth is retarded (zone III). Steric factors would be expected to be appreciable at this point in the crystallization process. Above 200°C. (zone III), there appears to be a second distinct crystallization process taking place. This is probably also accompanied by further ordering of the crystallites formed during primary crystallization. This new phase could represent crystallization of accumulated volumes of melt in pockets and other regions where the polymer chains have restricted movement.
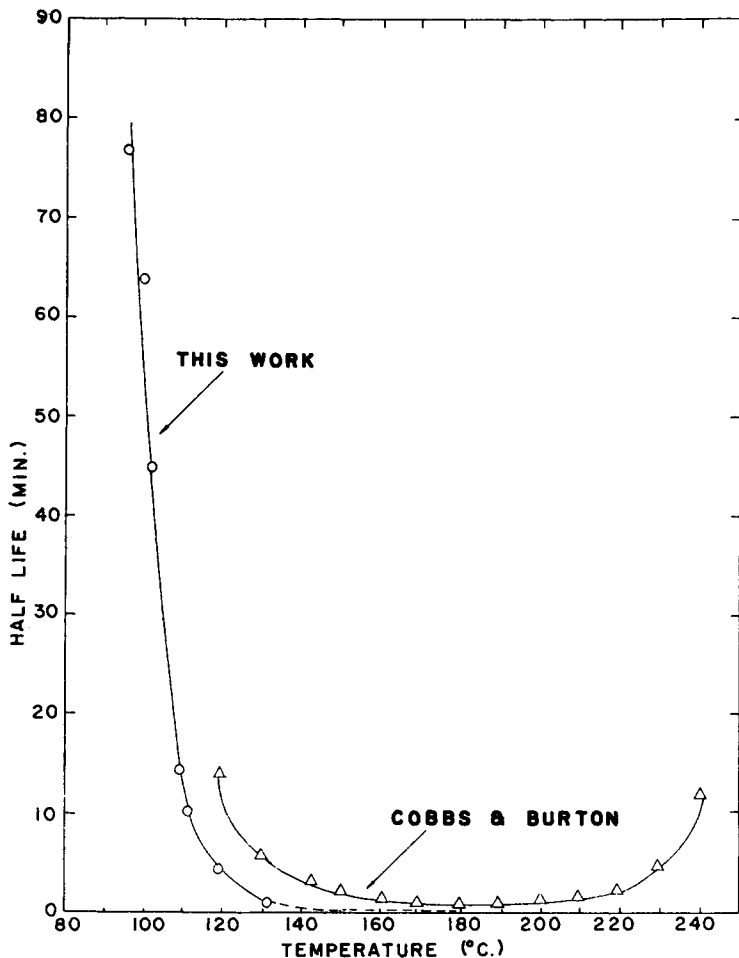
Fig. 6. Crystallization half-life of PET as a function of temperature.

The initial crystallization process is assumed to follow a first-order mechanism:

$$A \rightarrow A^* \rightarrow B$$

where A is the amorphous polymer, A^* may be thought of as a nucleated intermediate, and B is the crystalline polymer. The differential èquation defining this process is

$$- dx/dt = k_1(a - x)$$

where k is independent of a, x is the amount of crystalline polymer formed, and a is the amount of amorphous available for crystallization. The calculated rate constants are shown in Table I. By using standard techniques the rate constants can then be calculated from a knowledge of the half-lives
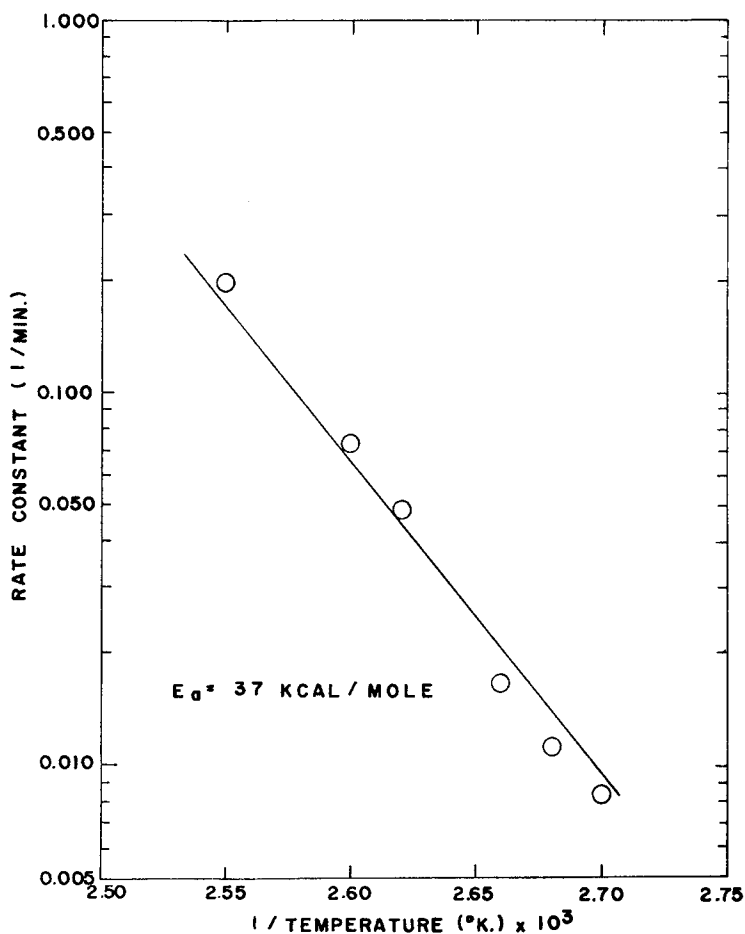
Fig. 7. Arrhenius plot employing rate constants as a function of temperature.

of crystallization. The density–time data were used as a basis for determining the half-lives. The half-lives were then obtained from Figure 5. Cobbs and Burton,[7] in their study of the crystallization of PET, reported

TABLE I
Rate Constants as a Function of Temperature

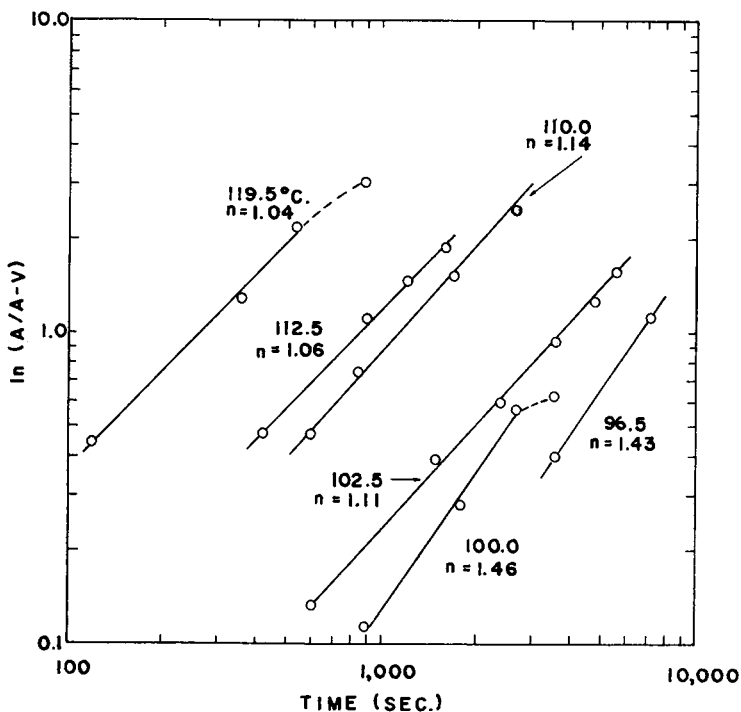| Crystallization temperature, °C.	Half-life, min.	Rate constant $k_1 \times 10^3$, min.$^{-1}$
96.5	84	8
100.0	64	11
102.5	43	16
110.0	14.5	48
112.5	9.5	73
119.5	3.5	198
132.0	1.0	Not determined

Fig. 8. Evaluation of the constant n from the Avrami equation.

half-lives over the range 120–240°C. These data have been reproduced along with the values from Table I in Figure 6. The two curves appear parallel, and if the actual numerical differences are ignored, the entire half-life curve can be pictured. The increase in half-life from 190 to 240°C. is not altogether unexpected and is consistent with theory.

The apparent activation energy for the primary crystallization process was calculated by using the Arrhenius relationship. In this case E_a is assumed to be independent of temperature over the range cited. Figure 7 gave an activation energy of approximately 37 kcal./mole of segment crystallized. This value is considerably higher than the 20 kcal./mole reported by Cobbs and Burton. Since the activation energy obtained by these authors was based on induction times, inherent errors could effect the results adversely if the system did not attain instantaneous thermal equilibrium. Heat transfer calculations based upon the parameters reported by these authors indicate that their system could not have attained equilibrium in the time reported. An activation energy based on induction times read from the transmission–time curves was also obtained for this work as 30 kcal./mole.

The theories evolved by Avrami[12,13] apply principally to metals. However, based upon the similarity between the properties of metals and polymers, these theories have been applied to phase changes in crystallizable

polymers. The Avrami equation as applied to polymer systems may be written as:

$$V_x = Z(1 - e^{Bt^n}) \qquad\qquad 1 < n < 4$$

where V_x is the volume fraction of the crystalline polymer, A the limiting volume fraction of crystalline polymer at a specific isothermal temperature, B contains nucleation and growth constants, and n may vary from 1 to 4, depending upon the geometry of nucleation and growth.

The density–time data were converted to crystalline volume fraction as a function of time and were applied to the above relationship. In this case the constant n is of primary importance, since it yields information about the crystal geometry. Results are shown in Figure 8.

The only conclusion that can be drawn from the values of n is that the crystallites favor linear growth during the primary stages of crystallization. Over the range of 120–240°C. Cobbs and Burton found that platelike growth is favored. However, since the data cover different temperature spans and since the methods of obtaining data for the calculation of n are different, the numerical results cannot be compared directly.

References

1. Daubeny, R. de P., and C. W. Bunn, *Proc. Roy. Soc. (London)*, **A226**, 531 (1954).
2. Kolb, H. J., and E. F. Izard, *J. Appl. Phys.*, **20**, 564 (1949).
3. Keller, A., G. R. Lester, and L. B. Morgan, *Phil. Trans. Roy. Soc.*, **A247**, 1 (1954).
4. Morgan, L. B., *Phil. Trans. Roy. Soc.*, **A247**, 13 (1954).
5. Hartley, F. D., F. W. Lowd, and L. B. Morgan, *Phil. Trans. Roy. Soc.*, **A247**, 23 (1954).
6. Smith, C. W., and M. Dole, *J. Polymer Sci.*, **20**, 327 (1956).
7. Cobbs, W. H., and R. L. Burton, *J. Polymer Sci.*, **10**, 275 (1952).
8. Bunn, C. W., *J. Appl. Phys.*, **25**, 820 (1954).
9. Naona, T., *J. Sci. Hiroshima Univ.*, **A24**, No. 3 (1960).
10. Hawkins, S. W., and R. B. Richards, *J. Polymer Sci.*, **4**, 515 (1948).
11. Kean, J. J., and R. S. Stein, *J. Polymer Sci.*, **20**, 327 (1956).
12. Avrami, M., *J. Chem. Phys.*, **7**, 1103 (1939).
13. Avrami, M., *J. Chem. Phys.*, **8**, 211 (1940).

Résumé

Des films amorphes coulés de téréphtalate de polyéthylène de 25 μ d'épaisseur ont été soumis à cristallisation à température constante dans une huile de silicone dans un domaine de température de 25 à 240°C. La cristallisation a été suivie en mesurant le pourcentage de lumière transmise à 4000 A. à travers ces films, en fonction du temps et de température déterminée. Entre 70 et 90°C la transmission croît à une valeur plus élevée que la valeur initiale, et elle ne décroît pas avec le temps. De 95 à 125°C les courbes montrent une augmentation similaire, suivie d'une diminution jusqu'à une valeur minimum, puis d'une nouvelle augmentation jusqu'à atteindre un nouveau maximum-palier. Les formes de ces courbes sont interprétées en tenant compte de la grandeur des sphérulites en croissance. Les premiers signes détectables de cristallisation sont observées à 96°C, ainsi qu'il ressort des mesures de densité. Le polymère passe par un domaine de température, débutant au point de transition vitreuse (66°C) et allant jusqu'à 93°C, où les réarrangements moléculaires de la chaîne se passent sans cristallisation. Les durées de demi-vie et les constantes de vitesse croissent exponentiellement

dans la région de 96,5 à 119,5°C. Au-delà d'environ 125°C le processus de cristallisation est tellement rapide qu'il est impossible d'obtenir des résultats précis. Les énergies d'activation ont été calculées au départ des constantes de vitesse et au départ des périodes d'induction évaluées sur les courbes de transmission de lumiére en fonction du temps. Ces valeurs s'élèvent respectivement à 37 et 30 Kcal/mole. Les résultats densité/temps correspondent à la relation d'Avrami. L'évaluation des constantes indiquent que la croissance initiale des cristaux est linéaire.

Zusammenfassung

Gegossene amorphe, ein Mil dicke Filme aus Polyäthylenterephthalat wurden in Siliconöl im Temperaturbereich von 25–240°C isotherm zur Kristallisation gebracht. Der Fortschritt der Kristallisation wurde durch Aufzeichnung der prozentuellen Transmission bei 4000 A. der Filme als Funktion der Zeit bei spezifischen Temperaturen verfolgt. Bei Temperaturen zwischen 70 und 90°C nahm die Transmission zu einem höheren Wert als dem der Anfangstransmission zu und fiel mit der Zeit nicht ab. Von etwa 95 bis 125°C zeigten die Kurven einen ähnlichen Anstieg, auf welchen eine Abnahme zu einem Minimum und darauf ein Anstieg zu einem neuen Maximum vor der Verflachung folgte. Die Gestalt dieser Kurven wurde in Zusammenhang mit der Grosse der wachsenden Sphärolithe gebracht. Die ersten erkennbaren Anzeichen für die Kristallisation wurden durch Dichte- und Densitometermessungen bei 96,5°C beobachtet. Es wird gezeigt, dass das Polymere durch einen beim Glasumwandlungspunkt (66°C) beginnenden und sich bis etwa 95°C erstreckenden Temperaturbereich geht, in welchem Molekül- und Kettenumlagerungen ohne Kristallisation auftraten. Die Halbwertszeit und die Geschwindigkeitskonstante nehmen im Bereich von 96,5–119,5°C exponentiell zu. Oberhalb von etwa 125°C erfolgte der Kristallisationsprozess mit einer so grossen Geschwindigkeit, dass keine genauen Geschwindigkeitsdaten erhalten werden konnten. Aus den Geschwindigkeitskonstanten und aus einer Abschätzung der Induktionsperioden aus den Lichttransmission–Zeitkurven wurden Aktivierungsenergien berechnet. Die Werte betruge 37 bzw. 30 kcal, Mol. Die Dichte–Zeitdaten konnten in die Form der Avrami-Beziehung gebracht werden. Die Ermittlung der Konstanten Zeigte, dass das anfängliche Kristallwachstum linear erfolgte.