Melting and Crystallization Behavior of Miscible Copolyester–Polycarbonate Blends

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Synopsis

The melting and crystallization behavior of Kodar, a copolyester formed from 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids, and its miscible blends with polycarbonate was examined. The results of the melting behavior are discussed in terms of crystallization-induced chemical rearrangements and the copolymeric character of Kodar and interchange reactions between components when polycarbonate is present in the blend. For various reasons, the melting behavior cannot be extrapolated to infinite crystal size using the Hoffman–Weeks approach. Crystallization kinetics follows the Avrami equation, with rates being higher when the crystallization temperatuare is approached from the glass rather than from the melt. The kinetic data are discussed in terms of modern theories. An approximate melting point depression analysis is used to estimate the interaction parameter for the blend, and the result obtained is compared to a value from another technique.

INTRODUCTION

Earlier reports[1–4] have shown that the copolyester formed from 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids, known commercially as Kodar A-150, is miscible in all proportions with bisphenol A polycarbonate and have described the mechanical,[2] transport,[3] and chemical behavior[4] of these blends. The melting and crystallization of the copolyester in these mixtures is of interest for numerous reasons but is complicated by several factors as described more fully here. Melting point depression analysis is a potentially useful way of characterizing the thermodynamics of mixing miscible polymers[5] when one is crystallizable. However, such an analysis may be obscured by variations in crystal size, which also influences the observed melting point. Stein[6] has suggested that this effect can be eliminated by extrapolation of the observed melting point versus crystallization temperature to infinite crystal size using the Hoffman–Weeks approach.[7] Recent work has shown that various chemical reactions may occur in this system.[4] Below the melting point, Kodar apparently undergoes crystallization-induced chemical rearrangements of the type described by Lenz and co-workers[8–11]; while in the melt state, the blend can experience interchange reactions between the components. As shown here, these factors along with perhaps accompanying physical issues frustrate attempts to incorporate the Hoffman–Weeks approach into the analysis of melting point depression for this system.

It has been estimated that approximately 20% of the dibasic acid units in Kodar are isophthalic acid,[4] which presumably will not fit into the crystal structure

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formed by sequences of terephthalic acid and 1,4-cyclohexanedimethanol units. Therefore, it is of interest to compare the behavior of Kodar with the related polyester, Kodel, which has no isophthalic acid units.

The blends used in this work were prepared by melt mixing in an extruder as described earlier.[2] These blends showed a single, composition-dependent glass transition temperature and experienced little or no interchange reactions during processing. The following describes a series of studies on the melting and crystallization behavior of Kodar and Kodel plus the above mentioned blends of Kodar with polycarbonate aimed at developing practical information about this important blend system and adding fundamental insight to these observations. The materials used have been described in detail in earlier reports.[2]

BACKGROUND

For lamellar polymer crystals, the melting point T_m depends on the lamella thickness L as follows[13]:

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{\Delta H_f L} \right] \tag{1}$$

where T_m^0 is the equilibrium melting point of the infinitely thick crystal, ΔH_f is the heat of fusion, and σ_e is the specific surface free energy of the end face of crystals. Hoffman and Weeks[7] developed a theory relating the observed melting point to the crystallization temperature as follows:

$$T_m = T_m^0 \left(1 - \frac{1}{\beta} \right) + \frac{T_c}{\beta} \tag{2}$$

If the parameter β is a constant, a plot of T_m vs. T_c is linear and should intersect the line $T_m = T_c$ at T_m^0, the equilibrium melting point of the infinitely large crystal. Thus, an experimental approach for ascertaining T_m^0 is offered which has often been used for this purpose.[13] In comparing observed melting points from blends of differing composition, L may inadvertently be variable, thus introducing a factor other than mixing thermodynamics into the analysis. Comparisons of T_m^0 obtained by the Hoffman–Weeks type extrapolation would be preferable in order to eliminate this possibility. However, a review of the literature shows that for a variety of reasons plots of T_m vs. T_c may not be so simple as suggested above. Figure 1 summarizes the situation seen in many cases.[13,14] The lower branch of the experimental plot of T_m vs. T_c may even have zero slope.[13] The upper branch in many cases behaves as predicted, but occasionally instances occur where it apparently never intersects the $T_m = T_c$ line as expected. There seem to be a variety of reasons for these and other departures from the behavior predicted by the Hoffman–Weeks theory, and they are not rare.

Since Kodar is a copolymer, it is relevant to consider the special problems this may pose in terms of crystallization and melting behavior. Two limiting cases have been delineated. The noncrystallizing monomer may be trapped in the crystal forming a defect (inclusion), or this unit may limit the crystal size (exclusion). In the latter case, crystal size is determined by available segment lengths not containing the noncrystallizing monomer. Owing to the distribution of segment lengths, a broad, diffuse melting point might be expected,[15] and strict adherence to the Hoffman–Weeks behavior may not occur since crystal size will become limited by segment lengths rather than nucleation.
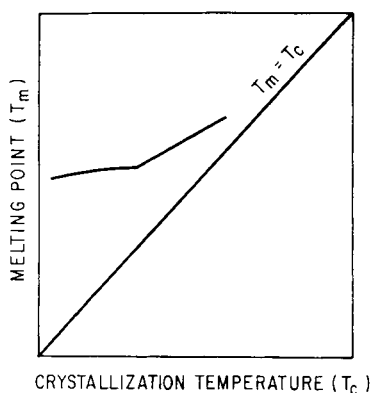
Fig. 1. Hoffman–Weeks plot typical of many polymer systems.

If there exists a chemical mechanism (e.g., interchange reactions) for reorganizing the monomer placements in a copolymer, crystallization may provide a driving force for reordering the segment length distribution into a blocklike structure with attendant changes in melting behavior. If a random copolymer did reorganize into a more blocklike structure, several changes might be observed. First, the melting point would tend to increase due to larger crystals. Second, X-ray diffraction peaks and the melting point should become sharper. Third, there should be an increase in crystallinity owing to conversion of segments too short to crystallize into longer segments which are able to do so. Several examples of crystallization-induced chemical reorganization have been reported. Schulken et al.[16] noted an increase in the observed melting point of poly(cis/trans-1,4-cyclohexanedimethanol terephthalate), i.e., Kodel, upon annealing at temperatures just below the melting point. Lenz and co-workers[8-11] made detailed studies of crystallization-induced reorganization in poly(ester-acetals), poly(cis/trans-1,4-butadiene), and various random and block copolyesters.

Lenz, Martin, and Schuler[8] offered four criteria which seem necessary for crystallization-induced chemical reorganization. First, the reorganization reaction should proceed at a reasonable rate at temperatures suitable for crystal growth. Second, either one material must be excluded completely from the crystal or a more stable crystalline form must be obtainable by exclusion. Third, material in the crystal is not allowed to participate in the reaction. Finally, either crystals must already be present, or conditions must be correct for spontaneous nucleation if sufficiently long segments are formed. Theil[17] has suggested that since free energy changes are path independent, the process can be considered in two steps. First, an entropically unfavored reorganization of uncrystallizable short segments into long blocks of crystallizable material occurs. The second step is the crystallization of the newly formed blocks which will provide the enthalpy of fusion to offset the unfavorable entropic effects and produce a negative net free energy required to drive the process. Evidence for such behavior with Kodar has already been reported.[4]

EFFECT OF THERMAL HISTORY ON MELTING BEHAVIOR OF KODAR AND KODEL

Kodar melting behavior was examined by a Perkin–Elmer DSC 2 using a heating rate of 10°C/min. All samples were heated to 330°C and held for 5 min
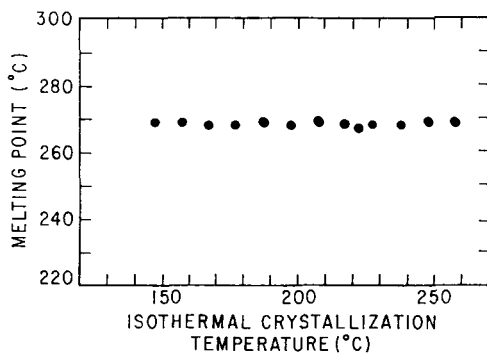
Fig. 2. Hoffman–Weeks plot for pure Kodar crystallized for 1 h or less.

to eliminate all vestiges of nucleation sites prior to rapid quenching (320°C/min) to the desired crystallization temperature at which the sample was held for a specified time. When this time was 1 h or less, results like those in Figure 2 were obtained showing a melting temperature (269 ± 1°C) substantially independent of crystallization temperature over a 100°C range. When much longer crystallization times were used, results like those in Figure 3 were obtained. For T_c < 217°C, the melting point observed is again independent of T_c although slightly higher (273 ± 2°C) than seen in Figure 2. Beyond 217°C, T_m does depend on T_c in a fashion more like that expected from the Hoffman–Weeks theory. There appears to be fundamental differences in the behavior for samples held at T_c for short (∼1 h) and long (∼20 h) times; and for future convenience, these conditions are referred to as crystallization and annealing, respectively, to distinguish them. Obviously, further elaboration is needed to understand what is occurring.

Insight into the behavior of Kodar may be had by comparing its melting and crystallization behavior with Kodel which does not have any noncrystallizing isophthalate units. Figure 4 shows the Hoffman–Weeks type plot for this polymer after crystallizing for short times at the temperatures indicated. For crystallization temperatures below 250°C, the melting point is somewhat scattered but relatively independent of T_c. However, beyond this, T_m vs. T_c behaves in accord with the Hoffman–Weeks theory, and an equilibrium melting point of 362°C is obtained by appropriate extrapolation. This is in sharp contrast to the behavior of Kodar for similar crystallization times (see Fig. 2).

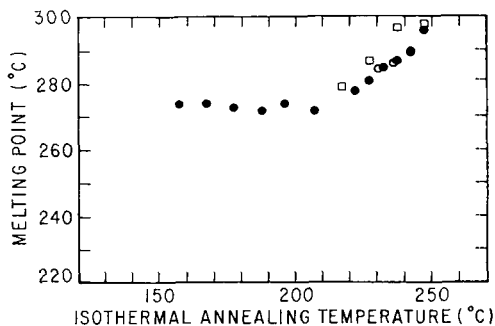Further comparisons between Kodar and Kodel are made in Figures 5–7.

Fig. 3. Hoffman–Weeks plot for pure Kodar held at the crystallization temperature for prolonged times: (●) 20 h; (□) 30 h.
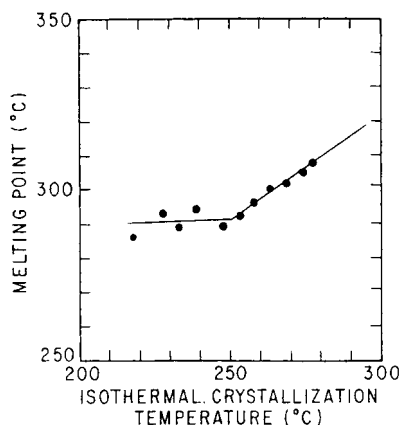
Fig. 4. Hoffman–Weeks plot for Kodel crystallized for less than 1 h.

Figure 5 shows that the melting endotherm for Kodar isothermally crystallized for short times is quite broad, whereas after annealing isothermally for long times, a sharp, well-defined endotherm develops.[4] The latter is similar in shape to that for Kodel crystallized for 1 h (see upper DSC trace in Fig. 5). Figure 6 shows wide-angle X-ray diffraction scans for these polymers at crystallization conditions indicated. Short-time crystallization of Kodar results in rather diffuse diffraction peaks which sharpen up significantly on long-time annealing and become very similar in both location and sharpness to Kodel. Figure 7 shows the effect of prolonged annealing at 227°C on the melting point of both Kodar and Kodel. Kodel shows an increase of only about 6°C over four days, while Kodar changes by nearly 30°C. Interestingly, the T_m for Kodar approaches that of Kodel at long annealing times.

Figure 8 compares the observed heat of fusion for Kodar isothermally crystallized for short times with that obtained by prolonged annealing. The former changes only slightly with T_c, whereas the latter increases greatly as T_c increases. The maximum heat of fusion observed for any Kodar sample was 17.8 cal/g after 72 h at 227°C. Kodel treated in a similar manner developed a value of 20.8 cal/g. It is interesting that the ratio of these results is very nearly the fraction of terephthalate (crystallizable) units in Kodar.
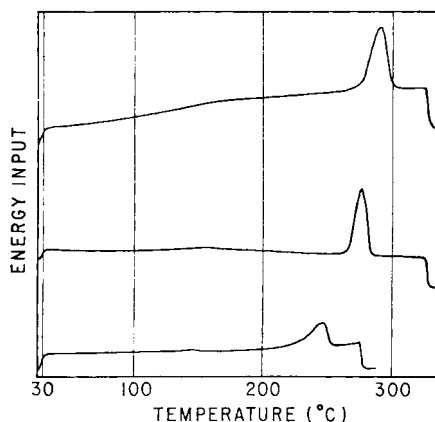

Fig. 5. DSC traces of melting of Kodel (top), annealed Kodar (middle), and Kodar isothermally crystallized 1 h (bottom).
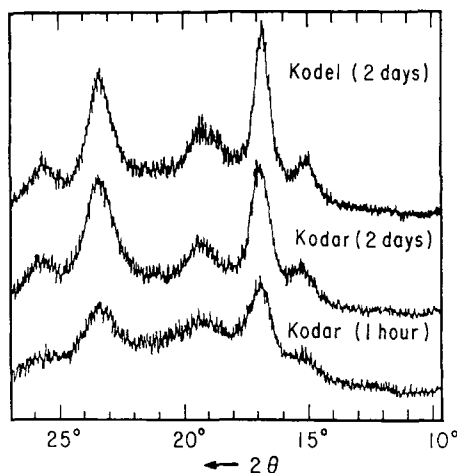
Fig. 6. X-Ray diffraction scans for Kodel and Kodar crystallized at 197°C for two days (upper two) and 1 h (lower one).

All of these results may be explained by the following physical picture. Crystal thickness in Kodel is controlled by nucleation phenomenon as postulated by the Hoffman–Weeks theory; thus, T_m responds to T_c in the expected manner except at very low T_c which is not uncommon in polymers. Kodar, on the other hand, is a copolymer (initially random) whose segment lengths of crystallizable terephthalate units are limited and larger crystals than this are not possible without chemical rearrangement. Thus, nucleation phenomenon does not control crystal size, so T_m for short crystallization times is independent of T_c. At long crystallization times and high crystallization temperatures, interchange reactions permit crystallization-induced chemical rearrangements to yield longer terephathate sequences and thus higher T_m and heats of fusion. Evidently, isophthalate units are excluded from the crystal. On prolonged annealing, Kodar becomes a blocklike polymer with crystal structure, melting temperature, and a heat of fusion (per gram of terephthalate units) which are essentially that of Kodel. Heating to temperatures well above the melting point scrambles this
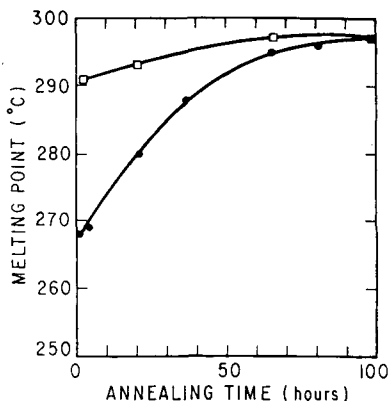

Fig. 7. Effects of annealing time at 227°C on Kodar and Kodel melting points: (●) Kodar; (□) Kodel.
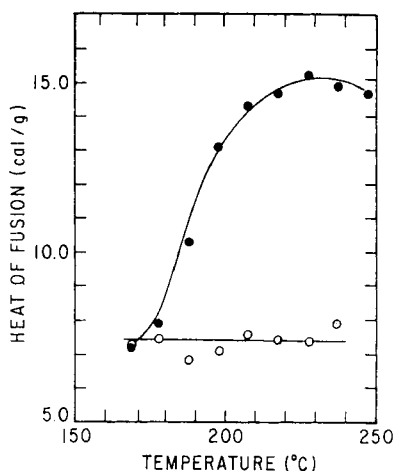
Fig. 8. Heat of fusion of Kodar after isothermal crystallization for 1 h (O) and 20 h (●) at the temperatures indicated.

ordered structure back to that of the original random copolymer through interchange reactions.

MELTING BEHAVIOR OF KODAR–POLYCARBONATE BLENDS

For blends of Kodar with polycarbonate, the additional possibility of interchange reactions between linkages in the two different polymers has to be considered. Prolonged heating in the melt state is known to cause such reactions,[4] and they could be an issue in long-term crystallization also. In fact, the question may be raised as to what extent such reactions occurred during melt processing to form the blend. Results in Figure 9 speak to this point. Here, blends were allowed to crystallize at 187°C for 20 h, and the measured heat of fusion (per gram of blend) following this treatment is plotted against blend composition. The low temperature of 187°C was chosen to minimize the possibility of interchange
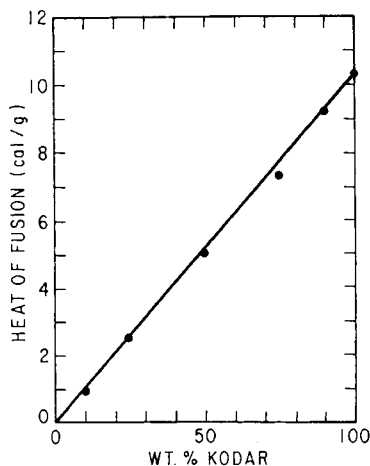

Fig. 9. Heat of fusion of Kodar-polycarbonate blends after crystallization at 187°C for 20 h.

reactions, and the long crystallization time was used to allow full development of Kodar crystallinity—the physical presence of polycarbonate is known to retard the kinetics of Kodar crystallization at high dilutions.[1-5] The results show a very good straight line connecting zero for pure polycarbonate to the value of pure Kodar. This means that the Kodar crystallinity is the same for all blends when kinetic restrictions are not present. This would not occur if a significant degree of interchange reaction in the blends had occurred during processing. Other evidence has also led to the conclusion that minimal reaction between Kodar and polycarbonate occurs during the short time in the melt needed for processing.[4]

Blends heated to high temperatures (300–330°C) in the DSC for several minutes experienced significant decreases in their ability to crystallize, apparently because of interchange reactions between the copolyester and the polycarbonate. This was most evident for blends containing less than 90% Kodar. Blends so treated and then quenched to room temperature failed to crystallize on heating at 10°C/min in the DSC, and they had much lower levels of crystallinity than indicated in Figure 9 following isothermal crystallization. Blends that had only been extruded crystallize readily on heating at 10°C/min. Apparently, similar reactions occur on prolonged annealing below the melting point as illustrated in Figure 10 for a 50% blend. Prolonged annealing at temperatures less than about 220°C increases the observed heat of fusion by about 20% compared to that seen for short crystallization times; however, above this temperature limit, the observed heat of fusion drops drastically, evidently by loss of crystallizable segments through interchange reactions. These results are in sharp contrast to what was observed during long-time annealing of pure Kodar (see Fig. 8).

Figures 11 and 12 show the melting point behavior for the Kodar in the 50% blends following isothermal crystallization and annealing. These samples were not held in the melt state to destroy nucleation sites prior to crystallization, since this would have resulted in a serious decline in crystallizability as noted earlier. When held at T_c for short times, a broad, diffuse melting peak resulted whose
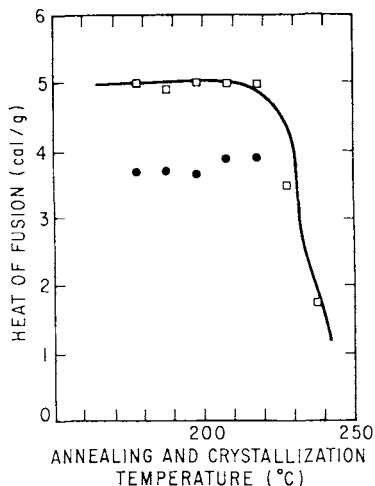

Fig. 10. Effect of crystallization temperature and time on the heat of fusion for blend containing 50% by weight of polycarbonate: (□) 20 h; (●) 1 h.
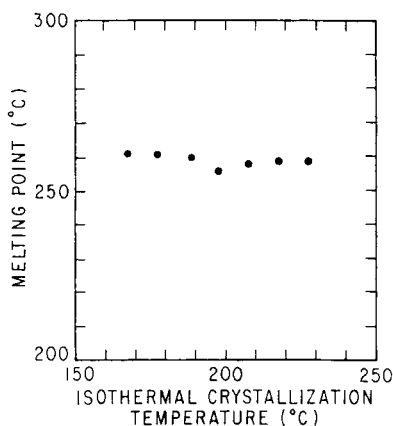
Fig. 11. Hoffman–Weeks plot for 50% Kodar blend using crystallization times of 1 h or less.

location, 258 ± 2°C, did not vary with crystallization temperature. However, after extended time at temperatures above 220°C, an elevation in T_m similar to that of pure Kodar (Fig. 3) is seen. The effect is not as large as seen in Figure 3 and is no doubt influenced considerably by the probable polyester–polycarbonate interchange reaction which ultimately outweighs the crystallization-induced reorganization reactions.

For 90% Kodar blends, evidence of interchange reactions between the two polymers is diminished by comparison. For example, holding this blend at 320°C for 5 min in the DSC only resulted in a decrease of heat of fusion from 6.5 to 4.5 cal/g. The melting point behavior for these blends shown in Figures 13 and 14 more or less parallels that seen for pure Kodar. For short crystallization times, the melting point (266 ± 2°C) was independent of T_c. For long times at low T_c, the melting point was also constant at a lower value of 259 ± 2°C, but significant increases in T_m are seen for $T_c > 220°C$. The heat of fusion was never observed to increase more than 20% above the value obtained following short-time isothermal crystallization. Evidently, interchange reactions with the polycarbonate compete with the crystallization-induced reorganization prevalent in pure Kodar.
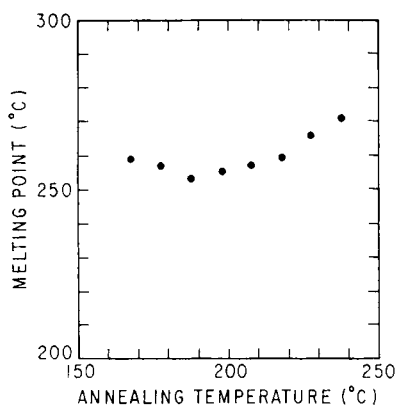

Fig. 12. Hoffman–Weeks plot for 50% Kodar blend using long crystallization times.
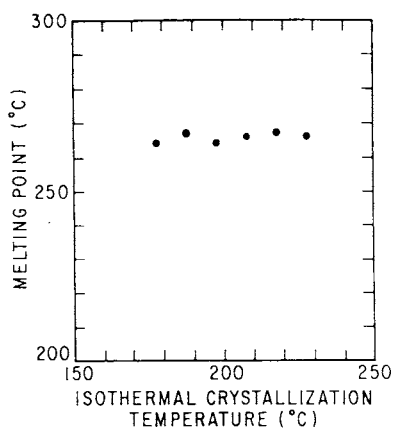
Fig. 13. Hoffman–Weeks plot for 90% Kodar blend using crystallization times of 1 h or less.

In principle, the melting point of a crystallizable blend component such as Kodar is depressed by the presence of an amorphous, miscible diluent such as polycarbonate as a result of the reduction in free energy caused by mixing. It would be of interest to quantify this effect by eliminating other factors such as crystal size using the Hoffman–Weeks method of extrapolation to infinite crystal thickness for each blend composition. However, the foregoing results clearly show that attempts to employ this technique introduces other, more complicating issues for the present system which preclude its use. Interestingly, the melting point of Kodar in the pure state and in blends seems to be relatively independent of crystallization conditions, except when the crystallization temperature is so high that chemical rearrangements occur. In view of this, a standardized method of crystallization ought to provide a reasonable estimate of the melting point depression caused by the single issue of the free energy change on mixing. A series of quenched blends were heated at 10°C/min in the DSC with crystallization occurring on heating. The measured melting points are shown in Table I; and where comparisons are possible, the values are the same as those obtained by isothermal crystallization. The peak melting points are plotted against the
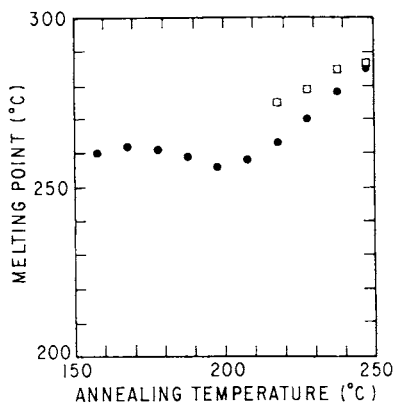

Fig. 14. Hoffman–Weeks plot for 90% Kodar blend using long crystallization times: (●) 18 h; (□) 30 h.

TABLE I
Melting Points of Kodar in Various Blends Obtained by Heating Quenched Specimens at 10°C/min in DSC

Kodar, wt %	Melting peak temperature, °C	Temperature of last trace of melting, °C
100	269	271
95	268	271
90	267	269
85	265	267
80	265	268
75	262	264

square of polycarbonate volume fraction in Figure 15. An analysis of melting point depression using the Flory–Huggins theory for components of very large molecular weights gives the following[18-20]:

$$T_m^0 - T_m = -T_m^0 \left(\frac{V_u}{\Delta H_u} \right) B \phi_1^2 \tag{3}$$

where T_m^0 is the melting point of the pure crystallizable component, $\Delta H_u / V_u$ is the heat fusion per unit volume, $B = RT (\chi_{12}/\tilde{V}_1)$ is the interaction parameter, and ϕ_1 is the volume fraction of amorphous component. The slope of the line drawn in Figure 15 is $d\Delta T_m/d\phi_1^2 = 100°C$ which can be used to estimate B or $\chi_{12}/\tilde{V}_1$, provided $\Delta H_u/V_u$ is known. For the latter, an estimated value for Kodel (see Appendix) is the only information available which should be an upper limit to the value applicable for Kodar. Using this value and $T_m^0 = 269°C$ gives

$$B = -6.3 \text{ cal/cm}^3$$

or

$$\chi_{12}/\tilde{V}_1 = -5.85 \times 10^{-3} \text{ cm}^{-3}$$

These values are compared with another estimate for the interaction parameter in a subsequent section.
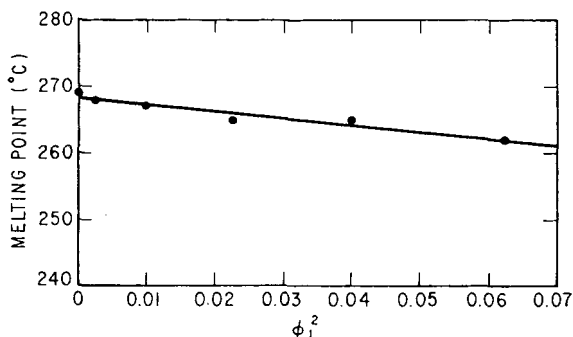

Fig. 15. Melting point depression for Kodar–polycarbonate blends. Peak melting temperatures from Table I are plotted.

CRYSTALLIZATION KINETICS

Crystallization kinetics of Kodar and its blends with polycarbonate was monitored by DSC by following the amount of heat released as a function of time at a given crystallization temperature. In one series of experiments, the samples were heated to 327°C for 5 min prior to cooling to T_c in order to destroy all active nuclei. However, as stated earlier, this severe thermal condition caused serious degrees of interchange reaction for blends containing more than 10% polycarbonate, so only pure Kodar and the 90% Kodar blend were examined in this way. A broader range of blend compositions was examined in a second series of experiments in which quenched blends were heated to T_c from the glassy state. In both cases, the fractional crystallization X_t, defined as the ratio of heat released in time t to that released in infinite time, was calculated by graphic methods as a function of crystallization time at T_c. These results were fitted to the Avrami equation

$$\ln(1 - X_t) = K_n t^n \qquad (4)$$

in the usual way.[21,22] A typical Avrami plot is shown in Figure 16, and the response is reasonably linear, permitting evaluation of K_n and n. Tables II and III give the parameters K_n, n, and the half-time for crystallization (i.e., time to reach $X_t = \frac{1}{2}$) for crystallization from the glass and the melt, respectively, for each composition studied.

As expected, crystallization from the glass was always faster than from the melt owing to the presence of residual nuclei in the former—compare $t_{1/2}$ values in Tables II and III. Figure 17 shows a plot of recipricol half-times against T_c for samples crystallized from the glassy state. The response for each composition is of the form expected. An interesting feature of these results is that the 90% Kodar blend crystallizes more rapidly than pure Kodar or any of the other blends. The data in Table III for samples crystallized from the melt also show that crystallization from the 90% blend is faster than from pure Kodar. No definitive reason for this unexpected result is presently available, although related behavior in other systems has been noted previously.[5]

A more detailed analysis of the data in Table III was made using modern theories of crystallization kinetics, but a similar analysis for the results obtained by heating from the glassy state was not done because the less well-defined initial state made this seem unjustified. The analysis employs a modified Turnbull–
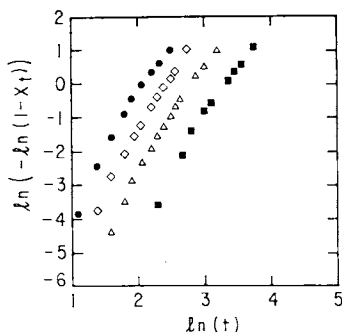

Fig. 16. Avrami plot for pure Kodar crystallized from the melt state at T_c indicated: (●) 187°C; (◇) 197°C; (△) 207°C; (■) 227°C.

TABLE II
Parameters for Crystallization Kinetics When T_c is Approached from the Glass

T_c, °C	Half-time, min	Avrami constants	
		n	$K_n \times 10^3$, (min)$^{-n}$
100% Kodar			
157	12.8	2.94	1.56
177	4.0	2.11	25.23
187	3.7	2.45	30.04
197	4.1	2.26	23.78
217	8.2	2.18	4.54
90% Kodar			
157	6.7	2.02	2.18
177	2.1	3.98	73.20
187	1.5	2.66	202.90
197	1.6	3.16	166.90
207	2.1	3.67	73.20
217	2.6	3.22	38.32
227	4.1	2.80	9.64
237	7.2	2.68	1.75
75% Kodar			
177	4.4	2.70	16.33
187	4.0	2.42	20.78
197	3.9	2.27	22.15
207	4.7	2.73	13.82
50% Kodar			
177	10.5	2.48	2.03
187	9.2	2.96	1.90
197	7.4	2.49	3.38
207	9.0	2.71	2.01

Fisher expression[7,23–31] to describe the Avrami rate parameter K_n, which results in the following[32]:

$$\frac{1}{n} \ln K_n + \frac{1500}{R(30 + T_c - T_g)} = A_0 - \frac{4b_0 \sigma \sigma_e T_m^0}{R \Delta H_f T_c (T_m^0 - T_c)} \tag{5}$$

TABLE III
Parameters for Crystallization Kinetics When T_c is Approached from the Melt

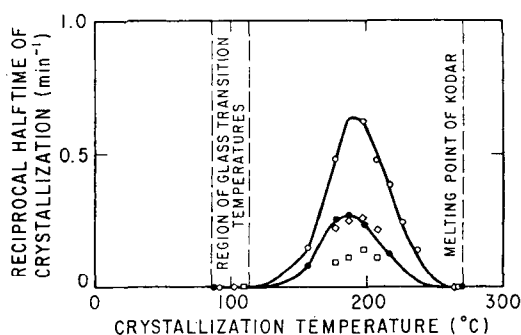| T_c, °C	Half-time, min	Avrami constant	
		n	$K_n \times 10^3$, (min)$^{-n}$
100% Kodar			
187	7.2	3.22	1.30
197	10.1	3.13	0.44
207	14.6	3.30	0.14
217	23.6	3.21	0.053
222	25.7	2.96	0.030
227	28.3	3.66	0.017
90% Kodar			
192	4.70	2.49	14.93
197	5.03	2.91	12.62
202	6.00	2.65	8.15
207	10.50	2.30	2.03
217	12.40	2.04	1.35

Fig. 17. Crystallization rates from the glassy state for Kodar–polycarbonate blends: (●) Kodar; (○) 90% Kodar; (◇) 75% Kodar; (□) 50% Kodar.

where A_0 is a preexponential constant not specified by the theory. The last term on the right-hand side stems from the free energy required to form a critical-sized nucleus from the melt. The various parameters have the following meaning: b_0 is the distance between adjacent chains, σ is the surface free energy parallel to chains, σ_e is the end-surface free energy, ΔH_f is the heat of fusion, and R is the gas constant. The second term on the left-hand side is a mobility correction of WLF form employing constants suggested by Hoffman et al.[24] Wang and Nishi[31] were able to describe the rate of poly(vinylidene fluoride) spherulite growth from blends with poly(methyl methacrylate) using a related modification of the Turnbull–Fisher theory.

Based on eq. (5), a plot of the left-hand side vs. $T_m^0/[T_c(T_m^0 - T_c)]$ should produce a straight line with a slope related to the parameters defined above. As seen in Figure 18, plots of this type do yield straight lines for Kodar and the 90% blend which are nearly parallel. Using available information,[32] the end-surface free energy σ_e can be estimated from the slopes to be in the range of 140 to 170 erg/cm^2. Typical chain-folded lamella have σ_e of the order of 50 erg/cm^2, while bundle-type lammella have values of the order of 150 erg/cm^2 according to Hoffman.[27] The latter form is thus inferred to be more applicable for Kodar crystallization.

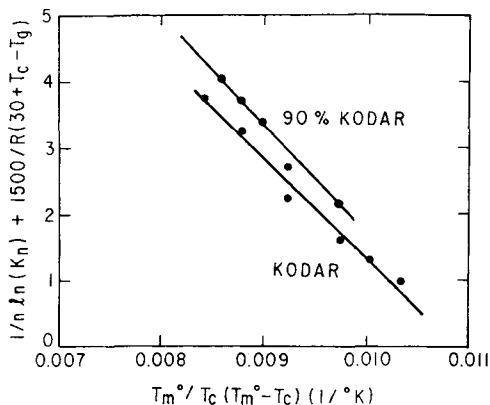The values of the Avrami exponent n vary considerably as seen in Tables II

Fig. 18. Analysis of the effect of crystallization temperatures on crystallization rate from the melt for pure Kodar and a 90% Kodar blend.

and III owing to the uncertainty of determining it, but generally the values found lie about $n = 3$, which is the typical range for polymers. Because of the many possibilities in mechanism and the experimental uncertainty, little can be said about the details of crystallization from these values.[15]

SUMMARY

The evidence presented here strongly suggest that the copolyester Kodar experiences crystallization-induced chemical rearrangements when held at high temperatures for long times. Similarly, miscible blends of Kodar with polycarbonate experience interchange reactions yielding a more complex copolymer under similar conditions. Crystallization kinetics are adequately described by modern theories. However, attempts to extrapolate observed melting points at various crystallization temperatures to obtain the equilibrium melting points of infinitely large crystals for this system do not follow the simple expectations of the Hoffman–Weeks theory owing on the one hand to the copolymeric nature of Kodar and to the above mentioned reactions on the other hand. These factors preclude the correction of melting point depression analysis for possible morphologic effects stemming from varying crystal size with blend composition. In view of this difficulty, an analysis of melting points without correction was made to obtain an estimate of the interaction parameter for this system. A sorption probe technique using CO_2 at 35°C for the same blend system has resulted in the following interaction parameters[3]:

$$B = -3.1 \text{ cal/cm}^3$$

or

$$\chi_{12}/\tilde{V}_1 = -0.00507 \text{ cm}^{-3}$$

which may be compared with the results from the melting point depression analysis. The values of B from the two methods differ by roughly a factor of 2; however, the $\chi_{12}/\tilde{V}_1$ values by the two methods are within 13% of each other. Note that the two means of expressing the interaction differ by a factor of T and that the absolute temperatures in the two experiments differ by a factor of 1.76, i.e., 269 vs. 35°C. Neither method may be argued to provide little more than an estimate of the interaction parameter, so it is not reasonable to speculate further about these results except to say that the values obtained are in reasonable accord with expectations from a variety of sources.

APPENDIX

ESTIMATION OF $\Delta H_u/V_u$ FOR KODEL

The heat of fusion per unit volume of poly(1,4-cyclohexanedimethanol terephthalate) crystals does not appear to have been determined previously. An estimate was made as follows. An amorphous Kodel sample was crystallized for 2 h at 180°C. By DSC, the heat of fusion was found to be 9.33 cal/g. The density of this sample was determined to be 1.222 ± 0.0005 g/cm³ using a glass pycnometer with heptane as the immersion fluid. Using an amorphous density of 1.195 g/cm³ and a crystalline density of 1.283 g/cm³ for Kodel,[33] a fractional crystallinity of 0.313 was calculated. Thus, the heat of fusion for 100% crystalline Kodel would be 9.33/0.313 = 29.8 cal/g. The crystalline

density at the melting point is estimated to be 1.15 g/cm^3 using a reasonable thermal expansion coefficient; thus, $\Delta H_u / V_u = 29.8 \times 1.15 = 34.3$ cal/cm^3.

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