

Influence of low molecular weight polyoxyethylene on bulk crystallization and melting behaviour of poly(oxymethylene diacetate)

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The effects of low molecular weight polyoxyethylene (POE) on crystallization kinetics, radial growth rate of spherulites and crystallite long period of melt crystallized poly(oxymethylene diacetate) (POMDA) have been investigated with different techniques (optical microscope, calorimetry, small- and wide-angle X-ray scattering). The results obtained suggest that the POE affects both the crystallization kinetics and equilibrium thermodynamic quantities of fusion of POMDA. This influence can probably be attributed to the lower concentration of defects in the crystalline layers of the polyoxyethylene lamellae and interaction of part of the additive with the amorphous phase.

INTRODUCTION

The problem of additives and their influence is of great importance in the technology and handling of plastic materials and in the mechanical behaviour of the finished product. Therefore it is interesting to investigate new substances which affect the overall properties of plastic materials.

Polyoxymethylene (POM) is a very useful commercial product, so the study of new additives is of interest.

Mikhailov *et al.*¹ carried out a systematic study of the influence of small quantities of a wide variety of organic low molecular weight, oligomeric and polymeric substances on the morphology and kinetics of growth of several structures which can be formed from melt crystallization of poly(oxymethylene diacetate) (POMDA).

However, the influence of these substances on some thermodynamic quantities, like equilibrium melting point and enthalpy, T_m^0 and ΔH_m^0 , respectively, and the surface free energy of the lamellae, has not yet been thoroughly investigated.

In this paper we study the effect of the concentration of a low molecular weight polymeric substance (with a low melting temperature) on the spherulitic growth determining parameters, on the average dimensions of the crystalline and amorphous zones and on melting and surface thermodynamic quantities.

EXPERIMENTAL

Mixing of additive

The poly(oxymethylene diacetate) (POMDA) used in this work was a commercial product with $\bar{M}_n \approx 5 \times 10^4$.

*Part of this paper was presented at the '1° Convegno Italiano di Scienza delle Macromolecole', S. Donato Milanese, 18–20 December 1975.

Poly(oxyethylene glycol), POE, with $\bar{M}_n \approx 3 \times 10^3$ and $T_m = 57^\circ\text{C}$, was added after fusion of the POMDA in a Brabender cell, in quantities of 1.5, 3.0 and 5.0% by wt and then homogenizing the melt for 10 min at about 200°C .

A portion of POMDA was melted in the same way, but without any addition of POE. This will be referred to as the reference sample. The purpose of this sample was to achieve independence of uncontrollable variables such as thermal and oxidative degradation of the polymer during the treatment in the cell.

Radial growth rate of spherulites

All the observations of isothermal radial growth rate (Figure 1) were made by means of a Reichert polarizing microscope, equipped with a Mettler hot stage; temperature was automatically held constant with a precision of $\pm 0.2^\circ\text{C}$. In order to make the thermal pretreatment standard, the sample was melted and kept at 200°C for 10 min before making any observations at the required crystallization temperature, T_c .

This procedure was also used for the experiments described below.

The increase of spherulite radius, G , with time was determined from micrographs taken at different times (Figure 1).

Only values averaged over at least five observations were considered.

With this technique, it was possible to measure G for T_c values in the range 156°C – 162°C . It was not possible to make observations at temperatures lower than 156°C because the nucleation rate was higher than the specimen cooling rate; the upper limit $T_c = 162^\circ\text{C}$ was due to the extremely low crystallization rate at temperatures higher than that.

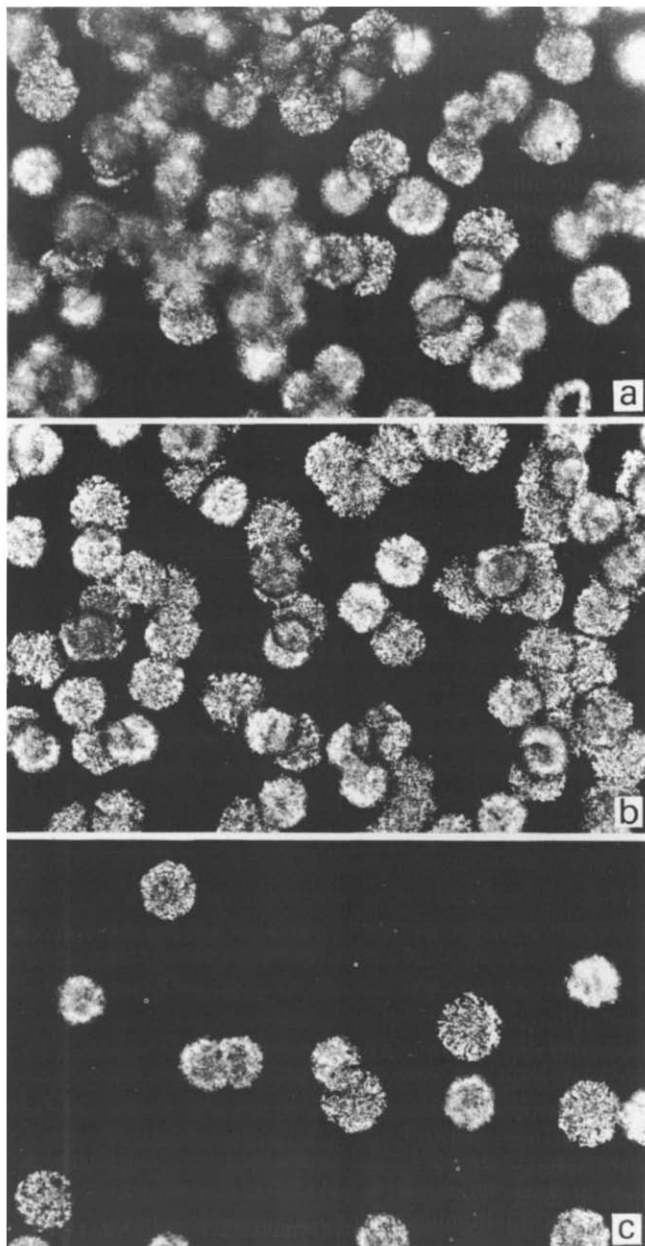


Figure 1 Micrographs of growing spherulites of POMDA: (a) reference POMDA; (b) POMDA + 1.5% POE; (c) POMDA + 5% POE

Bulk crystallization kinetics

The bulk crystallization isotherms were followed by means of a Perkin–Elmer DSC 1B differential scanning calorimeter. The relative degree of crystallinity at time t , χ_t , was measured as $\chi_t = A_t/A_\infty$, where A_t and A_∞ are the areas of the exotherms at time t and at the end of the crystallization, respectively. With this method, we could follow the isothermal crystallization kinetics in the temperature range 145°–161°C.

Determination of the thermodynamic equilibrium quantities

After crystallization in the d.s.c. sample holder, the samples were melted at high scanning speed (32°–64°C/min), to avoid any possible structural modification, taking the peak maximum temperature as melting point, T_m .

In this case, as well as for the plots in Figures 4, 12 and 13, the lines were drawn by the least squares method. The T_m^0 value is given by the point of intersection of the experi-

mental curve with the straight line $T_m = T_c$ (ref 2). Another way to obtain T_m^0 is by the equation^{3–4}:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H_m^0 L_c} \right) \tag{1}$$

after determining L_c and T_m by X-ray and d.s.c. measurements, respectively.

The thermodynamic equilibrium enthalpy of fusion, ΔH_m^0 , was also determined by two methods. The first one consists of the following simplified expression:

$$\chi = \frac{\Delta H_m}{\Delta H_m^0} \tag{2}$$

for which it is necessary to measure experimentally the degree of crystallinity, χ , and the apparent enthalpy of fusion, ΔH_m . The second method uses the Roe–Blair equation⁵:

$$\Delta H_m = \Delta H_m^0 - \frac{2q_e}{L_c} \tag{3}$$

The ΔH_m^0 value is obtained by plotting ΔH_m against $1/L_c$, and extrapolating to $1/L_c = 0$.

Crystallinity and long period measurements

Degree of crystallinity was determined from wide-angle X-ray diffraction spectral measurements, carried out on a Philips diffractometer, using an X-ray generator PW 1130, goniometer 1050/25, and normal electronic circuitry panel PW-1360.

To obtain the long period, L , small-angle X-ray diffraction was used. The spectra were recorded by photography in a pinhole collimated Rigaku–Denki camera (radiation $\text{CuK}\alpha$)^{6–8}.

Measurements were carried out on samples crystallized at temperatures between 140° and 160°C. In order to obtain values at 177°C, the samples were crystallized at 160°C and annealed under nitrogen at 177°C for about 2 h.

The crystal thickness, L_c , was obtained by two methods. By measuring the half-height peak width of wide-angle X-ray reflections, it is possible to find the mean crystallite dimensions, normal to diffracting planes, by applying the Debye–Scherrer law^{6,7}:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{4}$$

where K is a constant, assumed in our case to be 0.89; β is the peak half-height width, corrected for $\text{K}\alpha$ doublet separation and instrumental broadening b , according to a widely used method; λ is the wavelength of the radiation used; θ is Bragg’s angle.

From the reflection line broadening on the 105 planes, one can obtain a dimension D_{105} , normal to these planes. In order to find L_c , on the c axis, D_{105} must be multiplied by $\cos \delta$, where δ is the angle formed by the normal to the planes 105 and the c axis. Knowing the unit cell parameters of POM⁸ gives $\delta = 41^\circ 52'$.

Another method for L_c is to calculate it from long spacing, L , through the formula⁹:

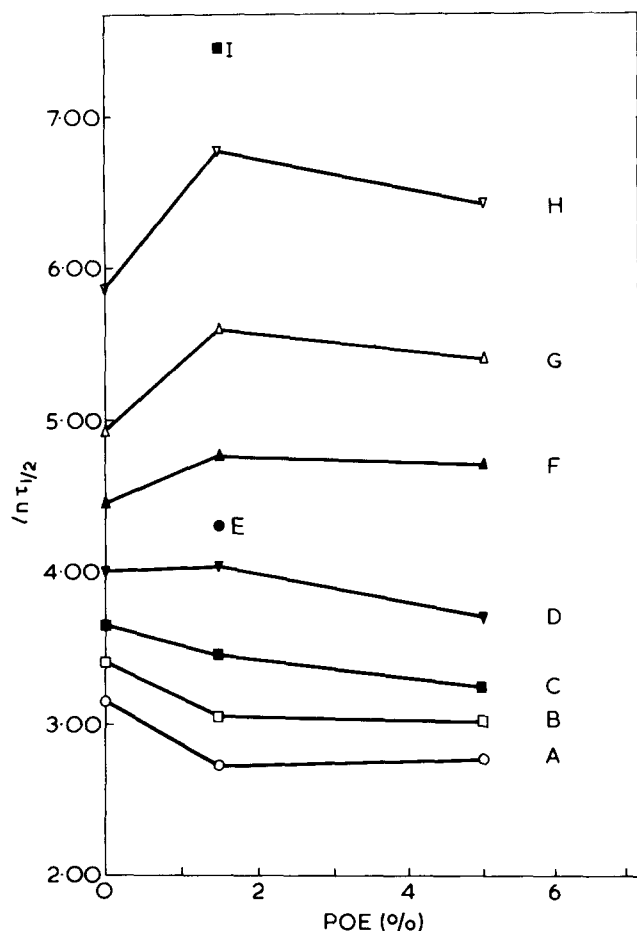


Figure 2 Crystallization half-time versus POE content of POMDA at different T_c . A, 145°C; B, 147°C; C, 149°C; D, 151°C; E, 153°C; F, 155°C; G, 157°C; H, 159°C; I, 161°C

$$L_c = \frac{\chi L}{\frac{\rho_c}{\rho_a}(1 - \chi) + \chi} \quad (5)$$

where ρ_c ($= 1.506 \text{ g/cm}^3$) and ρ_a ($= 1.25 \text{ g/cm}^3$) are the crystalline and amorphous densities, respectively⁸.

RESULTS AND DISCUSSION

Bulk isothermal crystallization kinetics

The crystallization half-time, $\tau_{1/2}$, obtained from the crystallization isotherms, is plotted as a function of POE percentage for each T_c in Figure 2. An inversion of the curve trends can be observed at a T_c of about 150°C; below this temperature the reference sample is the slowest and above it the fastest in crystallizing. A possible explanation of this phenomenon will be given below. Here we only note that the largest variation of $\tau_{1/2}$ with POE content is observed between 0 and about 1.5% independently of its sign. The kinetic parameter $\tau_{1/2}$ does not parallel (as does $1/\tau_{1/2}$) the G values in Table 1. The implication is, therefore, that the primary nucleation process is vastly different at different POE levels and effects the overall $\tau_{1/2}$.

The Avrami plots of the samples of reference POMDA and POMDA with 1.5, 3 and 5% of POE give Avrami exponents n within the limits of 3–4.

Radial growth rate

The spherulites radii versus time are plotted in Figure 3. The trend is generally linear although for the sample with 5% of POE one can observe a shift from linearity. This behaviour could be explained by a phase separation between solid POMDA and liquid POE during crystallization. Thus the melt enriches in polyoxyethylene, causing a decrease in G when the additive concentration in the liquid phase rises above a certain limit.

This suggestion seems to be confirmed by a comparison of the microphotographs in Figure 4, which show the morphologies of reference POMDA (a) and a sample of POMDA with 5% of additive (b), both crystallized at 160°C, after a Soxhlet extraction in CHCl_3 for 24 h. (The latter solvent is good for POE, but not for POMDA, even for very low molecular weights.) These results suggest that two polymers are inherently incompatible and, in the solid blend, always phase-separated.

Figure 3d shows the change of G with T_c , while Table 1 lists G values for $T_c = 157^\circ$ and 159°C . The sample admixed with 5% of POE has a higher growth rate with respect to the other samples, in almost the whole range of T_c studied. This difference is about 25% at low T_c and decreases as T_c increases: at $T_c = 160^\circ\text{C}$ the effect of additive disappears.

According to the kinetic theory of polymer crystallization, and assuming moderately low undercooling and that radial growth rate is a bidimensional coherent nucleation controlled process, the dependence of G on the temperature may be described thus^{4,10}:

$$\ln G = \ln G_0 - \frac{\Delta F^*}{KT_c} - \frac{4b_0\sigma\sigma_e T_m^0}{K\Delta H_m^0 T_c \Delta T} \quad (6)$$

where G_0 is a constant, depending practically only on the nature of the polymer chain, ΔF^* is the activation energy for the jump rate process at the supercooled liquid–solid interface, $4b_0\sigma\sigma_e T_m^0/\Delta H_m^0 \Delta T = \Delta\phi$ is the formation free energy of a nucleus with critical dimensions, σ_e and σ are the fold and lateral surface free energy of the lamellae, respectively, b_0 ($= 4.46 \text{ \AA}$ in our case) is the monomolecular layer thickness and $\Delta T = T_m^0 - T_c$ is the undercooling.

The dependence of ΔF^* on the temperature can be described by the Williams–Landel–Ferry equation¹⁷. Since the crystallization temperature range used was only 6°C (156° – 162°C) the ΔF^* (calculated from the WLF equation) change with T_c is negligible. Therefore the data from the kinetic investigations are represented graphically as the function $\ln G$ versus $T_m^0/T_c \Delta T$ (Figure 5).

The plots are linear for reference and admixed samples. From the slopes of the lines, the values of the product $\sigma\sigma_e$ were calculated (Table 3): these figures are about 10% smaller than those can be obtained by calculating ΔF^* from

Table 1 Kinetic data for POMDA and POMDA–POE

Sample	T_c ($^\circ\text{C}$)				
	145		157	159	
	$\tau_{1/2}$ (sec)	$\tau_{1/2}$ (sec)	G ($\mu\text{m}/\text{min}$)	$\tau_{1/2}$ (sec)	G ($\mu\text{m}/\text{min}$)
Reference POMDA	23	138	18.8	353	7.6
POMDA + 1.5% POE	15	269	19.0	882	7.5
POMDA + 5% POE	16	222	25.0	621	10.0

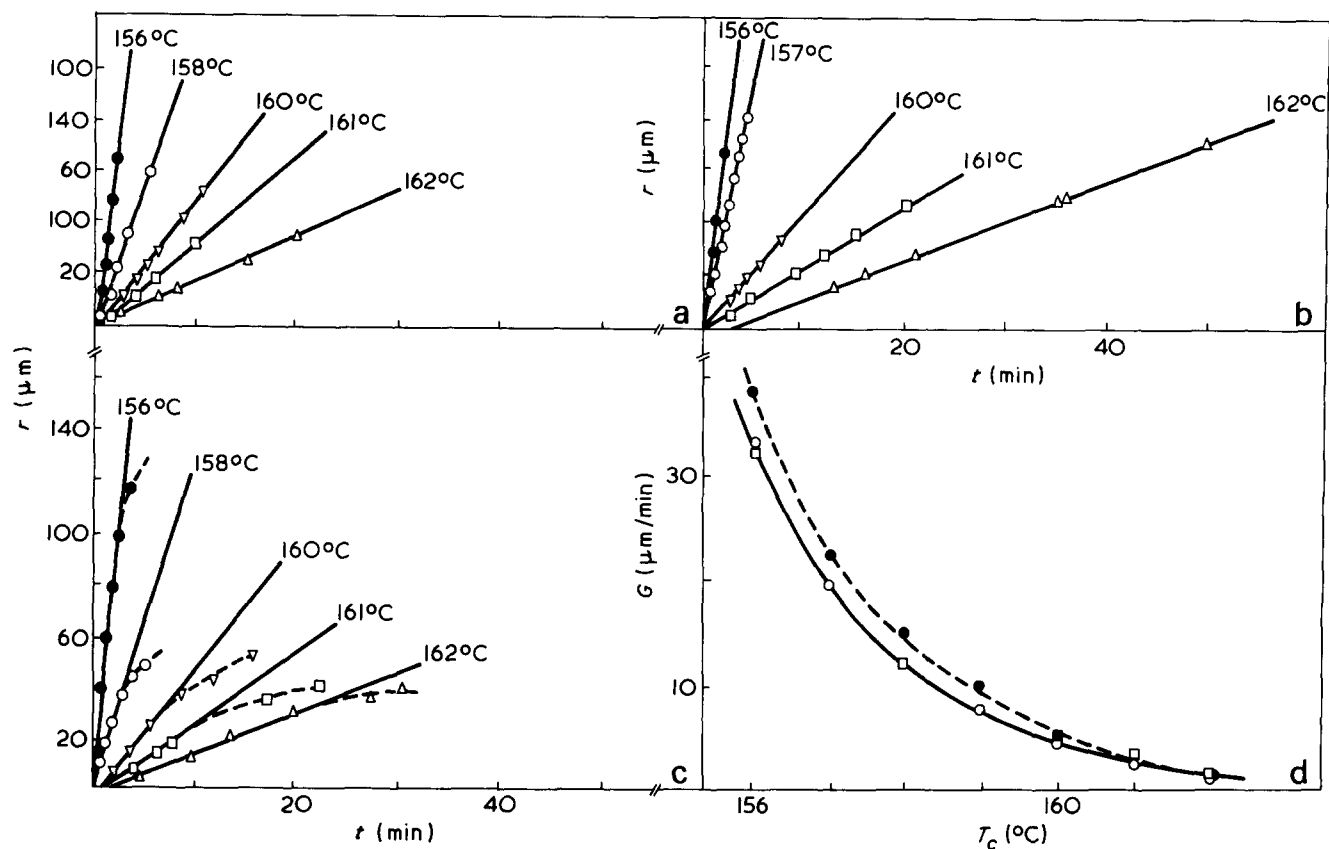


Figure 3 Spherulite radius versus time for pure (a) and mixed samples (b, 1.5%; c, 5% POE) of POMDA at different T_c . (d) Radial growth rate versus T_c : \square , reference POMDA; \circ , POMDA + 1.5% POE; \bullet , POMDA + 5% POE

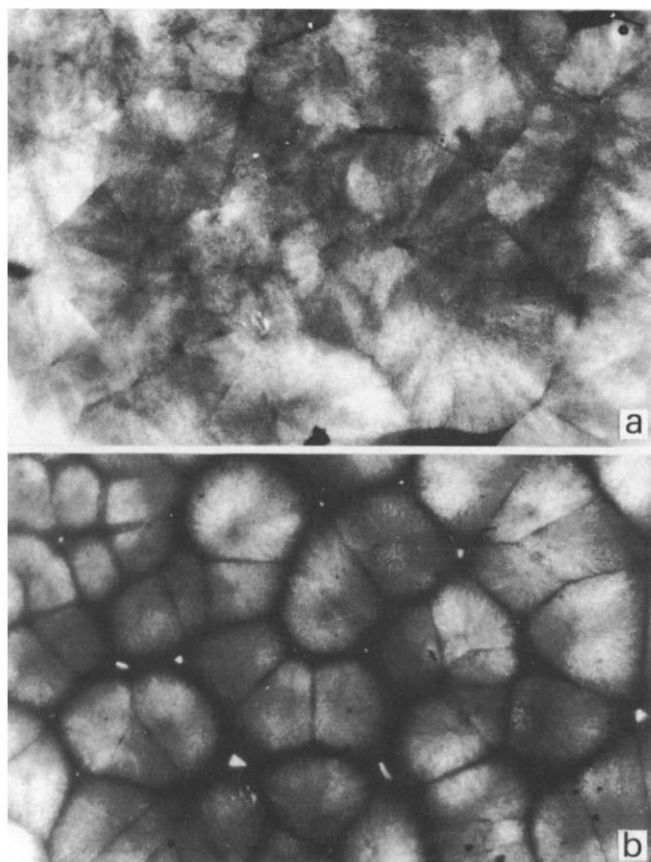


Figure 4 Micrographs of reference POMDA (a) and POMDA + 5% POE (b) etched with CHCl_3 for 24 h (see text)

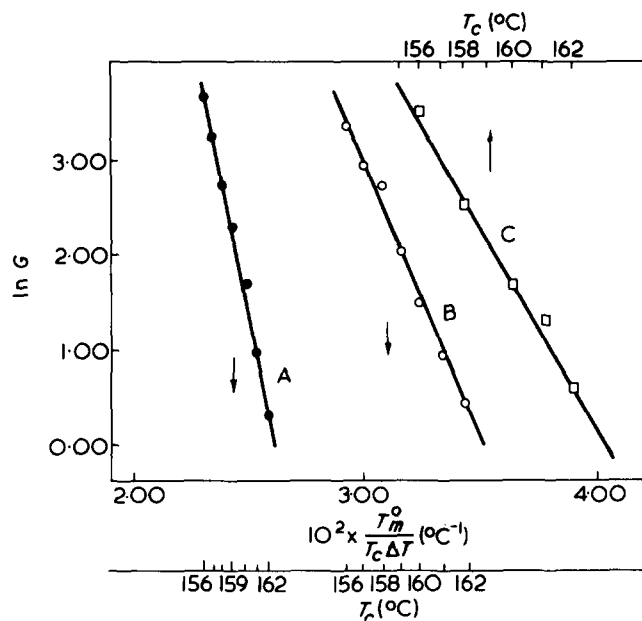


Figure 5 Plot of the dependence of $\ln G$ on $T_m^0/T_c \Delta T$. A, POMDA + 5% POE; B, POMDA + 1.5% POE; C, POMDA

the WLF equation and plotting $\ln G + (\Delta F^*/KT_c)$ versus $T_m^0/T_c \Delta T$.

In Figure 6 are plotted the values of $\Delta\phi$ versus POE content, for two different undercoolings. A sharp increase in the critical free energy of nucleation is observed with increasing content of additive and, as known, T_c .

Since, as will be seen later, σ is independent from the

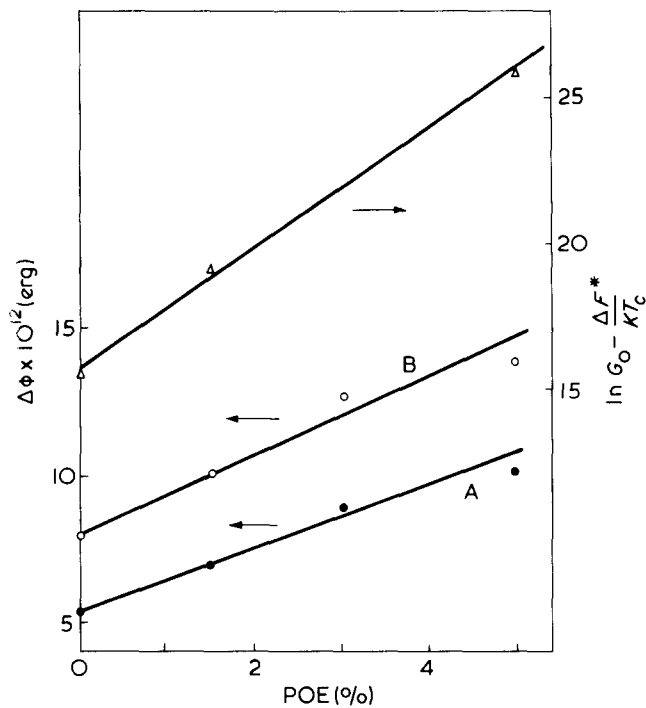


Figure 6 Free energy of formation for critical size nucleus $\Delta\phi$ and $\ln G_0 - \Delta F^*/KT_c$ for our samples. A, $T_c = 145^\circ\text{C}$; B, $T_c = 159^\circ\text{C}$

Table 2 Relative degree of crystallinity of POMDA and POMDA-POE

T_c ($^\circ\text{C}$)	χ (%)			
	POMDA reference	POMDA + 1.5% POE	POMDA + 3% POE	POMDA + 5% POE
140	73.0	71.0	70.9	67.1
145	73.1	72.3	71.3	68.6
150	75.4	72.7	70.9	69.1
155	76.9	73.5	73.2	70.8
160	80.0	74.9	74.0	73.5
177	95.5	82.4	77.4	79.5

addition of POE, σ_e is the only parameter on which $\Delta\phi$ depends, at constant ΔT .

The same plot also shows the quantity $(\ln G_0 - \Delta F^*/KT_c)$ as a function of POE percent. It can be seen that this value is proportional to the quantity of additive, since G_0 probably does not depend on unrelated substances, this result means that ΔF^* decreases with increasing additive. These two opposite effects, ΔF^* decreasing while $\Delta\phi$ increases with both POE content and T_c , could explain the behaviour of $\ln \tau_{1/2}$ versus % POE (Figure 2). At $T_c > 150^\circ\text{C}$, the effect of formation free energy of critical size nuclei overcomes the effect due to the lower melt viscosity, so that we have a slower overall crystallization rate for admixed samples. The kinetic effect becomes more apparent for samples with the highest POE content.

At $T_c < 150^\circ\text{C}$, we observe a decrease of $\tau_{1/2}$ with POE percentage. This acceleration of crystallization rate could be attributed to the predominant influence of lower melt viscosity for admixed samples at higher undercoolings.

Degree of crystallinity and crystallite dimensions

The values for degree of crystallinity obtained for several T_c and percent POE are presented in Table 2. χ increases

with increasing T_c for each sample, but it decreases with increasing POE content (Figure 7).

The values of L and L_c are plotted against T_c in Figure 8. It can be seen that there is good agreement between the L_c values obtained by the two methods.

L and L_c both increase with T_c for all specimens, but a comparison between these estimates is meaningful only at the same undercooling, as shown in Figure 9.

This plot shows that POE does not influence the L_c value. On the other hand, the variation of amorphous phase thickness, L_a , increases with POE percent, at the same ΔT , and the phenomenon is larger the smaller is the undercooling (Figure 10). This result agrees with that discussed above for the POE effect on degree of crystallinity. For high undercooling, when all samples show approximately the same χ , the differences in L_a are probably due to the presence of POE between lamellae; at low undercooling, when χ changes from 95.5% for the reference sample to about 79% for POMDA + 5% of POE, higher L_a values for admixed samples are also probably due to the increase of amorphous phase layer in POMDA.

Thermodynamic quantities

Figures 11 and 12 show plots of T_m against T_c and $1/L_c$, respectively, for our samples. Both methods used show an interesting result; T_m^0 is not constant, but increases with increasing POE content. The deviations between the T_m^0 values obtained from the two methods for the same sample, are most probably due to the different techniques employed.

From a standard analysis of the dependence of the melting temperature on the crystallization temperature for melt-crystallized samples, Wissbrun¹¹ reports $T_m^0 = 200^\circ\text{C}$, Majer¹²

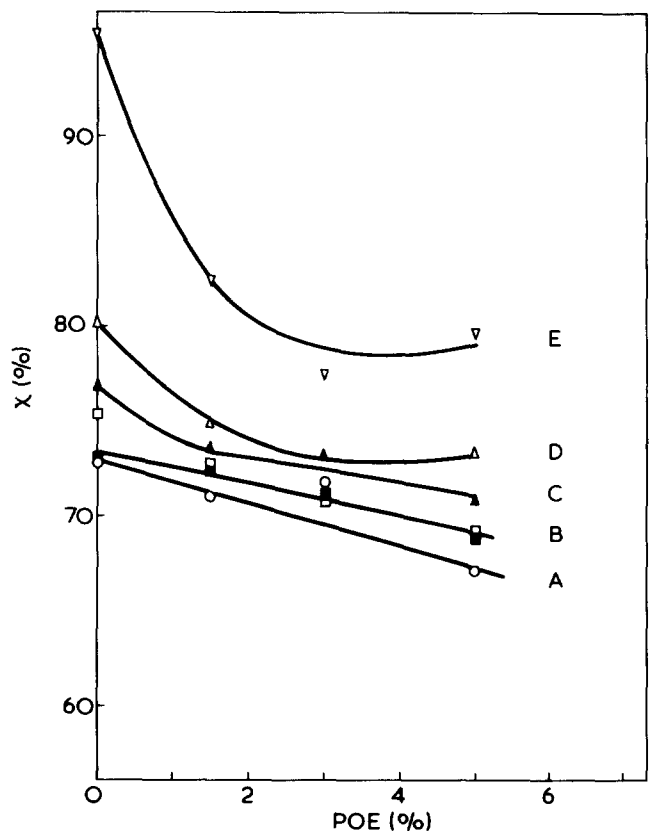


Figure 7 Degree of crystallinity versus POE content at different T_c . A, 145°C ; B, 150°C ; C, 155°C ; D, 160°C ; E, 177°C

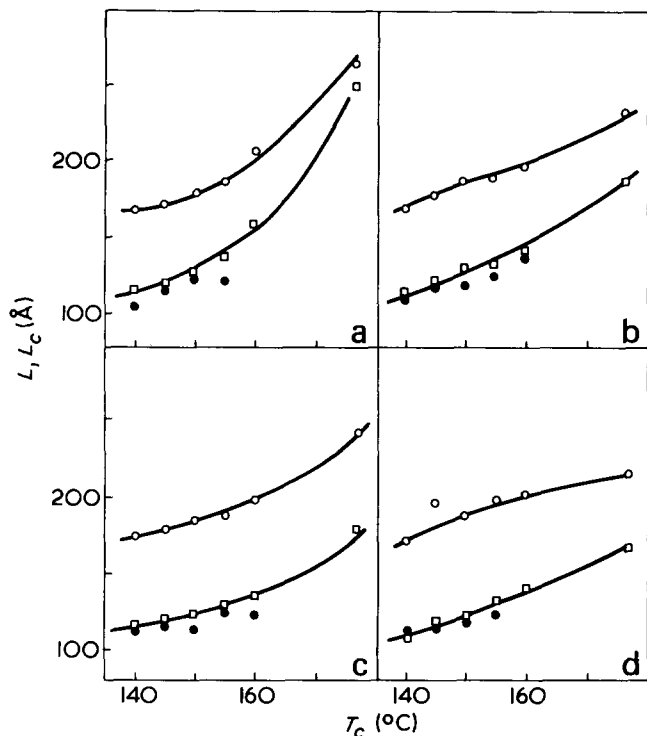


Figure 8 Long period L (\circ) and crystalline lamellae thickness L_c (\square , \bullet) versus T_c ; (\square) from SAXS and (\bullet) WAXS data. (a) POMDA; (b) POMDA + 1.5% POE; (c) POMDA + 3% POE; (d) POMDA + 5% POE

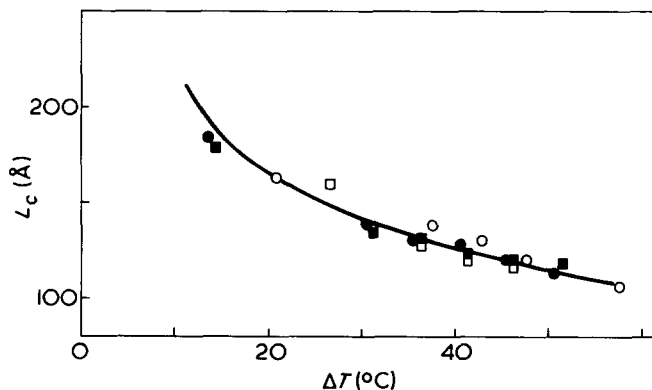


Figure 9 Crystalline phase thickness L_c versus under cooling ΔT for different POMDA samples. \square POMDA; \bullet POMDA + 1.5% POE; \blacksquare , POMDA + 3% POE; \circ , POMDA + 5% POE

206°C and Carter and Baer¹³ 202° ± 10°C. The last investigators also studied the relationship between T_m and L_c , and found $T_m^0 = 210^\circ \pm 10^\circ\text{C}$ for intense X-ray reflections; from weak X-ray reflections they deduce a $T_m^0 = 182^\circ \pm 2^\circ\text{C}$. As a result of our analysis and according to the above data, we consider that $T_m^0 \approx 185^\circ\text{C}$, generally used for POM, underestimates the true value by about 15°–20°C.

The ΔH_m^0 values, obtained from Figure 13, in which ΔH_m is plotted versus $1/L_c$, and from calorimetric measurements are in very good agreement. Again, both methods suggest that ΔH_m^0 depends upon additive concentration.

The generally accepted value of ΔH_m^0 is 1.78 kcal/mol $\text{CH}_2\text{-O}$ units⁸; this is in good agreement with our average value of 1.84 kcal/mol unit. However, we observe that a difference of about 15% between ΔH_m^0 for reference samples and 5% for POE samples, results from both methods; so we think it is a real difference.

Moreover, it should be emphasized that the increase of 10% in ΔH_m^0 is already obtained for samples mixed with 1.5% POE. The true value of ΔH_m^0 is probably about 2000 ± 100 cal/mol unit.

A possible explanation of this phenomenon could be a better packing of the crystalline phase, with a consequent decrease in the concentration of defects in the crystal, on account of a lower melt viscosity of the sample containing POE with respect to the reference sample, as seems to be suggested by the ΔF^* values discussed above.

The fusion and surface thermodynamic quantities are given in Table 3. The ΔS_m^0 value of the reference sample, 3.7 e.u./mol unit, is in good agreement with the value of 3.5 e.u./mol unit, determined by Inoue¹⁴ from depression of the melting temperature by means of diluent technique. ΔS_m^0 also increases from the reference sample to that with 5% of additive.

As already shown, it is possible to derive the end surface free energy, σ_e , from equation (1) (Table 3). σ_e changes from 31 erg/cm², for the reference sample, to 91 erg/cm² for a sample containing 5% POE. This trend seems to be confirmed by two experimental results: a decrease in degree of crystallinity and an increase in L_a at constant L_c .

The second result suggests a possible presence of POE in the amorphous layer between lamellae. As should be expected, when two polymers do not cocrystallize, σ is independent of POE content, because it has no effect on the lateral surface of the matrix crystallites.

The average value of $\bar{\sigma} = 29 \pm 2$ erg/cm², calculated from the slopes in Figure 5 ($\ln G$ versus $T_m^0/T_c \Delta T \times 10^2$), is almost twice the value calculated by the Thomas–Shaveley equation¹⁵:

$$\sigma = \alpha \Delta H_m^0 b_0 \quad (7)$$

where α is a constant, equal to 0.106, and $b_0 = 4.46$ Å for pure POM.

In the literature several very different values of σ_e and σ , are reported. Mikailov¹ reports $\bar{\sigma}_e$ values ranging from 14.5 to 27.8 erg/cm², depending on T_c ; Pelzbauer gives 95.5

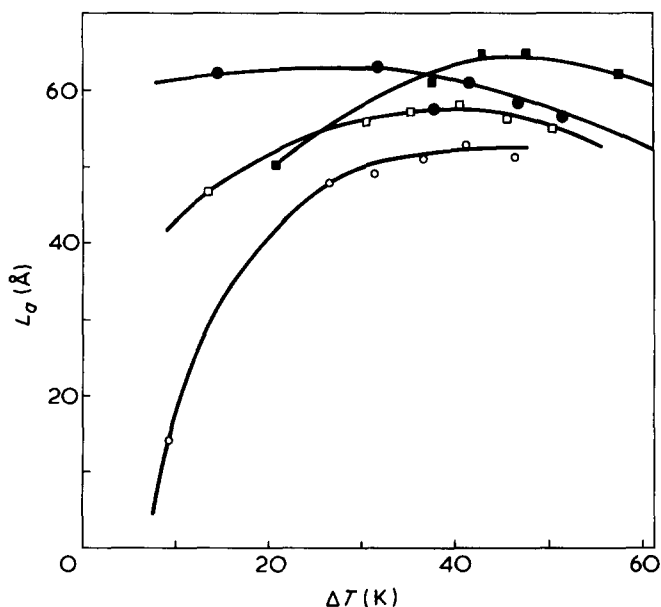


Figure 10 Amorphous phase thickness L_a versus undercooling ΔT for different POMDA samples. \circ , POMDA; \square , POMDA + 1.5% POE; \bullet , POMDA + 3% POE; \blacksquare , POMDA + 5% POE

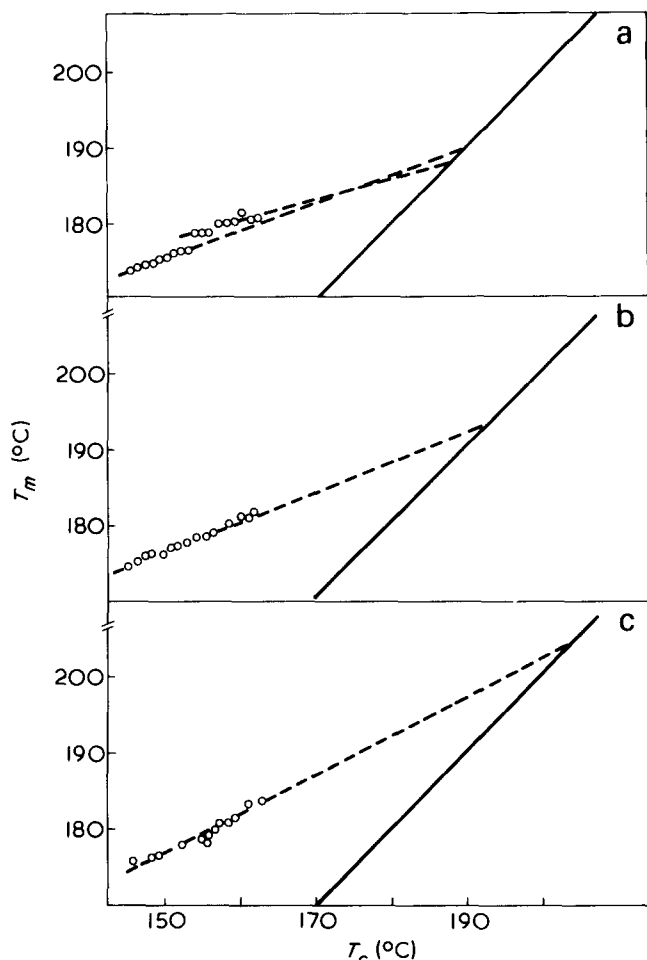


Figure 11 T_m versus T_c plots for reference and mixed POMDA (a) POMDA, $T_m^0 = 189.2^\circ\text{C}$; (b) POMDA + 1.5% POE, $T_m^0 = 193.2^\circ\text{C}$; (c) POMDA + 5% POE, $T_m^0 = 204.4^\circ\text{C}$

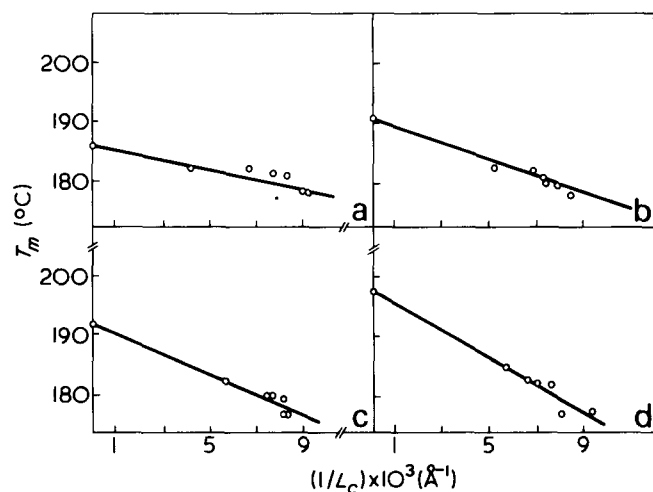


Figure 12 T_m versus $1/L_c$ plots for reference and admixed POMDA. (a) POMDA, $T_m^0 = 186.4^\circ\text{C}$; (b) POMDA + 1.5% POE, $T_m^0 = 190.6^\circ\text{C}$; (c) POMDA + 3% POE, $T_m^0 = 191.6^\circ\text{C}$; (d) POMDA + 5% POE, $T_m^0 = 197.7^\circ\text{C}$

and 183 erg/cm^2 , for T_c above and below 158°C , respectively, using equation (7) to calculate σ^{16} . However, if we also deduce σ from the same equation, then our data fit well with those of Pelzbauer, i.e. we get $\sigma = 17 \pm 2 \text{ erg/cm}^2$, from which we estimate that σ_e ranges from 57 to 154 erg/cm^2 for reference and 5% POE samples, respectively.

Carter and Baer found that, for $T_m^0 = 210^\circ \pm 10^\circ\text{C}$, $\sigma_e = 150 \pm 40 \text{ erg/cm}^2$, and $\sigma_e = 37 \pm 10 \text{ erg/cm}^2$, for $T_m^0 = 182^\circ \pm 2^\circ\text{C}$ ¹³. The trend of σ_e value with T_m^0 , shown in Table 3, in our case agrees with the above results of Carter and Baer.

The folding enthalpy, q_e , has been calculated from equation (8) and Figure 13. q_e increases considerably with increasing POE concentration from 530 to 810 erg/cm^2 , suggesting an increase in the number of molecular segments in the folds of matrix chains, and interactions between POE and POMDA molecular units in the non-crystalline zones.

According to the following equation:

$$\sigma_e = q_e - T_c s_e \quad (8)$$

and, knowing σ_e and q_e , we have deduced the entropy of folding, s_e , at the same undercooling, $\Delta T = 42^\circ\text{C}$. s_e also increases with additive quantity, thus confirming a higher degree of disorder between lamellae.

CONCLUSIONS

(i) POMDA admixed with 5% of POE, and melt-crystallized has a higher radial growth rate of spherulites compared with the other samples.

(ii) POE seems to be rejected, during the crystallization, from the crystalline phase and relegated to amorphous and interspherulitic zones.

(iii) The free energy of formation of a nucleus with critical dimensions, $\Delta\phi$, increases with addition of POE, while the activation energy for the jump rate process, ΔF^* , decreases. The temperature at which these two factors balance each other depends on the POE content.

(iv) The thickness of amorphous zones increases with POE concentration, while the degree of crystallinity decreases: crystal thickness is independent of it.

(v) The additive produces an increase of T_m^0 , ΔH_m^0 and ΔS_m^0 , most probably as a result of a lower defect concentration in the crystalline phase; meanwhile, end-surface, enthalpy and entropy of folding increase with POE concentration, suggesting a larger disorder in the fold region.

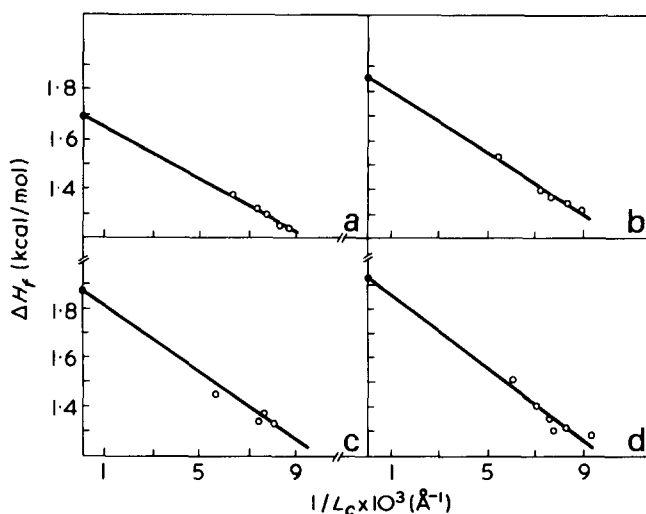


Figure 13 ΔH_m versus $1/L_c$ plots for reference and admixed POMDA. (a) POMDA, $\Delta H_f^0 = 1.69 \text{ kcal/mol}$; (b) POMDA + 1.5% POE, $\Delta H_f^0 = 1.86 \text{ kcal/mol}$; (c) POMDA + 3% POE, $\Delta H_f^0 = 1.87 \text{ kcal/mol}$; (d) POMDA + 5% POE, $\Delta H_f^0 = 1.93 \text{ kcal/mol}$

Table 3 Thermodynamic quantities for POMDA and POMDA-POE

Sample	T_m^0 (°C)		ΔH_m^0 (kcal/mol)		ΔS_m^0 (e.u./mol)	$\sigma\sigma_e$ (erg ² /cm ⁴)	σ_e (erg/cm ²)	σ (erg/cm ²)	q_e (erg/cm ²)	s_e (e.u./mol)
	A	B	A	C						
POMDA	186.4	189.2	1.69	1.70	3.7	966	31	31	530	3.3
POMDA + 1.5% POE	190.6	193.4	1.86	1.86	4.0	1531	56	27	675	4.0
POMDA + 3% POE	191.6	—	1.88	1.87	4.0	—	68	—	735	4.3
POMDA + 5% POE	197.7	204.4	1.93	1.91	4.1	2612	91	29	810	4.6

A, From small-angle X-ray scattering data; B, from T_m versus T_c data; C, from wide-angle X-ray scattering and calorimetric data; D, from G measurements

From this last point we would emphasize that the true value of T_m^0 for POM is very likely to be above 200°C.

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