Spherulitic crystallization in blends of poly(ethylene oxide) and poly(methyl methacrylate)

E. Calahorra, M. Cortazar and G. M. Guzmán
Departmento de Química-Física, Facultad de Ciencias Químicas, Alza, Apdo. 1072, *San Sebastián, Spain*

(*Received* 20 *October* 1981)

The crystallization kinetics of binary blends of poly(ethylene oxide) and poly(methyl methacrylate) were investigated. The isothermal spherulitic growth rates were measured by means of a polarized light microscope. The temperature and composition dependence on the growth rates have been analysed. The temperature range studied was from 44° to 58°C. The introduction of poly(methyl methacrylate) into poly(ethylene oxide) resulted in a reduction of the spherulitic growth rate as the proportion of poly(methyl methacrylate) was increased from zero to 40% by weight. Results have been analysed using the theoretical equations of Boon and Azcue for the growth rate of polymer–diluent mixtures. The experimental results are in good agreement with this equation. The temperature coefficient is negative as is the case in the crystallization of bulk homopolymers.

Keywords Crystallization; polymer–polymer mixtures; kinetics; poly(ethylene oxide); poly(methyl methacrylate); spherulitic growth rates

INTRODUCTION

The kinetics of the isothermal crystallization of poly(ethylene oxide) (PEO) have been the subject of much investigation[1-4].

The crystallization of a polymer can take place from mixtures which contain a low molecular weight diluent as an added ingredient and can also occur from mixtures which contain another polymer as an ingredient.

Recently, research on the effect of an amorphous polymer upon the crystallization of a crystalline polymer has reached some importance[5-10].

In a previous study[11], the polymer pair PEO–poly(methyl methacrylate) (PMMA) was found to be miscible at temperatures near the melting point of the PEO. This polymer pair provides a suitable system for studying the growth kinetics of spherulites, particularly with regard to the influence of an uncrystallizable polymer present in the blend. When two polymers are compatible in the melt, the diffusion of the non-crystallizable polymer plays an important role in the crystallization process.

The present work was undertaken in an attempt to understand the factors which determine the morphology, the rate of crystallization process and the spherulite size of POE crystallized in the presence of an amorphous polymer.

EXPERIMENTAL

Materials

Commercial polymer samples were used. PEO ($\bar{M}_w = 4.00 \times 10^6$) was supplied by Quimidroga S.A. PMMA was obtained from Critesa S.A. ($\bar{M}_w = 9.36 \times 10^4$). The molecular weights were measured by capillary viscometry.

Preparation of the blends

Both polymers were dissolved in chloroform. The ratios of PEO to PMMA in the mixtures refer to their weight proportions. The mixtures of polymers were maintained in solution for a period of two weeks with frequent agitation to assure homogeneity.

Films of PEO, PMMA and their mixtures were cast from chloroform solution onto a glass surface at room temperature; the solvent was allowed to evaporate very slowly under a stream of air. The resulting films were subjected to further drying under vacuum for a week. Average film thickness was about 0.3 mm.

Spherulitic growth rates

To prepare a typical specimen for microscopic examination, a piece about 6 × 6 mm in size was cut out from the film, mounted on a cover slip and covered with a 0.17 mm thick coverslip. The assembly was heated on a Mettler FP 52 hot stage to 80 ± 0.1°C and kept at this temperature for 10 min in order to destroy any traces of crystallinity. The temperature was then suddenly lowered to a desired crystallization temperature T to make the sample crystallize isothermally.

The growth rate of spherulites, $G = \frac{dR}{dt}$ (R = radius of spherulite) is calculated by measuring the size of the spherulites as a function of time during the isothermal crystallization process, taking photomicrographs, at appropriate intervals of time with a camera (Reichert Kam Aut) mounted on the microscope (Reichert Zetopan). The measurements were carried out only on samples having PEO contents above 60% and at crystallization temperatures between 44° and 58°C.

0032-3861/82/091322-03$03.00

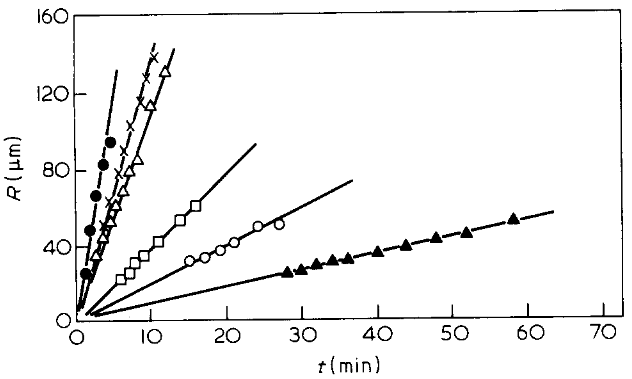

Figure 1 Radius of spherulites vs. time for the composition, on a weight basis, PEO/PMMA 70/30 at indicated crystallization temperatures: ●, 44°C; X, 46°C; △, 48°C; □, 50°C; ○, 52°C; ▲, 54°C

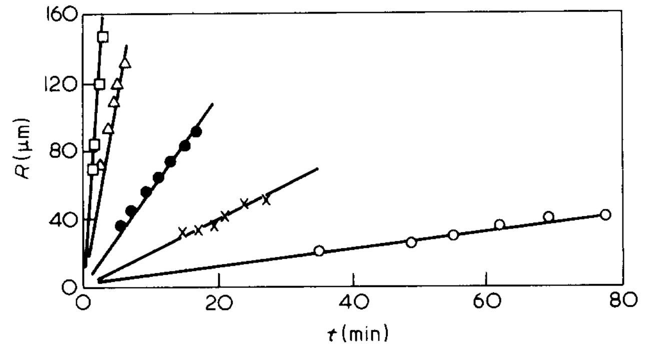

Figure 2 Radius of spherulites as a function of time at crystallization temperature of 52°C for the following compositions: □, 100/0; △, 90/10; ●, 80/20; X, 70/30; ○, 60/40

RESULTS AND DISCUSSION

A typical plot of the radius of the spherulite against crystallization time at different crystallization temperatures is shown in *Figure 1*. A set of straight lines was obtained for each sample. The lines represented the best least-squares fit to the data. The slopes of these lines were G. If the growth rates were influenced by local changes of composition in the melt due to rejection of non-crystallizable species from crystals, the growth rate would decrease with time in direct proportion to the concentration of PMMA at the growth front. It has been observed that the growth rate G does not decrease with time, regardless of the concentration of PMMA. This implies that the rejected non-crystallizable material is trapped between the growing fibrils of the spherulites[9,12].

However, it has been observed that the growth rate G is independent of the size of the spherulite. In *Figure 2* the radius of the spherulite is plotted against time at a given crystallization temperature for several compositions. It can be observed that the slope of the different lines decreases by increasing the proportion of PMMA, therefore there is a reduction in growth rates on addition of PMMA to the crystallizable polymer.

Radial growth rates of spherulites in PEO and its blends with PMMA are given in *Figure 3* as a function of temperature. As can be seen, the dependence of growth rates on temperature for the blends is very similar to that for homopolymers.

The values of the growth rates as a function of composition and crystallization temperature are given in *Table 1*.

Assuming that crystallization is by a single mechanism, polymer crystal growth rates, G, can be described in terms of a classical rate equation[13]:

$$G = G_0 \exp\left(-\frac{\Delta\varphi^*}{KT}\right)\exp\left(-\frac{\Delta F^*}{KT}\right) \quad (1)$$

T being the crystallization temperature, K the Boltzmann's constant, $\Delta\varphi^*$ the free energy required to form a critical sized nucleus from the melt, ΔF^* is the activation energy for transport of crystallizing units across the liquid–crystal interface, and G_0 is a constant.

The free energy of activation ΔF^* is usually estimated by using the William–Landel–Ferry expression for temperature dependence of the viscosity[14], from which the following equation for ΔF^* was derived[15]:

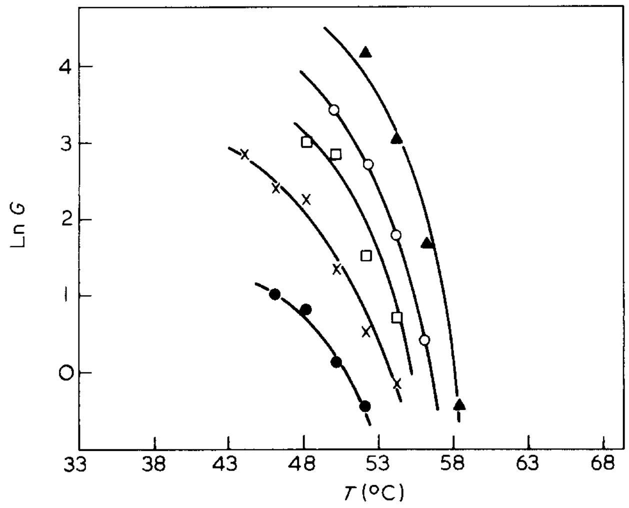

Figure 3 Growth rate of spherulites vs. crystallization temperature for blends PEO/PMMA at indicated compositions: △, 100/0; ○, 90/10; □, 80/20; X, 70/30; ●, 60/40

Table 1 Spherulitic growth rate as a function of composition and crystallization temperature

Composition PEO/PMMA	T (°C)	G (μm min^{-1})
100/0	58.0	0.645
	56.0	5.39
	54.0	21.0
	52.0	64.1
90/10	56.0	1.49
	54.0	5.91
	52.0	14.8
	50.0	34.7
80/20	54.0	2.03
	52.0	4.59
	50.0	17.2
	48.0	21.6
70/30	54.0	0.878
	52.0	1.70
	50.0	3.88
	48.0	9.66
	46.0	11.2
	44.0	17.3
60/40	52.0	0.628
	50.0	1.13
	48.0	2.28
	46.0	2.82

Table 2 Melting points, T_m, and glass transition temperatures, T_g for PEO and its blends with PMMA

Composition PEO/PMMA	T_m (°C)^a	T_g (°C)^b
100/0	67.7	−45
90/10	67.5	−37
80/20	67.0	−33
70/30	66.7	−30
60/40	65.7	−30

^{a} See ref. 11
^{b} Measured by differential scanning calorimetry at 10°C min^{-1} after samples had been quenched from the melt in liquid nitrogen

$$\frac{\Delta F^*}{KT}=\frac{4120}{R(51.6+T-T_g)} \tag{2}$$

where T_g is the glass temperature of the blend.

For polymer–diluent mixtures an additional term must be included to obtain the free energy required to form a critical sized nucleus[16,17]. This additional term, containing $\ln v_2$, represents the probability of selecting the required number of crystalline sequences from a mixture with polymer volume fraction v_2. For a two-dimensional nucleus, $\Delta\varphi^*$ can be expressed as[18]:

$$\frac{\Delta\varphi^*}{KT}=\left[-\frac{4b_0\sigma_u\sigma_e T_m}{KT\Delta H_v(T_m-T)}+\frac{2\sigma_u T_m \ln v_2}{b_0\Delta H_v(T_m-T)}\right] \tag{3}$$

where σ_u and σ_e are interfacial free energies per unit area parallel and perpendicular, respectively, to the molecular chain direction, b_0 is the thickness of a monomolecular layer; ΔH_v is the heat of fusion per unit volume, T_m is the melting point of the crystalline phase in the mixture.

By substituting equations (2) and (3) in equation (1) and multiplying the pre-exponential factor G_0 of equation (1) by v_2, due to the fact that the rate of nucleation is proportional to the concentration of crystallizable units[17], the growth rate of polymer–diluent mixtures can be represented by the following equation[9,18]:

$$G=v_2G_0\exp\left[-\frac{4120}{R(51.6+T-T_g)}\right]$$
$$\times\exp\left[-\frac{4b_0\sigma_u\sigma_e T_m}{K\Delta H_v T(T_m-T)}+\frac{2\sigma_u T_m(\ln v_2)}{b_0\Delta H_v(T_m-T)}\right] \tag{4}$$

Experimental data are usually analysed by plotting α against $\frac{T_m}{T(T_m-T)}$, α being given by:

$$\alpha=\ln G-\ln v_2+\frac{4120}{R(51.6+T-T_g)}-\frac{0.2\,T_m(\ln v_2)}{T_m-T} \tag{5}$$

If the spherulitic growth rate for the blends can be described by equation (4), we will obtain a straight line. The slope of this line is equal to $\frac{4\,b_0\sigma_u\sigma_e}{K\Delta H_v}$. The product $\sigma_u\sigma_e$ can be found from the known values of b_0, T_m and ΔH_v.

Using the empirical relation[19] $\sigma_u=0.1\,b_0\Delta H_v$ (6) and substituting into equation (4) $b_0^3=4.65\times10^{-8}$ cm, $\Delta H_v{}^{20}=2.13\times10^9$ erg cm^{-3} and for T_m and T_g the listed values in *Table 2*, a straight line is obtained in the plot, as shown in *Figure 4*. The correlation coefficient obtained in the least-squares fit is 0.98.

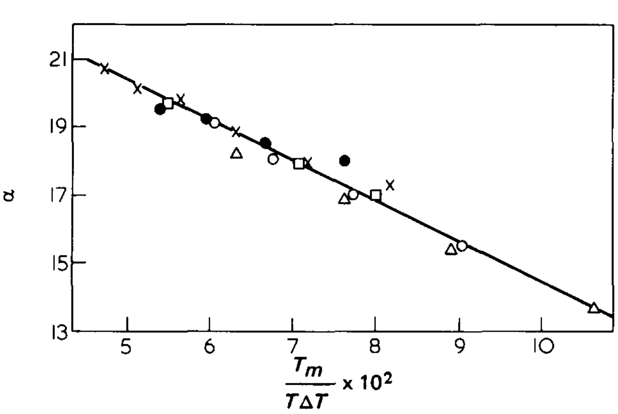

Figure 4 Plot of α against the ratio $T_m/T\Delta T$ for the compositions: △, 100/0; ○, 90/10; □, 80/20; X, 70/30; ●, 60/40

Considering *Figure 4*, from the intercept one obtains $G_0=4.1\times10^5$ cm/s. This result is in good agreement with the theoretical[15] value 5×10^5 cm/s.

From the slope of the line (*Figure 4*) it follows that $\sigma_e\sigma_u$ is 186 erg^2 cm^{-4}. Taking into account the empirical formula, equation (6), for the lateral surface free energy of a crystallite, we obtained a value of 9.90 erg cm^{-2} for σ_u. The σ_e value estimated from the product $\sigma_u\sigma_e$ is 18.8 erg cm^{-2}. The value of σ_e appears to be in reasonable agreement with those obtained by Godovsky[3].

In view of the above mentioned results, it is evident, that for the PEO–PMMA blend, the dependence of growth rate on temperature is very similar to that found in homopolymers. However, the good fit for our results in equation (4) must be accepted with caution, as the high concentration of diluent was not analysed here. Moreover, the range of temperatures analysed here is close to the melting point.

ACKNOWLEDGEMENTS

We thank Mr. D. J. Largo for assistance with the determination of the glass transition temperature.

REFERENCES

1 Mandelkern, L., Quinn, F. A. and Flory, P. J. *J. Appl. Phys.* 1954, **25**, 830
2 Beech, D. R., Booth, C. and Pickles, C. J. *Eur. Polym. J.* 1972, **8**, 799
3 Godovsky, Y. K., Slonimsky, G. L. and Garbar, N. M. *J. Polym. Sci. C* 1972, **38**, 1
4 Maclaine, J. Q. G. and Booth, C. *Polymer* 1975, **16**, 191
5 Riande, E., Fatou, J. G. and Alcazar, J. C. *Polymer* 1977, **18**, 1095
6 Yeh, G. S. Y. and Lambert, S. L. *J. Polym. Sci. A-2* 1972, **10**, 1183
7 Berghmans, H. and Overbergh, N. *J. Polym. Sci. A* 1977, **15**, 1757
8 Wang, T. T. and Nishi, T. *Macromolecules* 1977, **10**, 2
9 Ong, C. J. and Price, F. P. *J. Polym. Sci. C* 1978, **63**, 59
10 Aref-Azar, A., Hay, J. N., Marsden, B. J. and Walker, N. *J. Polym. Sci. A-2* 1980, **18**, 637
11 Cortazar, M., Calahorra, E. and Guzmán, G. M. *Eur. Polym. J.* in press
12 Keith, H. D. and Padden, F. J. Jr. *J. Appl. Phys.* 1964, **35**, 1286
13 Turnbull, D. and Fisher, J. C. *J. Chem. Phys.* 1949, **17**, 71
14 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
15 Hoffman, J. D. *Soc. Plast. Eng. J.* 1964, **4**, 315
16 Mandelkern, L. *J. Appl. Phys.* 1955, **26**, 443
17 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964, pp. 273
18 Boon, J. and Azcue, J. M. *J. Polym. Sci. A-2* 1968, **6**, 885
19 Thomas, D. G. and Staveley, L. A. K. *J. Chem. Soc.* 1952, 4569
20 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, New York, 1976