Miscible polymer blends: 2. Kinetics of the high pressure crystallization of poly(ethylene oxide) and poly(vinylidene fluoride) in blends with poly(methyl methacrylate)

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(Received 6 January 1988; revised 30 July 1989; accepted 20 November 1989)

The isothermal crystallization of poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF) in blends with poly(methyl methacrylate) (PMMA) has been studied in the pressure range 25.2–100.6 MPa. The energy parameters of nucleation have been calculated for pure polymers and their blends, and the bounds of the kinetic regimes of crystallization have been determined.

(Keywords: poly(ethylene oxide); poly(vinylidene fluoride); poly(methyl methacrylate); isothermal crystallization; nucleation; pressure; crystallization regime)

INTRODUCTION

Studies of isothermal crystallization of matter involve quantitative analysis of the kinetics of the process and calculation of energy parameters of nucleation from the crystallization models available. It has been shown[1,2] that crystallization of polymeric materials is accompanied by the chain folding mechanism, while the increasing pressure leads to alteration of the kinetic and energy parameters of the process; crystallization under pressure may bring along polymorphic and 'topomorphic'[3] transformations of polymers. Recently, with the increasing number of polymer blends studied, attention has been drawn to miscible polymer pairs, i.e. polymer pairs forming solutions at the molecular (segment) level. The systems poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF)/PMMA are traditional representatives of this class of polymer blends; their crystallization, phase composition and morphology have been studied in detail[4–8]. However, some aspects remain to be examined concerning the named systems as well as the whole class of polymers thermodynamically miscible in the melt. For example, it is not yet clear whether the crystallization of PEO and PVDF occurs in the homogeneous melt or in the heterogeneous melt; in what way crystallization in the blends of thermodynamically miscible polymers is affected by specific interactions between the melt components and the applied pressure; and what is the effect of the amorphous miscible polymer on the crystallization kinetics. In this paper we try to throw some light on these problems.

EXPERIMENTAL

The samples of polymers used throughout this work were PEO-2 ($M_n = 2 \times 10^3$), PEO-125 ($M_n = 125 \times 10^3$), PVDF ($M_n = 550 \times 10^3$) and amorphous component PMMA ($M_n = 500 \times 10^3$). The characteristics of the polymers and the technique of preparing blends have been described elsewhere[9].

The isothermal crystallization of PEO, PVDF and their blends with PMMA under high pressure was studied with the use of a modified high pressure dilatometer. The procedure was as follows. A sample of the polymer, or of the blend, was preliminarily heated in the chamber of the dilatometer at 25.2 MPa for 20 min. At the crystallization pressures 25.2, 50.3, 75.5 and 100.6 MPa, the overheating temperature was increased proportionally with $T_m(P)$ (ref. 10), where T_m is the melting temperature. At $P = 25.2$ MPa, the PEO samples were exposed to 373 K, the PVDF samples to 488 K. The melted sample was then cooled to the chosen crystallization temperature T at normal pressure, kept there for 20 min, and loaded instantaneously to the crystallization pressure. A range of crystallization temperatures was chosen in such a way that it would provide an induction period $\geqslant 30$ s. During the experiment, the variation of the sample height with time was recorded. The maximum determination error for the crystallization half-period $\tau_{0.5}$ was 3 min, that for crystallization temperature was 0.5 K. For a given composition, isothermal crystallization was studied on three samples.

RESULTS AND DISCUSSION

For all the samples studied, the dependence of the crystallization half-period on overcooling temperature, $1/T\Delta T$ ($\Delta T = T_m^0 - T$, where T_m^0 is the equilibrium temperature of melting PEO, PVDF crystallites), has been obtained at four different pressures. *Figure 1* shows, in a semilogarithmic plot, these dependences for the systems PEO-2/PMMA and PVDF/PMMA. The curves are satisfactorily approximated by straight lines. For PEO-2/PMMA, the values of $\tau_{0.5}$ at $w = 0.2$ and $w = 0.4$

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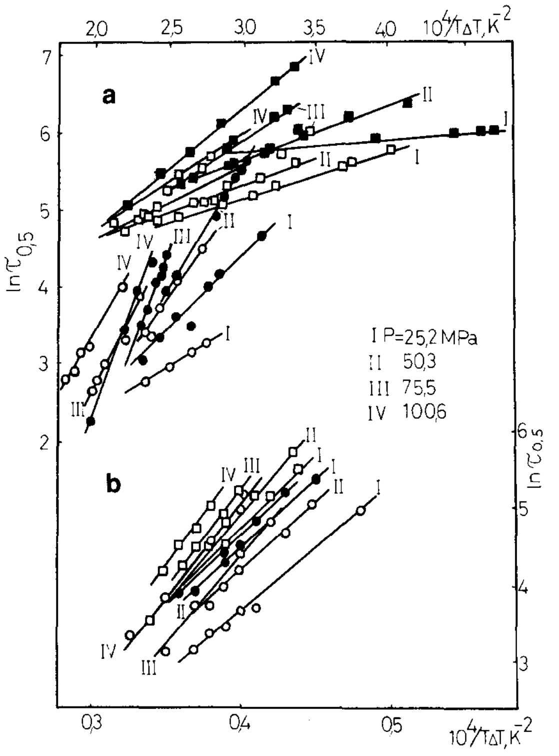

Figure 1 Temperature dependence of the half-period of crystallization for (a) PEO-2/PMMA and (b) PVDF/PMMA: ○, blends with $w=0$; ●, 0.1; □, 0.2; ■, 0.4

are a few orders of magnitude higher than those for pure PEO-2 at the same overcooling. The composition with $w=0.1$, however, crystallizes faster than PEO-2. An increase in crystallization pressure leads to an increase in $\tau_{0.5}$ at any composition, and shifts the crystallization temperature range towards greater overcooling. For the blends PEO/PMMA and PVDF/PMMA, $\tau_{0.5}$ grows with increasing w and crystallization temperature.

Kinetic data has been analysed in terms of the bi-exponential equation

$$G = G_0 \exp(-\Delta E/kT)\exp(-\Delta F/kT) \qquad (1)$$

where G_0 is the pre-exponential (frequency) factor, $\Delta E/kT$ is the activation energy of the molecular transfer through the melt–crystal interface, $\Delta F/kT$ is the free nucleation energy for a crystal of a critical size and T is a crystallization temperature. To account for the inconstancy of the values of $\Delta F/kT$ in the temperature, pressure and composition ranges under study, we have used the approximation $\Delta E/kT = B/(T-T_0)$, where B and T_0 are the parameters of the Vogel–Tamman equation. For PEO-2, PEO-125 and PVDF, in the temperature range $T<T_m$, the values of B and T_0 determined by measuring the Newtonian viscosity of the melt at normal pressure[11] are: $B=840$ K, $T_0=180$ K; $B=810$ K, $T_0=180$ K; $B=3250$ K, $T_0=162$ K, respectively. Taking into account inverse proportionality between the parameter B and the bulk thermal expansion coefficient α[1], we calculated the composition dependence of B based on our earlier experiments[9]. The composition and pressure dependences of T_0 were calculated on the assumption that $T_0/T_g=$ const. (where T_g is the glass transition temperature of the polymer) and $dT_0/dP = dT_g/dP$, where dT_g/dP was determined from Ehrenfest's second equation[7].

From analysis of the temperature dependences of the kinetic lines we calculated, setting $\ln G = -\ln \tau_{0.5}$[1,2], the slopes $W = ab_0\sigma_1\sigma_2 T/\Delta H_v$ in the coordinates $-\ln \tau_{0.5} + B/(T-T_0)$ *versus* $10^4/T\,\Delta T$ (*Figure 2*), where $a=2$ or 4 depending on the crystallization regime (see below), and σ_1 and σ_2 are the lateral and surface free energy of the crystallites, respectively. For PEO and its blends, $b_0 = 4.65 \times 10^{10}$ m and $\Delta H_v = 2.64 \times 10^5$ kJ m^{-3} (ref. 11); for PVDF and its blends, $b_0 = 4.96 \times 10^{-10}$ m and $\Delta H_v = 1.99 \times 10^5$ kJ m^{-3} (ref. 11). For T_m^0 for PEO-2 and its blends, we made use of the experimental values of T_m, since in the temperature range under study PEO-2 is crystallized in a linear conformation[10]. For PEO-125, setting $\Delta T_m^0 = \Delta T_m$ and $\Delta T_m^0/dP = dT_m/dP$, we used $T_m^0 = 348$ K[11]. For PVDF we used $T_m^0 = 481$ K.

The value $\sigma_1 = 0.1 b_0\,\Delta H_v$, required for calculation at high pressure, was found from the formula $\sigma_1 = \text{const.} \times (V_{cr}/V_a)^4$, where V_{cr} and V_a are the specific volumes of the crystal and melt, respectively, which were evaluated in our earlier experiments[9]. The value of V_{cr} was adopted according to the additivity rule for 100% crystallinity of PEO and PVDF.

Table 1 presents the results obtained from experimental data. For pure PEO-2, PEO-125 and PVDF, σ_2 has, at $P_{cr} = 25.2$ MPa, the values of 18.5×10^{-3}, 22.9×10^{-3} and 112×10^{-3} kJ m^{-3}, respectively, which, with allowance for measurement errors and the dependence $\sigma_2(P)$, is in good agreement with the previous results[1].

At $w=0.2$ and $w=0.4$, the blend PEO-2/PMMA exhibits kinetic lines of a smaller slope and smaller σ_2, by factors of 2.3 and 2.6, respectively. A decrease in σ_2, in principle, should lead to a faster crystallization at the expense of a lowering of the energy barrier of nucleation ($\Delta F/kT$). However, as has been mentioned (see *Figure 1*), at $w=0.2$ and $w=0.4$, the system PEO-2/PMMA undergoes a slower crystallization than pure PEO-2. It has been shown[12] that, in the system PEO/PMMA, as well as in the blends containing PMMA with molecular weight lower than critical, $\sigma_2(w)$ decreases just as in our case. All these data show that, for the system PEO-2/PMMA, a decrease in $\sigma_2(w)$ at $w=0.2$ and 0.4 can be explained by either the absence of the entanglement

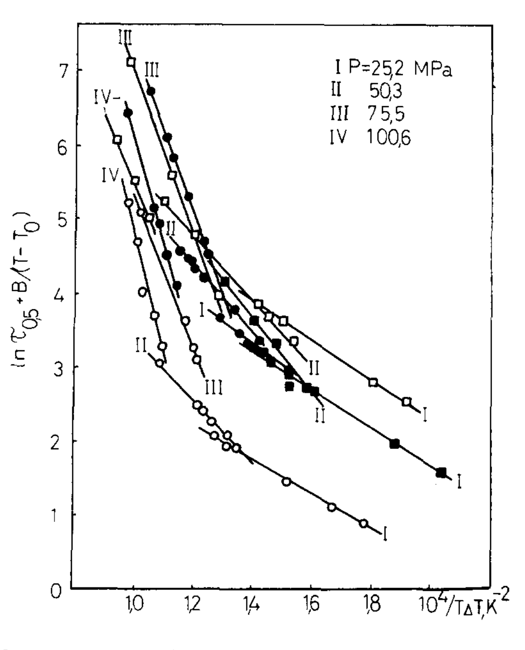

Figure 2 Temperature dependence of $\ln \tau_{0.5} + B/(T-T_0)$ for the blends PEO-125/PMMA: ○, blends with $w=0$; ●, 0.1; □, 0.2; ■, 0.4

Table 1 Crystallization parameters for PEO and PVDF in blends with PMMA at high pressure

w	P_{cr} (MPa)	$T_m^0(P)$ (K)	B (K)	T_0 (K)	$-W \times 10^{-4}$ (K^2)	$\ln G_0$	Z	σ_1 (10^{-3} J m^{-2})	σ_2 (10^{-3} J m^{-2})
PEO-2/PMMA^a									
0	25.2	326.4	1050	182	1.76	9.54	2.74	11.5	18.5
	50.3	330.3	1211	184	3.75	11.94	2×10^{-6}	10.7	21.2
	75.5	333.7	1357	186	5.23	18.06	2×10^{-11}	10.4	30.9
	100.6	337.2	1458	188	8.03	23.21	2×10^{-20}	10.0	48.2
0.1	25.2	326.4	1544	182	2.63	14.62	4×10^{-3}	10.7	14.9
	50.3	330.3	1607	184	3.70	17.25	2×10^{-6}	10.4	21.5
	75.5	333.7	1675	186	5.60	22.09	2×10^{-12}	10.2	33.1
	100.6	337.2	1906	188	6.51	24.95	9×10^{-16}	10.0	39.0
0.2	25.2	326.4	1607	183	1.07	9.60	48.57	10.0	13.0
	50.3	330.3	1712	185	1.32	10.76	1.17	9.7	16.4
	75.5	333.7	1831	187	2.39	13.96	4×10^{-4}	7.2	20.5
	100.6	337.2	2316	189	2.45	17.43	1×10^{-7}	6.2	23.2
0.4	25.2	323.4	1810	186	1.37	11.78	0.91	8.7	9.6
	50.3	327.1	1920	188	2.16	14.41	1×10^{-3}	8.6	15.3
	75.5	330.7	2187	190	2.52	17.38	4×10^{-7}	8.5	18.0
	100.6	334.2	2500	192	3.07	21.05	4×10^{-7}	8.5	21.9
PEO-125/PMMA^b									
0	25.2	353.4	977	182	2.38	5.09	332	11.5	22.9
	50.3	358.8	1143	184	4.13	7.55	1.86	11.3	40.3
	75.5	364.2	1308	186	11.18	16.78	3×10^{-2}	11.1	54.2
	100.6	369.6	1475	188	16.90	21.71	3×10^{-6}	10.8	83.0
0.1	25.2	353.0	1048	206	3.04	7.56	87	11.1	27.4
	50.3	358.4	1214	208	5.28	10.78	0.84	10.4	50.8
	75.5	363.8	1381	210	10.85	18.06	3×10^{-2}	10.1	53.7
	100.6	369.0	1548	212	13.78	19.76	1×10^{-4}	9.7	71.0
0.2	25.2	352.7	1152	206	2.65	7.62	84	10.1	26.2
	50.3	358.0	1317	208	4.13	9.73	0.65	9.7	42.6
	75.5	363.4	1486	210	10.40	17.23	2×10^{-2}	9.7	53.6
	100.6	368.5	1651	212	13.58	19.00	1×10^{-4}	9.6	70.7
0.4	25.2	352.4	1187	206	2.55	6.81	36	9.1	28.0
	50.3	357.6	1353	208	5.60	11.46	2×10^{-3}	9.1	51.5
	75.5	362.8	1520	210	–	–	–	9.0	–
	100.6	368.0	1684	212	–	–	–	9.0	–
PVDF/PMMA^c									
0	25.2	490.1	3450	169	25.09	19.40	4×10^{-2}	12.6	112
	50.3	499.1	3645	176	27.85	20.58	1×10^{-3}	11.6	133
	75.5	508.2	3842	184	39.72	25.74	6×10^{-4}	11.4	137
	100.6	517.2	4040	191	49.66	29.65	2×10^{-10}	11.2	237
0.1	25.2	486.1	5359	171	29.01	27.93	1×10^{-3}	12.0	138
	50.3	495.1	6254	178	32.64	32.54	4×10^{-5}	11.3	161
	75.5	504.2	7153	186	39.04	37.83	1×10^{-7}	10.9	197
	100.6	517.2	8038	193	50.02	44.94	1×10^{-11}	10.7	252
0.2	25.2	482.1	5950	172	28.23	30.16	5×10^{-3}	12.5	130
	50.3	491.1	6845	179	29.69	33.71	4×10^{-4}	11.5	145
	75.5	500.2	7153	187	31.08	35.01	9×10^{-5}	11.3	152
	100.6	509.2	8626	194	47.31	46.32	6×10^{-10}	11.1	232

[a] Z for $1/T\,\Delta T = 2.8 \times 10^{-4}$ K^{-2}

[b] Z for $1/T\,\Delta T = 1.3 \times 10^{-4}$ K^{-2}

[c] Z for $1/T\,\Delta T = 4 \times 10^{-5}$ K^{-2}

network[1] in the crystallizing PEO-2 or the 'orientation' effect due to specific interactions between the hydroxyl end-groups of PEO-2 and carbonyl groups of PMMA, which do not restrict the mobility of the major parts of the PEO-2 chains. One of these factors, or their combined effect, may eventually result in a decrease in $\sigma_2(w)$.

For the system PEO-2/PMMA with $w = 0.1$, an increase in W, and correspondingly in σ_2, may be explained, to our thinking, by maximum levelling of the specific interactions between PEO-2 and PMMA. In this situation, an increase in the free energy of the end planes of the growing PEO-2 crystallites is accompanied not by an increase but by a decrease in the crystallization half-period $\tau_{0.5}$.

For the blends PEO-125/PMMA and PVDF/PMMA, with measurement errors taken into account, a dependence $\sigma_2(w)$ has not been found. To our thinking, this result is not at variance with the composition dependence of the thermodynamic characteristics of the melts we have established earlier[9], since the characteristics of the crystalline phase (lattice parameters, melting heat) remain unchanged.

For all the blends studied, increasing pressure causes an increase in the kinetic line slopes W and, correspondingly, the parameter σ_2. This may be explained by variations of the conformation folds[13] due to an increase in the melt density, rather than by those of the lattice constants, or by the enthalpy and entropy of melting. It is evident that, similarly to the case of *cis*-isoprene[13], the PEO-125 and PVDF folds have two conformations corresponding to the two local free energy minima, respectively. An increase in pressure, then, leads to a gradual transition of part of the folds from one conformation to the other. For the PEO-2-based blends, the $\sigma_2(w)$ dependence is evidently due to variations in the structure of the edge planes of the crystal nuclei.

For the PEO/PMMA blends studied, the slopes of the pressure dependence coefficients $\mathrm{d}\ln\sigma_2/\mathrm{d}P$ lie within the range $(1.1\text{–}1.7)\times10^{-2}\,\mathrm{MPa}^{-1}$. The slopes increase as w decreases, running through the current values of 0.4, 0.2, 0.1, 0 in the system PEO-2/PMMA; then follow PEO-125/PMMA. The isothermal compressibility coefficients of the melt vary with composition similarly[9]. The higher values of $\mathrm{d}\ln\sigma_2/\mathrm{d}P$ figured out for the system PEO-125/PMMA evidently reflect the difference between the end plane structure of PEO-2 and that of PEO-125. For the blends PVDF/PMMA, $\mathrm{d}\ln\sigma_2/\mathrm{d}P=6.4\times10^{-1}\,\mathrm{MPa}^{-1}$.

Table 1 also gives the values of Louritzen's criterion[14]

$$Z\approx10^3(L/2b_0)^2\exp(ab_0\sigma_1\sigma_2T^0_{\mathrm{m}}/\Delta H_{\mathrm{v}}T\,\Delta T) \qquad (2)$$

where L is the thickness of the lamellae. This criterion is of primary importance, since it enables one to judge the regime of the polymer crystallization, even when the temperature dependence of $\ln G$ has no fracture surfaces; regime I recognized at $Z\leqslant0.01$, regime II at $Z>1$. In crystallization under kinetic regime I, each surface nucleation event has a short duration, so that a new lamella forms on the substratum before a new nucleus appears. As a result, the growth rate, G, is proportional to the nucleation rate and $a=4$ (see Reference 2 and the foregoing discussion). Kinetic regime II takes place when the nucleation rate is so high that multiple nuclei appear on the substratum surface before the surface is completely filled with the growing lamellae; $a=2$.

The thickness of the lamellae in PEO has been determined from the large period values derived from the small angle X-ray diffraction studies[10]; for PVDF, we have taken $L=16.5\,\mathrm{nm}$[14]. It has turned out that, in pure PEO-2, an increase in P_{cr} leads, starting from $P_{\mathrm{cr}}=50.3\,\mathrm{MPa}$ and higher, to transition from regime II to regime I. The pressure increase shifts the temperature range of isothermal crystallization to the region of stronger overcooling, which may be explained by a decrease in the rate of secondary nucleation. resulting from the growth of the energy barrier ($\Delta F/kT$) and density of the melt. This leads to a shift of the temperature boundary between regimes I and II towards lower temperatures (*Figure 3*).

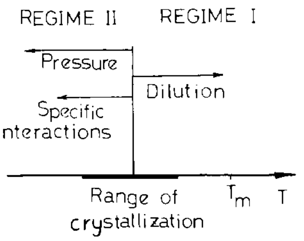

Figure 3 Schematic diagram of the influence of some thermodynamic quantity on the position of the temperature boundary between crystallization regimes I and II

For PEO-2/PMMA of compositions $w=0.2$ and $w=0.4$, the regime II to I transition occurs at a higher pressure ($P_{\mathrm{cr}}=75.5\,\mathrm{MPa}$), which is equivalent to a temperature boundary shift towards higher temperatures. The system PEO-2/PMMA of composition $w=0.1$, in the temperature and pressure ranges studied, undergoes crystallization under regime I only. Evidently, the specific PEO-2–PMMA interactions lead to a slowing down of the secondary nucleation rate, which is equivalent to a shift of the crystallization interval to the region of milder overcooling.

In PEO-125, the regime II to I transition takes place at a higher crystallization pressure ($P_{\mathrm{cr}}=75.5\,\mathrm{MPa}$) than in PEO-2. The explanation is evidently that, in PEO-125, the nucleation rate is lower than that of the substratum filling. In the blends $w=0.1$, 0.2 and 0.4, the regime I to II transition shifts are the same as in pure PEO-125, which is probably due to the fact that the parameter σ_2 is independent of composition.

A characteristic feature of pure PVDF is that, in the range of temperatures and pressures studied, it crystallizes in regime I. The same is true for the blends $w=0.1$ and $w=0.2$, since here, by analogy with PEO-125, σ_2 is independent of composition.

CONCLUSIONS

From the results of the high pressure studies of isothermal crystallization of PEO and PVDF in blends with PMMA we reach the following conclusions.

For PEO and PVDF, a decrease by a few orders of magnitude in the crystallization rate is proportional to the amount of the non-crystallizing PMMA in the blends, i.e. the crystallization of PEO and PVDF in blends occurs from the macroscopically homogeneous melt[9].

The existence of specific interactions between the components of the blends[9] leads to a growth of the nucleation energy barrier. However, the expected slowing down of the crystallization process does not take place. The independence of the parameter σ_2 of composition in the blends of PEO-125 and PVDF with PMMA is evidently explained by the existence of the entanglement network in the overcooled melt of the crystallizing polymers. For the blends PEO-2/PMMA, the composition dependence of the parameter σ_2 does exist: σ_2 decreases as w increases.

Increasing pressure leads to a slowing down of crystallization in all the blends studied, due to a change in the edge plane structure of the crystal nuclei as a result of the increasing density of the melt. In this case, the specific interactions between the blend components make no significant contributions to the magnitude of the slowing down of crystallization.

In the temperature and pressure range under consideration, the introduction of a non-crystallizing component shifts the temperature boundary between the crystallization regimes I and II towards mild overcooling. The increasing crystallization pressure, as well as superposition of the specific interaction effects, may lead to the opposite results: to the shift of the regime I–II boundary towards the region of stronger overcooling.

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