Thermochimica Acta, 137 (1988) 115–121
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRYSTALLIZATION KINETICS OF BINARY POLYMER BLENDS

E. PEDEMONTE, A. TURTURRO and G. SEMINO

Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, 16132 Genova (Italy)

(Received in final revised form May 2, 1988)

ABSTRACT

Isothermal crystallizations of several polymer blends with one regular component are studied as a function of composition, by differential scanning calorimetry. The overall crystallization rate constant K is calculated according to the Avrami equation. The miscibility between the crystallizable and the amorphous polymer strongly influences the results; K has the same value in both the pure polymer and mixtures only when no specific interaction is active in the liquid state.

INTRODUCTION

It is well known that the crystallization of a macromolecular component from a binary polymer mixture generates a pure ordered phase, in which only the crystallizable polymer is present. Consequently, interactions between structural elements of the different macromolecules located in the amorphous phase are confined to the interlamellar regions [1-3].

Evaluation of miscibility is not easy [3]. From a qualitative point of view, determination of the glass transition temperature is often hindered by both the small amount of amorphous phase in the blend and superposition of other phenomena, such as annealing and melting.

On the other hand, quantitative evaluation of the depression of the equilibrium melting temperature requires the use of the Hoffman-Week procedure, which is currently a matter of debate. Secondary crystallization and crystal perfection actually take place both at the crystallization temperature, T_C, after the primary crystallization, and between T_C and the melting temperature,

0040-6031/88/$03.50

T_m, during the scanning. Therefore, T_m may not correspond to the fusion of the crystals originally present in the specimen, and the correlation with T_c would not be straightforward.

The aim of this paper is to investigate the influence of a polymer on the isothermal crystallization rate of another macromolecular component of a binary mixture [4,5], with a view to proposing a qualitative method capable of evidencing any specific interaction in the amorphous regions. A preliminary approach to the evaluation of the interaction parameter from these data is also indicated.

EXPERIMENTAL

Materials

Our measurements were mainly performed on commercial products free from additives and used without further purification and fractionation.

Poly(ε-caprolactam), PA6, supplied by Enichem Tecnoresine, Italy, as Nivionplast 2.7, was characterized by GPC analysis. Average values of $M_n=20.4\times10^3$ and $M_w=68.9\times10^3$ were calculated.

Poly(vinylidenfluoride), PVDF, was supplied by Solvay, Italy, as Solef 2010 ($M_n=68.0\times10^3$; $M_w=152.0\times10^3$); poly(vinylpyrrolidone), PVP, by Serva ($M_v= 350.0\times10^3$) and poly(carbonate), PC, by Enichem Tecnoresine, Italy, as Synvet 201 ($M_n=20.0\times10^3$).

Poly(ethyleneoxide), PEO, and poly(propyleneoxide), PPO, were laboratory products from Fluka and Polysciences respectively. The molecular weights were $M_v= 6.0\times10^3$ and 3.0×10^3 for PEO (in the following PEO 6K and PEO 3K) 4.0×10^3, 2.0×10^3 and 400 for PPO (in the following PPO 4K, PPO 2K and PPO 400).

Specimens preparation

PVDF/PVP films, about 0.5 mm thick, were prepared by dissolving the polymers in a common solvent (N,N-dimethylformamide) and casting the solutions at room temperature with fast evaporation.

PEO/PPO mixtures were prepared from dilute solutions in toluene by freeze-drying evaporation; PA6/PC mixtures by melt blending [6].

Measurements and technique

The isothermal crystallizations were carried out with a Perkin Elmer DSC

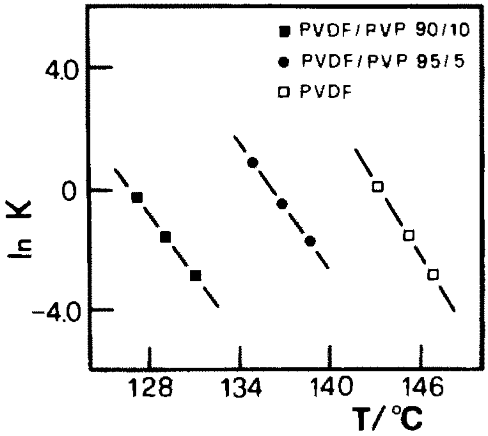

Fig.1. Kinetic data of PVDF/PVP blends with different compositions.

2 calorimeter, equipped with the model 3600 Data Station. The specimen was rapidly cooled to the selected temperature after 5 mins above the melting temperature of the crystallizable component: 267 °C for PA6/PC, 207 °C for PVDF/PVP and 87 °C for PEO/PPO.

The crystallization data were processed with the well-known Avrami equation [7]:

$$x = 1 - \exp(Kt^n) \qquad (1)$$

where :
x = degree of crystallity
K = overall rate constant, which includes both growth and nucleation rate
n = Avrami index, depending on the nucleation and growth mechanism

RESULTS AND DISCUSSION

Completely miscible components-PVDF/PVP

It is well known that PVDF and PVP are completely miscible over the whole range of composition, irrespective of their molecular weights, in the molten and solid amorphous states [8].

PVP hinders the PVDF phase transition. The latter ceases to crystallize when the PVP content of the mixture exceeds 40% [9]; our data (Table 1) show that the PVDF overall crystallization rate constant is depressed by several orders of magnitude by few per cent of amorphous component. The semilog plot in Fig. 1

TABLE 1

Kinetic data of PVDF/PVP blends with different compositions.

	PVDF		PVDF/PVP 95/5		PVDF/PVP 90/10	
$T_c/°C$	n	K	n	K	n	K
127	-	-	-	-	3.0	0.85
129	-	-	-	-	2.7	0.22
131	-	-	-	-	2.7	0.060
135	-	-	2.6	2.6	-	-
137	-	-	2.6	0.65	-	-
139	-	-	2.7	0.16	-	-
143	2.6	1.2	-	-	-	-
145	2.5	0.21	-	-	-	-
147	2.0	0.059	-	-	-	-

K in $\min^{-n}$

strongly underlines this behaviour.

These results indicate that segregations of crystalline phases from polymer-polymer mixtures are greatly impeded when strongly specific interactions are active in the amorphous: considerable lowering of the overall crystallization rate constant can be regarded as an index of miscibility between the components.

The data in Table 1 can be plotted versus $1/T_c(T_m^o - T_c)$ using the T_m^o of PVDF; the straight lines of mixtures can superimpose the pure polymer one by traying, leading to values of supercooling as a function of concentration. A value of $\chi_{12} = -6.0$ was found for the interaction parameter with the Flory eqn. (2)

$$(T_m^o - T_{m,b}^o) = -T_m^o\,(V_{2u}/V_{1u})\,(RT/\Delta H_2)\,\chi_{12}\,\phi_1^2 \qquad (2)$$

where:

T_m^o = equilibrium melting temperature of pure PVDF

$T_{m,b}^o$ = equilibrium melting temperature of PVDF/PVP blend

V_{2u}, V_{1u} = molar volume of repetition unit of PVDF and PVP

ΔH_2 = heat of fusion of PVDF

ϕ_1 = volume fraction of PVP

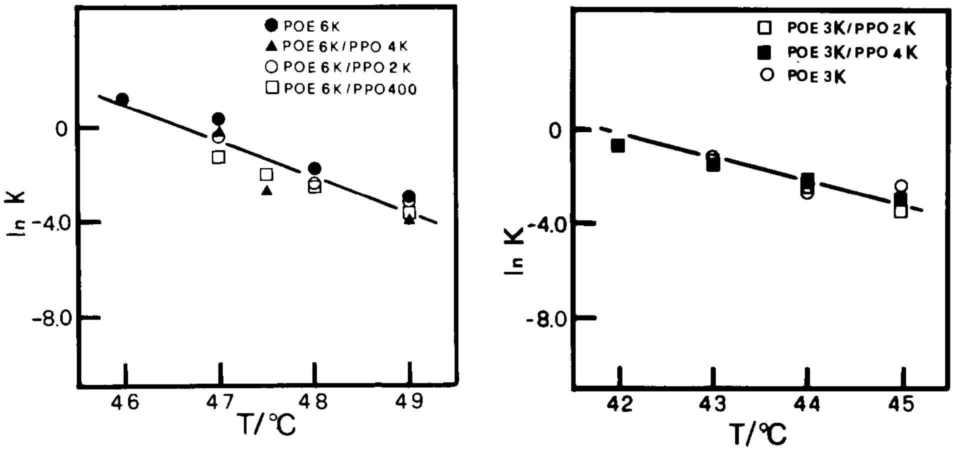

Fig. 2. Kinetic data of PEO/PPO 90/10 blends with different molecular weights of the components.

TABLE 2

Kinetic data of POE 6K/PPO 90/10 blends with several PPO molecular weights.

	POE 6K		PEO6K/PPO4K		POE6K/PPO2K		POE6K/PPO400	
T_c/°C	n	K	n	K	n	K	n	K
46.0	2.4	3.2	-	-	-	-	-	-
47.0	2.1	1.4	2.0	0.73	1.9	0.65	1.8	0.28
47.5	-	-	-	-	-	-	2.2	0.13
48.0	1.8	0.15	2.1	0.11	1.8	0.26	1.9	0.08
48.5	-	-	-	-	1.8	0.08	-	-
49.0	1.9	0.05	1.9	0.02	2.1	0.04	2.0	0.03

K in min^{-n}

Completely immiscible components-PEO/PPO

Tables 2 and 3 and Fig. 2 summarize the kinetic data for five blends obtained by mixing two samples of PEO with PPO of different molecular weights. The results show that the PEO overall crystallization rate constant has the same values in the pure homopolymer and blends containing large amounts of PPO. This behaviour does not depend on the molecular weights of the components.

Since recent papers have shown that PEO and PPO are completely immiscible

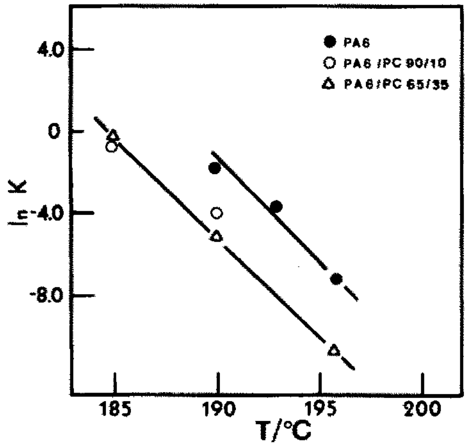

Fig. 3. Kinetic data of PA6/PC blends with different compositions.

TABLE 3

Kinetic data of POE 3K/PPO 90/10 blends with several PPO molecular weights.

	POE3K		POE3K/PPO4K		POE3K/PPO2K	
T_c/°C	n	K	n	K	n	K
42	-	-	1.8	0.58	-	-
43	2.1	0.34	1.9	0.28	1.7	0.27
44	2.3	0.07	1.7	0.11	2.0	0.10
45	1.7	0.10	1.7	0.05	2.0	0.03

K in min^{-n}

in both the molten and the solid state [10], our results lead to the conclusion that the crystallization of a polymer mantains its own characteristic when no interaction with a second polymer is active in the amorphous.

PA6/PC mixtures

Finally, if we look at PA6/PC mixtures (Fig. 3), we observe a substantial reduction of the PA6 overall crystallization rate when the amorphous polymer is present. One might be tempted to conclude that PA6 and PC are partially miscible, but the morphological analysis clearly shows that they are immiscible [11].

It must be realized that preparation of the blends by melt extrusion involves both a molecular degradation and the formation of a small amount of PA6/PC copolymers that acts as an interfacial agent, leading to a partial solubility of the lowest molecular species of PC in the molten PA6.

CONCLUSIONS

Results with completely miscible (PVDF/PVP) and completely immiscible (PEO/PPO) binary blends show that the crystallization behaviour of the regular component depends on the strength of the active interactions between the structural elements of the two types of macromolecules. The overall rate constant has exactly the same values in both the mixtures and the pure polymer when no interaction takes place in the amorphous, but is lowered by several orders of magnitude when specific interactions occur. Therefore the overall rate constant, which can be evaluated by calorimetry quite easily, can be regarded as a qualitative index of the miscibility of crystallizable polymers.

REFERENCES

1 D.R. Paul, Proceeding ACS 187th Meeting, St. Louis, 1984, 1-10.
2 D.R. Paul, in D.J. Walsh, J.S. Higgins and A. Maconnachie (Eds.), Polymer Blends and Mixtures, Nato ASI Series E89, Nijhoff, Dordrecht, 1985, 1-23.
3 D.J. Walsh and S. Rostami, Adv. Polym. Sci., 70 (1985) 119-169.
4 D.R. Paul and J.W. Barlow, in D. Klempner and K.C. Frisch (Eds.), Polymer Alloys II, Plenum Press, New York, 1980, 239-253.
5 P. Runt and L.M. Martynowicz, in D.R. Paul and L.H. Sperling (Eds.), Multicomponent Polymer Materials, ACS, Washington (1986), 111-123.
6 G. Gattiglia, A. Turturro and E. Pedemonte, J. Appl. Pol. Sci., in press.
7 A. Sharples, Introduction to Polymer Crystallization, Arnold, London (1966).
8 M. Galin, Makrom. Chem. Rapid Commun., 5 (1984) 119-124.
9 E. Musso, Thesis, University of Genova, Italy, 1987.
10 D.R. Cooper and C. Booth, Polymer, 18 (1977) 164-174.
11 E. Gattiglia, A. Turturro, E. Pedemonte and G. Dondero, J. Appl. Pol. Sci., in press.