

The effect of some additives on the Form II to Form I phase transformation in polybutene-1

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Abstract

The influence of various nucleating agents of polypropylene on the crystallization and Form II–Form I crystal transformation in polybutene-1 is studied by differential scanning calorimetry. It has been found that the quinacridone dye permanent red E3B and a pimelic acid–calcium carbonate mixture are more effective in promoting the crystallization and transformation than other additives and are comparable with the most effective additive, polypropylene. A good correlation between the effectiveness of an additive as a nucleating agent for crystallization and its effectiveness in promoting the phase transformation was observed for the present additives apart from polypropylene.

INTRODUCTION

The polymorphs of isotactic polybutene-1 (PB-1) have been investigated by many authors [1–3]. It is well known that the tetragonal crystal modification (Form II) forms from the melt and then transforms slowly to the hexagonal modification (Form I), resulting in changes of mechanical, thermal and physical properties. A major drawback of PB-1 is its slow crystallization kinetics compared with other polyolefins such as polyethylene and isotactic polypropylene. This, combined with the Form II to Form I phase transformation, which may require several days for completion, make PB-1 complicated and slow to process. Because of its significance with respect to the processing of PB-1, methods for the acceleration of both crystallization and transformation have been broadly investigated. The use of nucleating agents is the most convenient way to enhance crystallization kinetics and crystal transformation. Certain organic compounds, such as adipic acid, 1-naphthylacetamide etc. [4–6] were found to be effective in promoting the transformation, but isotactic polypropylene (IPP) has a greater effect than

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any of the known nucleating agents of PB-1 [7,8]. With the aim of finding additives which are as effective as IPP in enhancing the crystal transformation of PB-1, we describe here a study of certain selected additives. From the study, two of them are found to be more effective than the remainder.

EXPERIMENTAL

Materials

Polybutene-1 having a melt flow index of 0.3 dg min^{-1} and a viscosity average molecular weight of 1 320 000 was supplied by Mitsui Petrochemical Industries, Ltd. IPP (molecular weight 400 000) was supplied by Xiangyang Chemical Works. The following substances were selected as nucleating agents: adipic acid, pimelic acid, azelaic acid, the quinacridone dye permanent red E3B (E3B), *p*-chloro-*p*'-methyldibenzylidenesorbitol (E. C. Chemicals, Japan) (EC-4), bis(*p*-ethylbenzylidene)sorbitol (Mitsui Toatsu Chemicals, Japan) (NC-4), calcium carbonate, and pimelic acid–calcium carbonate mixture (1:1 by weight). These substances were known to be effective as nucleating agents for IPP crystallization from the melt [9]. The named nucleating agents (1% by weight) in powder form were homogeneously dispersed into the carbon tetrachloride solution of PB-1, then the solvent was evaporated under vacuum.

Instrumentation

The crystallization and melting were performed using a Perkin–Elmer DSC-2C differential scanning calorimetry/thermal analysis data station (TADS) system. The samples (about 7 mg) were heated or cooled at a scanning rate of $20^\circ\text{C min}^{-1}$. The melting temperature T_m or crystallization temperature T_c was obtained from the maximum of the endotherm or the minimum of the exotherm, respectively. The apparent enthalpies of fusion of Form I or Form II were calculated from the area of the respective endothermic peaks. Indium was employed to calibrate the temperature scale and the heat of transition.

For spherulitic size measurement, a polarizing microscope (Olympus BH-2) equipped with a Mettler FP52 hot stage was employed. The specimens were prepared by melting thin films of the samples between cover glasses and were maintained at 180°C for 10 min, then cooled from 180°C to ambient temperature at a cooling rate of $20^\circ\text{C min}^{-1}$ on the hot stage.

RESULTS AND DISCUSSION

The effectiveness of the present additives as nucleating agents for crystallization was tested by measuring their T_c in DSC and their spherulitic

TABLE 1

Composition, code number, DSC crystallization temperature and spherulitic diameter for additive-containing polybutene-1 samples

Sample	Code	Peak temperature (°C)	Spherulitic diameter (μm)
Polybutene-1	PB-1	60.0	43
1% EC-4 + PB-1	PB-E	61.0	28
1% NC-4 + PB-1	PB-N	73.3	18
1% Adipic acid + PB-1	PB-A	62.7	25
1% Pimelic acid + PB-1	PB-P	64.4	20
1% Calcium carbonate + PB-1	PB-C	62.7	40
1% Azelaic acid + PB-1	PB-Az	69.0	16
1% E3B + PB-1	PB-R	72.7	3
0.5% Pimelic acid + 0.5% calcium carbonate + PB-1	PB-PC	75.0	3
20% IPP + PB-1	PB-PPA	65.7	
20% IPP + 0.5% pimelic acid + 0.5% Calcium carbonate + PB-1	PB-PPB	74.7	

diameter in the polarizing microscope. The T_c of each sample was measured at a fixed cooling rate of $20^\circ\text{C min}^{-1}$. If a nucleating effect is present, we would expect to observe a higher T_c than for the un-nucleated PB-1 sample. The results in Table 1 clearly show that the substances are effective nucleating agents except EC-4 and calcium carbonate. Among them, the most effective ones are E3B and the pimelic acid–calcium carbonate mixture. Although calcium carbonate is found to be only slightly effective in promoting the crystallization of PB-1, it has a significant synergic effect with respect to pimelic acid-containing PB-1. In order to measure spherulitic diameter, each of the additive-containing PB-1 samples was crystallized from the melt by cooling at a rate of $20^\circ\text{C min}^{-1}$, then their size was measured by means of the polarizing microscope. If a nucleating effect is present, we would expect to observe a smaller spherulitic diameter than for the un-nucleated PB-1 sample. The spherulitic diameter data in Table 1 also demonstrate that the most effective nucleating agents are E3B and the pimelic acid–calcium carbonate mixture.

It has been proved by several investigators that the experimental data for the isothermal crystallization of PB-1 can be described by the Avrami equation [6]

$$1 - X_c = \exp(Kt^n) \quad (1)$$

where X_c is the weight fraction of material that can crystallize at time t , K is the crystallization rate constant and depends on the rates of nucleation and growth, and n is the Avrami exponent, the value of which depends

both on the nature of the primary nucleation and the growth geometry of the crystalline entities. Usually eqn. (1) can be written as

$$\log[-\ln(1 - X_c)] = n \log t + \log K \quad (2)$$

where the plot of $\log[-\ln(1 - X_c)]$ vs. $\log t$ will give a straight line of slope n and intercept $\log K$. The rate constant K can also be calculated from the half-time of primary crystallization $t_{1/2}$ and the value of n

$$K = \ln 2 / (t_{1/2})^n \quad (3)$$

When the calorimetric method is used to study the isothermal crystallization kinetics, the weight fraction of crystallized material at any time t can be evaluated by taking the ratio of the heat evolved up to that time to the total heat released as represented by the equation

$$X_c = \frac{\Delta H_t}{\Delta H_\infty} = \frac{\int_0^t dH/dt dt}{\int_0^\infty dH/dt dt} \quad (4)$$

Evaluation of the integrals was performed by the TADS using partial area software. Typical double logarithmic plots according to eqn. (2) for PB-R are shown in Fig. 1. The half-time of crystallization $t_{1/2}$ and values of kinetic parameters are summarized in Table 2. As can be appreciated from Table 2, the values obtained for the exponent are not in agreement with the simplified Avrami theory, where integral values for n are required except for PB-1 at 85–87°C. Because fractional values of n were obtained in this study, it is not possible to postulate a well determined mechanism of crystallization, particularly for the most interesting samples PB-R and PB-PC.

Figure 2 shows the variation of $t_{1/2}$ with crystallization temperature for PB-1, PB-A, PB-Az, PB-R and PB-PC. It is clear that E3B and pimelic

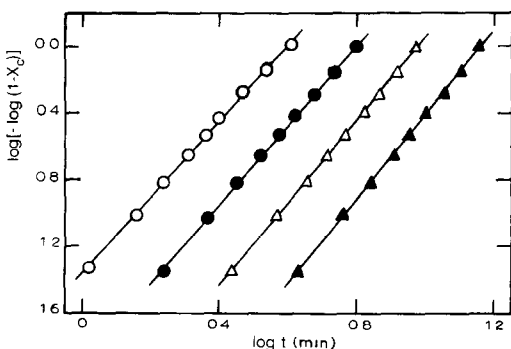


Fig. 1. Avrami plots for PB-R at 91°C (○), 93°C (●), 95°C (△), 97°C (▲).

TABLE 2

Results of Avrami analysis of the Form II crystallization kinetics in polybutene-1

Sample code	Crystallization temperature (°C)	$t_{1/2}$ (min)	n	$K \times 10^2 \text{ min}^{-n}$
PB-1	81	3.72	2.60	2.27
	83	4.63	2.55	1.39
	85	7.29	2.06	1.16
	87	9.17	2.00	0.82
PB-A	83	3.37	2.43	3.65
	85	4.39	2.48	1.78
	87	5.58	2.40	1.13
	89	8.05	2.56	0.33
PB-Az	83	1.55	1.93	29.60
	85	2.65	2.17	8.38
	87	4.00	2.24	3.09
	89	5.74	2.25	1.37
PB-R	91	2.32	2.30	10.00
	93	3.83	2.38	2.84
	95	5.85	2.48	0.87
	97	8.92	2.51	0.29
PB-PC	91	1.64	2.20	23.40
	93	2.58	2.25	8.22
	95	4.05	2.28	2.86
	97	7.76	2.45	0.46

acid–calcium carbonate decrease the undercooling most markedly and are more effective nucleating agents than adipic acid, the well-known nucleating agent for PB-1.

The effectiveness of the present additives on the crystal transformation rate of PB-1 was studied by comparing the values of the apparent heats of

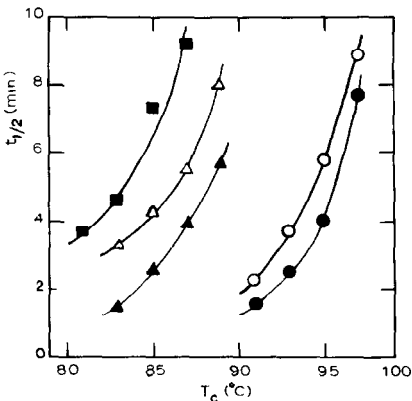


Fig. 2. Plot of $t_{1/2}$ vs. T_c (from Table 2) for PB-1 (■), PB-A (△), PB-Az (▲), PB-R (○) and PB-PC (●).

TABLE 3

Effect of additives on the thermal properties for polybutene-1 after ageing for 27 h at room temperature

Sample code	T_{m_I} (°C)	$T_{m_{II}}$ (°C)	ΔH_I (J g ⁻¹)	ΔH_{II} (J g ⁻¹)
PB-1	124.8	111.2	13.32	25.39
PB-E	126.0	112.0	15.14	22.15
PB-N	128.1	113.1	32.31	16.10
PB-A	125.7	111.9	14.88	21.99
PB-P	126.4	112.3	16.31	22.52
PB-C	125.0	112.7	14.66	23.46
PB-Az	128.1	112.9	31.46	17.57
PB-R	129.3	113.5	33.29	14.91
PB-PC	129.0	112.9	34.58	14.45

fusion of Form I and Form II for an ageing time of 27 h at room temperature for each of the additive-containing PB-1 samples. The results obtained are summarized in Table 3. From Table 3 it can be concluded that E3B and pimelic acid–calcium carbonate were most effective in promoting the crystal transformation in polybutene-1 among the listed additives, as the PB-R and PB-PC samples after ageing for 27 h exhibit the highest value of ΔH_I and the lowest value of ΔH_{II} . The value of ΔH_I , which is the measure of effectiveness in promoting the crystal transformation, is plotted as a function of T_c (from Table 1) in Fig. 3. A good correlation between the effectiveness in promoting the crystallization and the crystal transformation was observed.

Some previous investigators have also applied the Avrami equation to the analysis of the phase transformation of Form II to Form I [6,10]. The

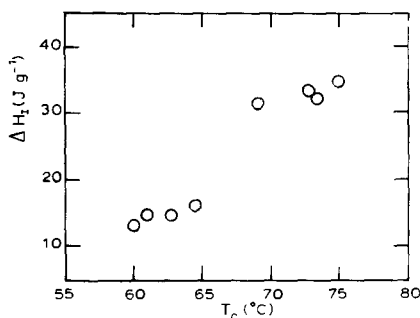


Fig. 3. The relationship between the apparent enthalpy of fusion of Form I in additive-containing PB-1 samples (from Table 3) and crystallization temperature (from Table 1).

TABLE 4

Results of Avrami analysis of the Form II to Form I phase transformation in polybutene-1

Sample code	$t'_{1/2}$ (h)	m	$k \times 10^3 \text{ hr}^{-m}$
PB-1	82.6	1.32	2.04
PB-A	50.1	1.33	3.80
PB-Az	38.0	1.35	5.11
PB-R	26.9	1.51	4.81
PB-PC	25.1	1.37	8.38
PB-PPA	21.4	1.40	9.51
PB-PPB	16.2	1.26	20.74

degree Y of crystal transformation of Form II changes with time according to the equation

$$1 - Y = 1 - \exp(-kt^m) \quad (5)$$

in which m is the Avrami exponent and k is the rate constant for the transformation. The values of m were determined from the slopes of the straight lines obtained by plotting $\log(-\log Y)$ versus $\log t$. The rate constant k (Table 4) was calculated from the $t'_{1/2}$ and the Avrami index m according to the relationship

$$k = \ln 2 / (t'_{1/2})^m \quad (6)$$

The Avrami plots of additive-containing PB-1 aged at room temperature are shown in Fig. 4. The values of m and k were calculated from eqns. (5) and (6) and are listed in Table 4. As may be seen from Table 4, E3B, pimelic acid–calcium carbonate and IPP are more effective in promoting the transformation than the other additives. Although IPP has slightly

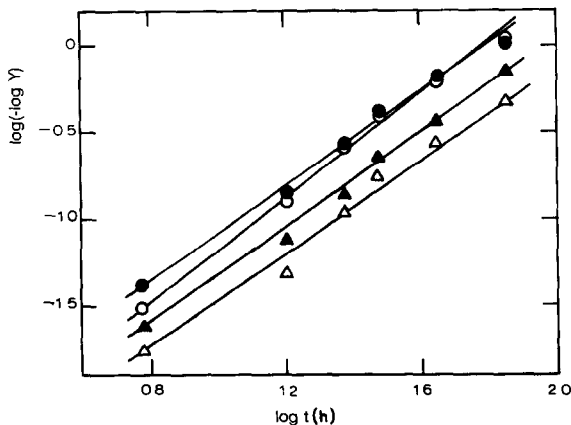


Fig. 4. Avrami plots of crystal transformation for PB-A (Δ), PB-Az (\blacktriangle), PB-R (\circ) and PB-PC (\bullet) aged at room temperature.

more effect at the concentration used than E3B or the mixture, it should be noted that IPP is present in fairly high concentration (20%) in a mechanical blend. The fact that m does not change significantly with the additive may indicate that the additives do not disturb the basic mechanism of the crystal transformation. It has been suggested that the known nucleating ability of the component crystallizing first towards the supercooled melt of the other may result from epitaxy of the polymer onto another polymer or the apolar part of the nucleating agent [11]. The epitaxial relationship between IPP and PB-1 is clear, as they both possess crystallographic faces in which the side-groups form well aligned rows. The concept of epitaxial crystallization may be also used to explain the nucleating activity of E3B and pimelic acid–calcium carbonate towards PB-1 as they are also effective nucleating agents of IPP.

CONCLUSIONS

Pimelic acid, azelaic acid, quinacridone dye E3B, pimelic acid–calcium carbonate mixture, *p*-chloro-*p*'-methyldibenzylidenesorbitol and bis(*p*-ethylbenzylidene)sorbitol exhibit an accelerating effect on the isothermal crystallization and Form II–Form I transformation in polybutene-1. Among them, E3B and pimelic acid–calcium carbonate mixture exhibit the greatest effect. For these additives, a correlation between the effectiveness in promoting the crystallization and the rate of crystal transformation was observed.

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