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Effect of Nucleating Agents Upon the Kinetics of Polybutene-1 Crystallization

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SUMMARY

The influence of various nucleating agents on the crystallization parameters of polybutene-1 is reported. Isothermal crystallization is investigated by differential scanning calorimetry. The morphology induced by the differents nucleating agents has been observed by hot stage polarizing microscopy. It has been stated that the addition of a nucleating agent affects the crystallization rate, dimension and homogeneity of spherulitic sizes. The induction time t_i, the semicrystallization time $t_{1/2}$, the crystallization rate constant K, and the Avrami coefficient n were measured and related to the different characteristics of the specimens. Because of the fractional values of n obtained in this study, it is not possible to propose well determined mechanisms of crystallization.

INTRODUCTION

Heterogeneous nucleation is the most frequent type of nucleation in the crystallization of polymers from the melt. This nucleation is caused by the surfaces of foreign bodies (MANDELKERN 1964) (SHARPLES 1969) (ZETTLEMOYER 1969) (WUNDERLICH 1976).
The control of the primary nucleation in the crystallization of polymeric materials is of scientific and technological importance (HAMMER et al. 1959) (STARKWEATHER and BROOKS 1959). Physical, mechanical, and chemical properties depend on the number and size of the spherulites (INOUE 1963) (BECK and LEDBETTER 1965) (BECK 1967). However, although there have been many attempts to improve some of these properties by controlled nucleation, the present knowledge is mainly empirical, and an unambiguous correlation between chemical composition, crystal structure, or physical properties of the nucleator additive and polymer has not yet been well established (CHATTERJEE and PRICE 1975) (BINSBERGEN 1977) (COLE and PIERRE 1978). The properties for a nucleating agent to be effective have not been fully known. For this reason the selection of nucleants is usually empirical.

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Nucleating agents for polyethylene (HARA and SCHONHORN 1972) and polypropylene (BECK and LEDBETTER 1965) (RYBNIKAR 1969) (BINSBERGEN 1970a,b) have been repeatedly studied in the bibliography. In orden to have a wider idea of the nucleating ability of substances in polyolefins, we have investigated the nucleating effect of different organic compounds on the crystallization of polybutene-1 (PB-1).
The present paper deals with the isothermal crystallization from the melt state of plain and filled polybutene-1, in a temperature range just below the melting point transition.

EXPERIMENTAL

The following organic substances were selected as nucleating agents: adipic acid, salicylic acid, p-aminobenzoic acid, sodium benzoate, sorbic acid. These substances were chosen mainly because they have structural and chemical characteristics that might be considered suitable to act as active nucleators. The named nucleating agents (3% by weight) in powder form were homogeneously dispersed into the polybutene-1 by mechanical mixing in the melt.The isotactic polybutene-1 was supplied by Aldrich European Division. The premelting history before crystallization was as follows; the polybutene-1 was mantained at 170°C for 20 min, so that the samples would not keep memory neither of the previous thermal history nor of the morphology when cooled to a particular crystallization temperature. The crystallization kinetics were carried out by calorimetry. A Dupont 990 differential scanning calorimeter (DSC) was employed, working in a nitrogen flux to avoid any possible degradation of the samples. In the DSC experiments, samples of about 7 mg were used. For optical investigation a polarizing microscope (Reichert Zetopan) equipped with an electric hot stage (Mettler FP52) was employed. The specimens were prepared by melting thin films of the samples between the cover glasses and maintained at the desired temperature by means of the hot stage. The polymer was crystallized from the melt mixed with the nucleating agents in the above indicated percentage, (Table 1).

TABLE 1

Characteristics of the samples

Sample	Description
A	PB-1 unfilled
B	PB-1-adipic acid
C	PB-1-salicylic acid
D	PB-1-p-aminobenzoic acid
E	PB-1-sodium benzoate
F	PB-1-sorbic acid

RESULTS AND DISCUSSION

As has been proved the Avrami equation (AVRAMI 1939, 1940, 1941) is of considerable importance in the study of the kinetics of nucleation and growth of crystalline polymers (MANDELKERN 1964) (SHARPLES 1969). The theory of isothermal crystallization for the overall change in crystallinity shows that the experimental data for the crystallization of polymers can be fitted by the equation:

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

Where X_t 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, while 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.
As usual eq. (1) can be written:

$$\log \left[-\ln (1 - X_t)\right] = n \log t + \log K \qquad (2)$$

Where it is observed that the plot of the left-hand side of eq. (2) as a function of 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 crysrallization $t_{1/2}$ and the value of n:

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

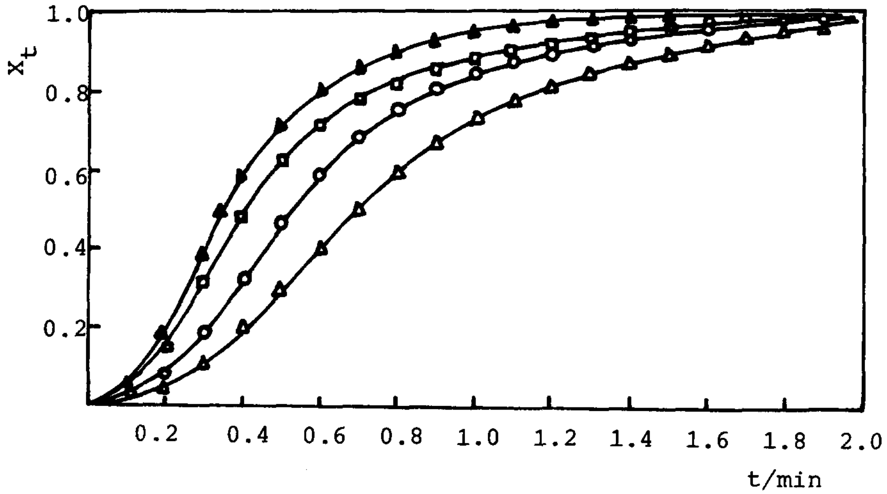

Fig. 1.- Crystallization isotherms for sample A at different temperatures ▲ 345K, ☐ 347K, ○ 351K, △ 353K

The DSC isotherms, obtained by plotting X_t as a function of t, are reported in Fig. 1 for the sample A. All the isotherms show a characteristic sigmoidal shape for all the samples studied in this paper.
Avrami plots of our measurements are shown in figure 2 where it is represented the equation 2 for the sample A.

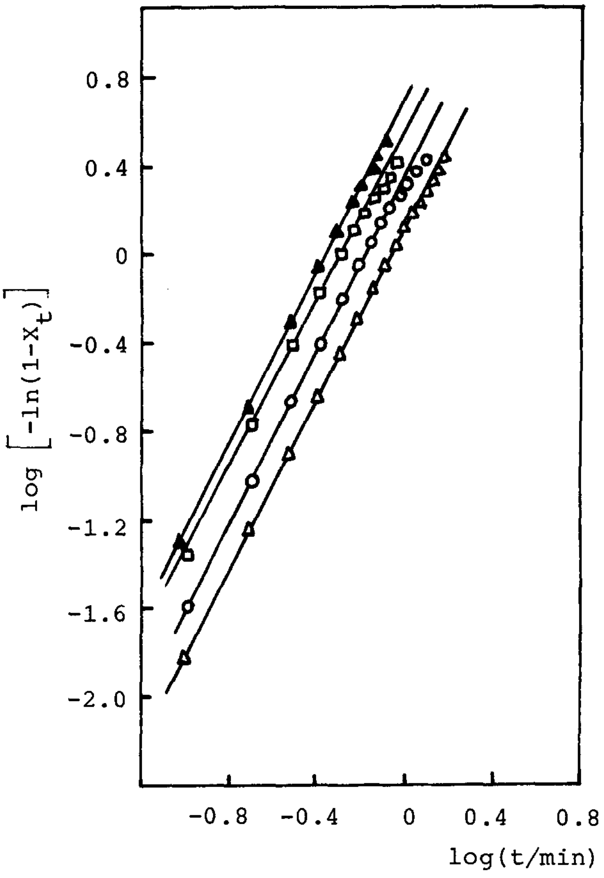

Fig. 2.- Avrami plots of log $\left[-\ln(1-X_t)\right]$ againts log t for sample A at different temperatures ▲ 345K, □ 347K, ○ 351K, △ 353K.

The values of kinetic parameters, semicrystallization time $t_{1/2}$, rate constant of isothermal crystallization K, and the Avrami exponent n, are summarized in table 2. As it can be appreciated in table 2 the samples B and D, polybutene-1 nucleated with adipic acid and p-aminobenzoic acid, respectively, have been crystallized at higher temperatures than the unfilled polybutene-1. This is due to the fact that the crystallization performed to the temperatures of the sample A was too quick for samples B and D to be registered with accuracy, showing that adipic acid and p-aminobenzoic acid decrease considerably the undercooling.

The induction period t_i has been obtained from the corresponding intercept with the x-axis of the linear part of the sigmoid curve. It is well known that the period of induction increases when the crystallization temperature increases. It can be appreciated in table 2 that the adipic acid and the p-aminobenzoic acid decrease considerably the times of induction with respect to the unfilled polybutene-1 taking into consideration that such times have been obtained at smaller undercooling (crystallization temperatures higher than those of the unfilled polybutene-1).

TABLE 2

Kinetic parameters from crystallization isotherms obtained by DSC measurements.

Sample	T_c(K)	$t_{1/2}$(s)	n	K (s^{-n})	t_i (s)
A	353	43.8	1.9	$5.27\text{x}10^{-4}$	13.2
	351	32.4	2.0	$6.60\text{x}10^{-4}$	9.6
	347	25.2	1.9	$1.51\text{x}10^{-3}$	7.8
	345	22.2	2.0	$1.41\text{x}10^{-3}$	6.6
B	376	35.2	2.1	$3.92\text{x}10^{-4}$	12.8
	373	28.2	2.2	$4.47\text{x}10^{-4}$	9.6
	369	22.8	2.1	$9.75\text{x}10^{-4}$	7.2
	363	18.0	2.1	$1.60\text{x}10^{-3}$	4.8
C	351	36.0	2.5	$8.91\text{x}10^{-5}$	13.2
	349	28.2	2.6	$1.18\text{x}10^{-4}$	12.0
	347	19.2	2.6	$3.19\text{x}10^{-4}$	7.8
D	369	48.0	2.0	$3.01\text{x}10^{-4}$	14.4
	365	39.6	1.9	$6.39\text{x}10^{-4}$	13.2
	361	36.0	2.0	$5.35\text{x}10^{-4}$	12.0
	359	32.4	2.0	$6.60\text{x}10^{-4}$	10.8
E	351	30.0	3.2	$1.30\text{x}10^{-5}$	13.2
	349	24.6	3.0	$4.66\text{x}10^{-5}$	9.6
	347	21.0	2.6	$2.53\text{x}10^{-4}$	7.8
	345	17.4	2.2	$1.29\text{x}10^{-3}$	6.6
F	351	45.0	2.5	$5.10\text{x}10^{-5}$	13.8
	349	30.6	2.5	$1.34\text{x}10^{-4}$	13.2
	347	21.6	2.4	$4.35\text{x}10^{-4}$	7.2
	346	18.0	2.5	$5.04\text{x}10^{-4}$	6.0

It can be also appreciated in table 2 the decrease suffered in the period of semicrystallization and the rate constant by the samples B and D with respect to the other studied samples. Therefore, we can conclude that the presence of adipic acid and p-aminobenzoic acid in the polybutene-1

exhibits an accelerating effect on the isothermal crystallization.
As it is well known, a polymeric spherulite is composed of crystallites and amorphous parts. In this sense, a value 2 of the Avrami exponent obtained by calorimetry, indicates a predeterminated nucleation and a spherulitic growth (GODOVSKY et al. 1972) (GODOVSKY et al. 1974). Therefore, the reasonably good fit of the Avrami equation with exponent n=2-see table 2- for unfilled polybutene-1, suggests that crystallization from the melt consists of a predeterminate mode of nucleation and a spherulitic growth.
As it can be appreciated in table 2, the values obtained for the exponent are near to 2 for the samples nucleated with adipic acid and p-aminobenzoic acid, but the values of n obtained for the other nucleated samples are not in agreement with the simplified Avrami theory where integral values for n are required. Similar experimental results were found for other nucleated polymers (CECCORULLi and MANESCALCHI 1973) (GROENINCKX et al. 1974), where the values of n are not integrals and also vary with the type of nucleating agent used. Due to the fractional values of n obtained in this study, it is not possible to propose well determined mechanisms of crystallization. These non integrals values might be explained by a special growth morphology; perhaps growth of a disordered structure of the type of interlamellar crystal.
We can conclude that the Avrami theory results insufficient to elucidate the type of structures in growing for the samples treated with certain nucleants. By means of the polarizing microscope it has been observed that, in the range of temperature here studied, the nucleation density increases considerably in the presence of the nucleating agents, and so, the spherulites can not be distinguished by optical microscopy because of their small size. As a consequence, the primary nucleation frequency and the growth rate of the spherulites cannot be followed by this method.

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