

# Crystallization and Melting Behavior of 1,2-Syndiotactic Polybutadiene

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Received 10 March 2003; accepted 4 November 2003

**ABSTRACT:** 1,2-Syndiotactic polybutadiene was synthesized at  $-30^{\circ}\text{C}$  using the catalyst system  $\text{CrCl}_2(\text{dmpe})_2\text{-MAO}$ . The syndiotactic index of the butadiene sequences, expressed as a percentage of syndiotactic pentads [rrrr], was evaluated by  $^{13}\text{C-NMR}$  measurements. WAXD and SAXS techniques were employed to characterize the crystalline structure of the polymer. The thermal behavior of the polybutadiene was investigated by differential scanning calorimetry. The isothermal crystallization kinetics were described by means of the Avrami equation, which suggested a three-dimensional growth of crystalline units, developed by het-

erogeneous nucleation, followed by a secondary crystallization stage. Polybutadiene isothermally crystallizes from the melt according to regime II of crystallization described by Lauritzen–Hoffman secondary nucleation theory. Nonisothermal crystallization kinetics were elaborated using the Ziabicki and Avrami methods modified by Jeziorny. The equilibrium melting temperature was calculated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1680–1687, 2004

**Key words:** differential scanning calorimetry (DSC); polybutadiene; syndiotactic; crystallization; melting point

## INTRODUCTION

In the past years the study of the synthesis and the properties of butadiene homo- and copolymers has received a renewed impulse, due to the introduction of more active and stereospecific catalysts based on methylaluminoxane. Highly crystalline *trans*-1,4 polybutadiene was obtained with the system  $\text{V}(\text{acac})_3\text{-MAO}$ .<sup>1,2</sup> Highly *cis*-1,4 polybutadiene was prepared with  $\text{Co}(\text{acac})_3\text{-MAO}$ ,<sup>1</sup>  $\text{Ni}(\text{acac})_2\text{-MAO}$ ,<sup>3,4</sup> and catalysts based on Nd(allyl) compounds.<sup>5</sup> 1,2-Syndiotactic polybutadiene and 3,4-polyisoprene, having an essentially syndiotactic structure, were obtained with catalysts based on iron(II) complexes with aromatic bidentate amines (i.e., bipyridine phenanthroline) and methylaluminoxane<sup>6,7</sup> and with the system  $\text{CrCl}_2(\text{dmpe})_2\text{-MAO}$ .<sup>8</sup> This latter catalyst was found to copolymerize butadiene and isoprene, having a 1,2/3,4 structure.<sup>9</sup>

In a previous paper we reported on the thermal characterization of butadiene–isoprene copolymers of various composition prepared at two different temperatures using  $\text{CrCl}_2(\text{dmpe})_2\text{-MAO}$  as the catalyst system.<sup>10</sup> We determined the influence of the copolymer composition and stereoregularity on the thermal properties.

In the present article we report structural characteristics and thermal properties of 1,2-syndiotactic polybutadiene (1,2-PB) obtained with the system

$\text{CrCl}_2(\text{dmpe})_2\text{-MAO}$  at  $-30^{\circ}\text{C}$ . 1,2-PB has characteristics of both a thermoplastic polymer and an elastomer<sup>11,12</sup> and is generally used in films, footwear soles, tubes, and hoses.

In particular, this paper reports on the melting behavior and the isothermal and nonisothermal crystallization kinetics of 1,2-PB. The Lauritzen–Hoffman secondary nucleation theory was applied to the isothermal growth rate data to investigate the regime of crystallization of 1,2-PB.

## EXPERIMENTAL

### Polymer synthesis

Butadiene (4 mL) and toluene (21.5 mL) were introduced into a 50-mL glass reactor and then the solution so obtained was brought to the polymerization temperature of  $-30^{\circ}\text{C}$ . Methylaluminoxane (MAO;  $1 \times 10^{-2}$  mol, 6.3 mL of a 10 wt % toluene solution) and  $\text{CrCl}_2(\text{dmpe})_2$  ( $1 \times 10^{-5}$  mol, 4.2 mL of a 1 mg/mL toluene solution) [dmpe = 1,2-bis(dimethylphosphino)ethane] were added. The polymerization was stopped after 10 days by the addition of methanol. The polymer was then coagulated with a large amount of methanol containing a small amount of hydrochloric acid and the antioxidant octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate (Ciba Irganox 1076,  $\leq 1\%$  by weight with respect to the polymer weight). The polymer so obtained was then repeatedly washed with methanol and then dried *in vacuo* at room temperature. Yield was 2.25 g with 80% conversion.

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### Polymer structural characterization

$^{13}\text{C}$ -NMR measurement was performed with a Bruker AM 270 instrument. The spectrum was obtained in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $103^\circ\text{C}$  using hexamethyldisiloxane as internal standard. The concentration of the polymer solution was about 10 wt %.

The wide-angle X-ray diffraction (WAXD) data were obtained at  $20^\circ\text{C}$  using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000W tube ( $\text{CuK}_\alpha$  radiation,  $\lambda = 0.154$  nm). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 5 to  $40\ 2\theta^\circ$  at  $0.02\ 2\theta^\circ$  intervals.

The small-angle X-ray scattering (SAXS) measurement was conducted at  $20^\circ\text{C}$  with a Kratky compact camera. Monochromatized  $\text{CuK}_\alpha$  radiation was supplied by a stabilized Siemens Krystalloflex 710 generator and a Siemens FK 60-04, 1500W Cu target tube operated at 40 kV and 25 mA. The scattered intensity was counted for 400 s at  $203$  angles of measurement in the range from  $0.1$  to  $3.0\ 2\theta^\circ$  using a step scanning proportional counter with pulse height discrimination.

### Thermal characterization

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 instrument under a nitrogen atmosphere ( $60\ \text{mL min}^{-1}$ ). The run was carried out from  $50$  to  $550^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$ .

The isothermal and nonisothermal crystallization kinetics and the melting behavior of 1,2-syndiotactic polybutadiene were investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 system equipped with a liquid subambient device. The instrument was calibrated with indium standard. The sample weight was  $\sim 3$  mg and a fresh specimen was used for each run.

In a typical isothermal crystallization run, the polymer was heated up to  $230^\circ\text{C}$  and held at this temperature for 3 min to cancel previous thermal history. Then, the sample was cooled at a nominal rate of  $500^\circ\text{C min}^{-1}$  to the selected crystallization temperature ( $T_c$ ). The heat flow evolved during the isothermal crystallization was recorded as a function of time. Finally, the isothermally crystallized sample was heated with a scan rate of  $20^\circ\text{C min}^{-1}$  from  $T_c$  to  $220^\circ\text{C}$  determining the melting temperature ( $T_m$ ).

The following standard procedure was employed in nonisothermal crystallization analysis: the samples were heated up to  $230^\circ\text{C}$  and kept for 3 min and then cooled at various cooling rates ranging from 1 to  $60^\circ\text{C min}^{-1}$ . The exothermic crystallization peak was recorded as a function of temperature.

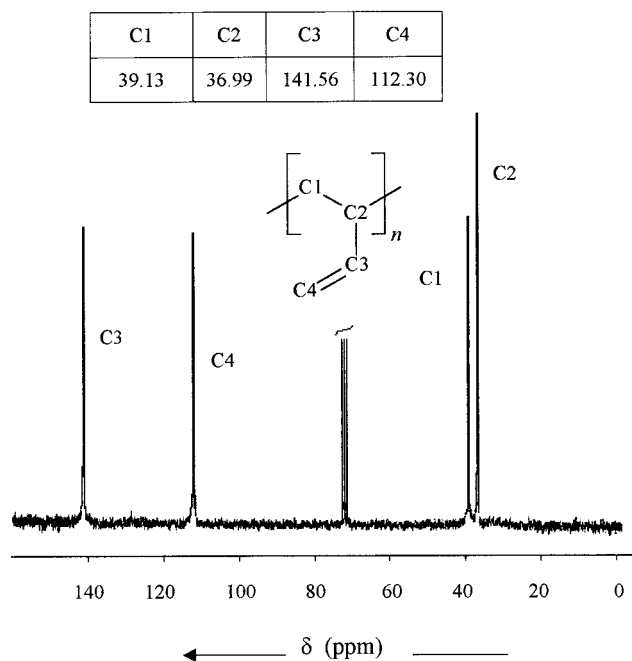


Figure 1  $^{13}\text{C}$ -NMR spectrum of 1,2-PB.

## RESULTS AND DISCUSSION

### Polymer structural characterization

The catalyst system  $\text{CrCl}_2(\text{dmpe})_2$ -MAO polymerizes butadiene to crystalline 1,2-syndiotactic polymer.<sup>8,9</sup> As reported in our previous paper,<sup>10</sup> the stereoregularity and, consequently, the thermal properties of polybutadiene depended on the temperature of the polymerization reaction. In fact, polymers synthesized at  $-30^\circ\text{C}$  presented  $T_m$  values higher than those prepared at  $20^\circ\text{C}$ .

Highly syndiotactic structure is indicated by the  $^{13}\text{C}$ -NMR spectrum (Fig. 1). The syndiotactic index of the butadiene sequences, represented as a molar fraction of the syndiotactic pentads [rrrr], was evaluated from the integrated areas of the peaks around 112 ppm, corresponding to the different butadiene pentads.<sup>13-15</sup> The [rrrr] value was about 0.95.

The WAXD profile of the synthesized 1,2-PB is reported in Figure 2. The position at maximum intensity of the diffraction angles,  $2\theta$ , for the four higher registered peaks corresponds to the spacings of 0.652, 0.544, 0.418, and 0.375 nm, respectively. These values are very similar to the ones reported in the literature for syndiotactic 1,2-polybutadiene, where the unit cell structure was estimated to be orthorhombic.<sup>16,17</sup>

The angular dependence of SAXS data is expressed in terms of the scattering vector  $h = (4\pi/\lambda) \sin\theta$ , where  $\theta$  is half the scattering angle. The blank scattering was subtracted from the sample scattering after correction for the sample thickness and absorption. The additional constant scattering component was de-

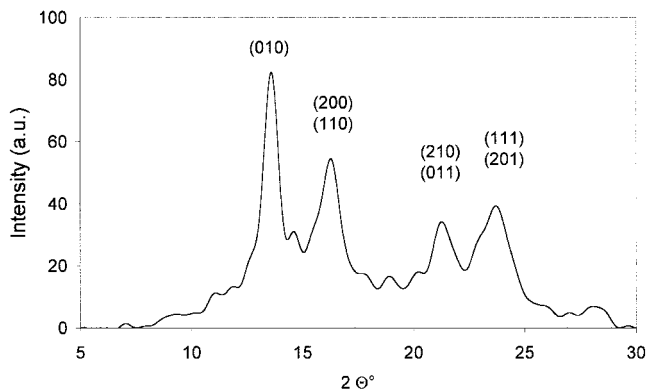


Figure 2 X-ray powder spectrum of 1,2-PB.

terminated and subtracted according to Porod.<sup>18</sup> Figure 3 reports the Lorentz corrected intensity profile for a sample of 1,2-PB isothermally crystallized from the melt at 179°C for 30 min. The long period ( $L_P$ ) of 14.7 nm was calculated by

$$L_P = 2\pi/h_m \quad (1)$$

where  $h_m$  is the abscissa value at the maximum of the plot.  $L_P$  is defined as the distance of the centers of two adjacent lamellae.

### Thermal characterization

#### Thermogravimetry

The TGA curve of 1,2-PB, reported in Figure 4, shows that the chain fragmentation with the formation of volatile products occurs only at temperatures higher than 300°C. In fact, the weight loss calculated at 300°C is ~1%. The maximum rate of degradation takes place at 468°C and the decomposition is complete at ~500°C.

#### Isothermal crystallization kinetics

The rate of isothermal crystallization of 1,2-PB, determined by DSC, is influenced from the temperature. In

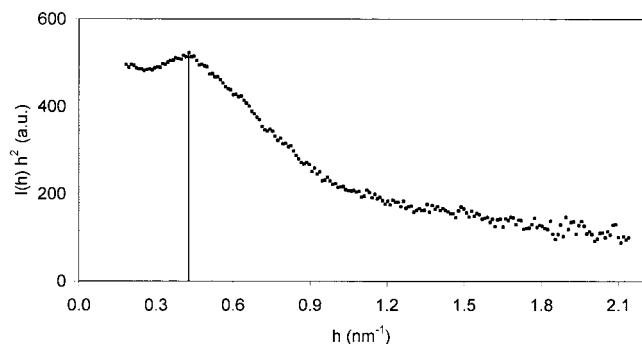


Figure 3 Lorentz-corrected plot of 1,2-PB isothermally crystallized from the melt at 179°C.

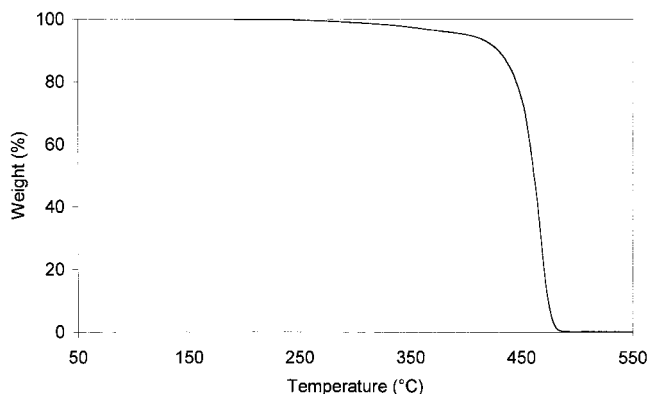


Figure 4 Thermogravimetric curve of 1,2-PB in nitrogen at 5°C min<sup>-1</sup>.

Figure 5 the fraction of the material crystallized at time  $t$ ,  $X_t$ , is reported at nine different crystallization temperatures in the range from 176 to 180°C. In Table I the half-time of crystallization  $t_{0.5}$ , defined as the time taken for half of the crystallization to develop, is reported for different  $T_c$ .

The isothermal crystallization of 1,2-PB was described by means of the Avrami equation:<sup>19</sup>

$$1 - X_t = \exp(-K_n t^n), \quad (2)$$

where  $n$  and  $K_n$  are parameters depending on the type of nucleation and on the geometry of the growing crystals. Table I collects the values of  $n$  determined from the slope of the straight lines obtained by plotting  $\log[-\ln(1-X_t)]$  versus  $\log t$  and the values of  $K_n$  calculated by means of the relationship

$$K_n = \ln 2/t_{0.5}^n \quad (3)$$

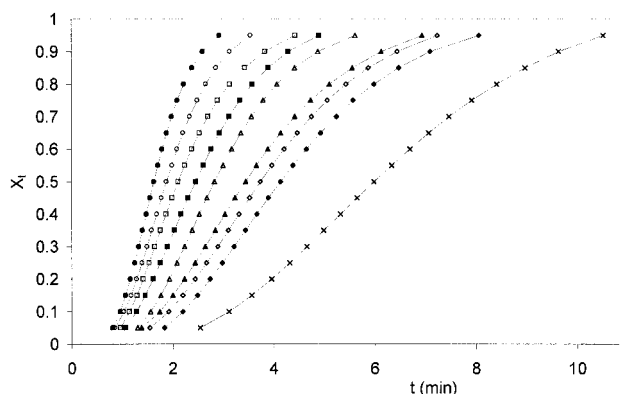


Figure 5 Development of relative crystallinity with time for isothermal melt crystallization at the adopted  $T_c$  (°C): 180 (x), 179.5 (◆), 179 (◇), 178.5 (▲), 178 (Δ), 177.5 (■), 177 (□), 176.5 (○), 176 (●).

**TABLE I**  
Isothermal Crystallization Kinetic Parameters of 1,2-PB from the Avrami Equation

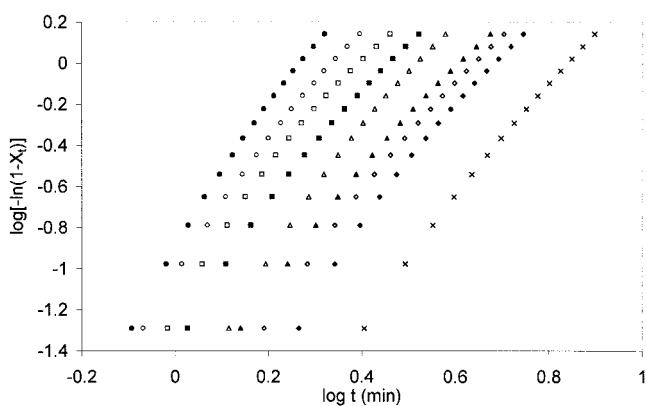
$T_c$ (°C)	$t_{0.5}$ (min)	$n$	$K_n$ (min <sup>-n</sup> )	$n'$
176	1.63	3.2	0.1452	2.2
176.5	1.87	3.0	0.1060	2.1
177	2.10	2.8	0.0868	1.8
177.5	2.45	2.9	0.0516	2.0
178	2.82	3.0	0.0309	1.9
178.5	3.44	2.7	0.0247	2.0
179	3.73	2.8	0.0174	2.1
179.5	4.13	2.9	0.0113	2.1
180	5.97	2.9	0.0039	2.0

In Figure 6 the Avrami plots obtained at different isothermal crystallization temperatures for 1,2-PB, are reported. For all  $T_c$  investigated, a straight line with a good correlation was generally observed for  $X_t$  values included between 0.05 and 0.75. The value of the Avrami exponent,  $n$ , about 3 indicates a three-dimensional growth of crystalline units, developed by heterogeneous nucleation. The primary crystallization was followed by a secondary stage generally due to the effect of slower crystallization caused by the impingement of the spherulites, characterized by a value of 2, of the Avrami exponent,  $n'$  (Table I).

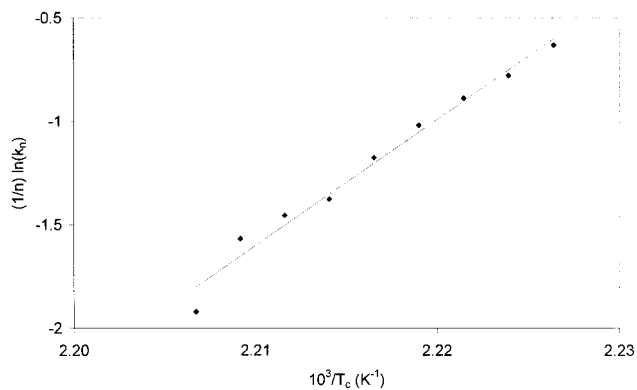
The value of the activation energy for the primary crystallization process was calculated assuming that the crystallization rate parameter  $K_n$  can be approximately described by an Arrhenius form:<sup>20</sup>

$$K_n^{1/n} = K_0 \exp(-\Delta E/RT), \quad (4)$$

where  $K_0$  is a temperature independent preexponential factor,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.  $\Delta E$  is the total activation energy and consists of the transport activation energy and the



**Figure 6** Avrami plots of  $\log[-\ln(1-X_t)]$  versus  $\log t$  for isothermal melt crystallization of 1,2-PB at the adopted  $T_c$  (°C): 180 (x), 179.5 (◆), 179 (◇), 178.5 (▲), 178 (Δ), 177.5 (■), 177 (□), 176.5 (○), 176 (●).



**Figure 7** Arrhenius plot of  $(1/n) \ln(k_n)$  versus  $1/T_c$  for determining the activation energy of crystallization.

nucleation activation energy.<sup>21</sup> The  $\Delta E$  value of -509 kJ/mol was calculated from the slope of the Arrhenius plot of  $(1/n) \ln(K_n)$  versus  $1/T_c$  (Fig. 7).

**Nonisothermal crystallization kinetics**

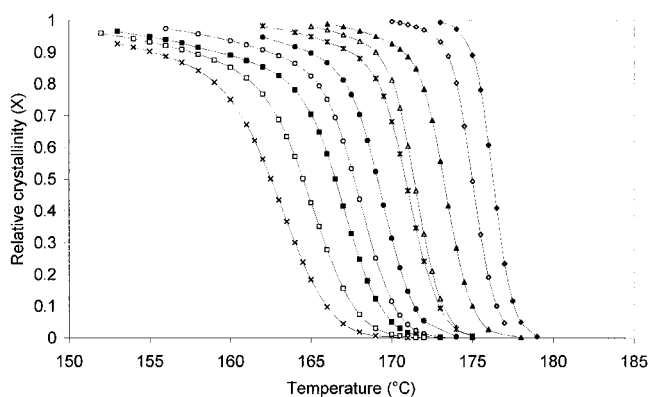
The development of relative crystallization with temperature, determined by DSC, for nonisothermal melt crystallization of 1,2-PB at different cooling rates, ranging from 1 to 60°C min<sup>-1</sup>, is presented in Figure 8.

According to the relationship between time ( $t$ ) and temperature ( $T$ ),

$$t_x = (T_i - T_x)/\Phi, \quad (5)$$

where  $\Phi$  is the cooling rate, and  $T_i$  and  $T_x$  are the temperature at the initial time and a time  $x$  during the cooling run, respectively; the dependence of relative crystallinity on time can be calculated.

The temperature at the maximum of the exothermic peak ( $T_{max}$ ) shifted to lower temperature region as the cooling rate increased. The  $T_{max}$  values, the corre-



**Figure 8** Relative crystallinity versus temperature for nonisothermal crystallization of 1,2-PB at the adopted cooling rates (°C min<sup>-1</sup>): 60 (x), 40 (□), 30 (■), 20 (○), 15 (●), 10 (\*), 7.5 (Δ), 5 (▲), 2 (◇), 1 (◆).

TABLE II  
Nonisothermal Crystallization Parameters of 1,2-PB

$\Phi$ ( $^{\circ}\text{C min}^{-1}$ )	$T_{\text{max}}$ (K)	$t_{\text{max}}$ (min)	$\Delta H_c$ (J/g)	$\omega_c^a$
1	449.4	1.96	44.0	0.43
2	448.1	1.13	48.7	0.47
2.5	447.7	0.90	47.9	0.47
5	446.4	0.52	46.4	0.45
7.5	444.6	0.36	47.7	0.46
10	444.2	0.30	46.4	0.45
15	442.6	0.22	48.8	0.47
20	441.2	0.18	49.6	0.48
30	440.1	0.13	50.6	0.49
40	438.2	0.11	51.7	0.50
60	436.5	0.08	52.4	0.51

<sup>a</sup> Calculated assuming  $\Delta H^0 = 102.8 \text{ J/g}$ .<sup>15</sup>

sponding times ( $t_{\text{max}}$ ), the crystallization enthalpy ( $\Delta H_c$ ), and the relative crystallinity ( $\omega_c$ ), are reported in Table II.

In a nonisothermal crystallization, the activation energy  $\Delta E$  can be calculated considering the variation of crystallization peak temperature  $T_{\text{max}}$  with the cooling rate  $\Phi$ , by the Kissinger equation:<sup>22</sup>

$$-\Delta E = R[d(\ln \Phi/T_{\text{max}}^2)/d(1/T_{\text{max}})], \quad (6)$$

where  $R$  is the universal gas constant. The  $\Delta E$  value of  $-502 \text{ kJ/mol}$  was calculated from the slope by plotting  $\ln(\Phi/T_{\text{max}}^2)$  versus  $1/T_{\text{max}}$  (Fig. 9). This value of  $\Delta E$  is very close to the one calculated for the isothermal crystallization.

The crystallization rate coefficient (CRC), defined as the variation in cooling rate required to change the undercooling of the polymer melt by  $1^{\circ}\text{C}$ , was introduced by Khanna.<sup>23</sup> The CRC can be obtained from the slope by plotting the cooling rate versus  $T_{\text{max}}$  and can be used as a guide for ranking the polymers on a scale of crystallization rates. A CRC value of  $203 \text{ h}^{-1}$  was calculated for 1,2-PB using the  $T_{\text{max}}$  obtained by cooling the sample at 10 different rates ranging from 1

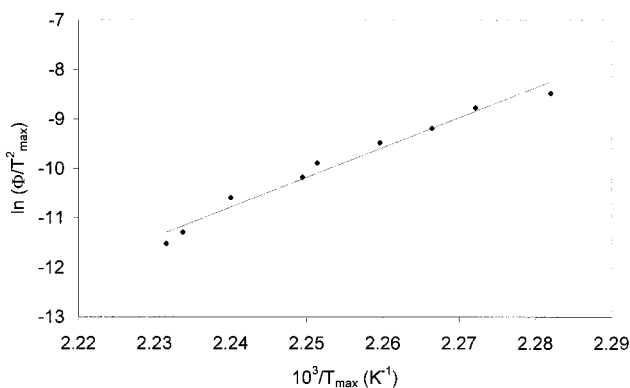


Figure 9 Plot of  $\ln(\phi/T_{\text{max}}^2)$  versus  $1/T_{\text{max}}$  according to the Kissinger method.

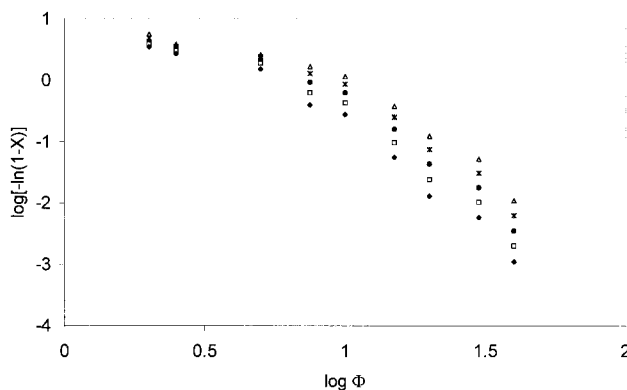


Figure 10 Ozawa plots of  $\log[-\ln(1-X)]$  versus  $\log \phi$  for nonisothermal crystallization of 1,2-PB at various temperatures ( $^{\circ}\text{C}$ ): 172 ( $\blacklozenge$ ), 171.5 ( $\square$ ), 171 ( $\bullet$ ), 170.5 ( $*$ ), 170 ( $\triangle$ ).

to  $40^{\circ}\text{C min}^{-1}$ , i.e., the interval rates adopted by Khanna.<sup>23</sup> The CRC values are higher for faster crystallizing systems. To the best of our knowledge, the CRC value obtained for 1,2-PB is the highest reported CRC for polyolefins.

The Ozawa equation is a modification of the Avrami equation which considers the effect of the cooling rate on crystallization from the melt, replacing the crystallization time in isothermal conditions with the cooling rate  $\Phi$ :<sup>24</sup>

$$1 - X = \exp[-K_c(T)/\Phi^m], \quad (7)$$

where  $X$  is the relative crystallinity at temperature  $T$ ,  $K_c(T)$  is the cooling function of the process, and  $m$  is the Ozawa exponent dependent on the crystal growth and nucleation mechanism. The results of the Ozawa analysis are presented in Figure 10 by plotting  $\log[-\ln(1-X)]$  versus  $\log \Phi$  for temperatures in the range from 170 to  $172^{\circ}\text{C}$ . The nonlinear trend in Figure 10 means that the parameter  $m$  is not a constant during crystallization. As observed for some polymers,<sup>25–29</sup> the crystallization under nonisothermal condition could not be described using the Ozawa equation. The isothermal crystallization measurements showed that the primary crystallization of 1,2-PB was immediately followed by a secondary crystallization event. The nonisothermal crystallization of 1,2-PB does not follow the Ozawa equation probably because of its inaccurate assumption about secondary crystallization.

As suggested by Jeziorny,<sup>30</sup> the kinetics of nonisothermal crystallization can be characterized directly on the approximate theory formulated by Ziabicki where the crystallization can be presented by means of the equation for first-order kinetics:<sup>31–33</sup>

$$dX/dt = [1 - X]K(T), \quad (8)$$

where  $X$  is the relative crystallinity, and  $K(T)$  is the rate constant dependent only on temperature. A  $K(T)$

TABLE III  
Nonisothermal Crystallization Kinetic Parameters  
of 1,2-PB

$\Phi$ ( $^{\circ}\text{C min}^{-1}$ )	$D$ (K)	$K_{\text{max}}$ ( $\text{min}^{-1}$ )	$G$ ( $\text{K min}^{-1}$ )	$G_c$
1	2.243	0.556	1.328	1.328
2	2.521	0.965	2.588	1.294
2.5	2.661	1.171	3.318	1.327
5	2.991	2.119	6.746	1.349
7.5	3.015	3.156	10.127	1.350
10	3.491	3.435	12.764	1.276
15	3.818	4.521	18.373	1.225
20	4.132	5.395	23.727	1.186
30	4.461	7.882	37.427	1.248
40	5.227	8.622	47.971	1.199
60	5.965	10.526	66.832	1.114

value can be determined at a temperature  $T$  in the range of temperatures between glass transition and melting temperatures.

According to Ziabicki's theory, Jeziorny derived an equation to calculate the quantity  $G$ , defined as "the kinetic crystallizability," by means of nonisothermal crystallization:<sup>30</sup>

$$G = \int_{T_g}^{T_m} K(T)dT = (\pi/\ln 2)^{1/2}K_{\text{max}}D/2 \quad (9)$$

where  $K_{\text{max}}$  is the value of  $K(T)$  at the maximum crystallization rate, and  $D$  is the half-width of the crystallization peak. The parameter  $G$  must be corrected considering the effect of cooling rate ( $dT/dt$ ), and its final form is as follows:

$$G_c = G/(dT/dt), \quad (10)$$

where  $G_c$  is the kinetic crystallizability at unit cooling rate.

Calculation of the  $G_c$  parameter was made possible by knowing the  $D$  and  $K_{\text{max}}$  values appearing in eq. (9). The half-width  $D$  can be directly determined from the thermogram, while the  $K_{\text{max}}$  value can be calculated as

$$K_{\text{max}} = C_k/t_{\text{max}}, \quad (11)$$

where

$$C_k = \int_0^{t_{\text{max}}} (dH/dt)dt / \int_{t_{\text{max}}}^{\infty} (dH/dt)dt, \quad (12)$$

where  $t_{\text{max}}$  is the time from the start of crystallization to reaching the maximum rate of crystallization.

The calculated parameters characterizing the 1,2-PB nonisothermal crystallization, according to the Jezi-

orny approach, are shown in Table III. The  $G_c$  values show a quite constant value for all investigated cooling rates, i.e., the kinetic crystallizability is related only to the intrinsic structure of the polymer.

### Melting behavior

The observed melting temperature ( $T_m$ ), determined by DSC, linearly increases with the isothermal crystallization temperature ( $T_c$ ), for 1,2-PB. The experimental data can be fitted using the Hoffman-Weeks equation:<sup>34</sup>

$$T_m = (1/\gamma)T_c + (1 - 1/\gamma)T_m^{\circ}, \quad (13)$$

where  $\gamma$  is the morphological factor and  $T_m^{\circ}$  is the equilibrium melting temperature. In Figure 11 the melting temperatures registered at the maximum of the peak for the isothermally crystallized 1,2-PB are reported as a function of  $T_c$ . On the basis of eq. (13) the extrapolation of the straight line to the intersection with the  $T_m = T_c$  line yielded the equilibrium melting temperature of 208°C.

### Surface free energy and Lauritzen Z-test

Assuming that the crystallization from the melt of 1,2-PB is of lamellar type, the overall rate constant of crystallization,  $K_n$ , derived from the Avrami calculation on primary crystallization, can be written as

$$(1/n)\ln K_n + U^*/R(T_c - T_{\infty}) = \log A_0 - (K_g/T_c\Delta Tf), \quad (14)$$

where  $U^*$  is the activation energy for the transportation of segments of molecules across the melt/solid surface boundary and is usually given by a universal value of 6280 J/mol.<sup>35</sup>  $T_{\infty}$  is the temperature below which all segmental motion ceases (i.e.,  $T_{\infty} = T_g - 30$

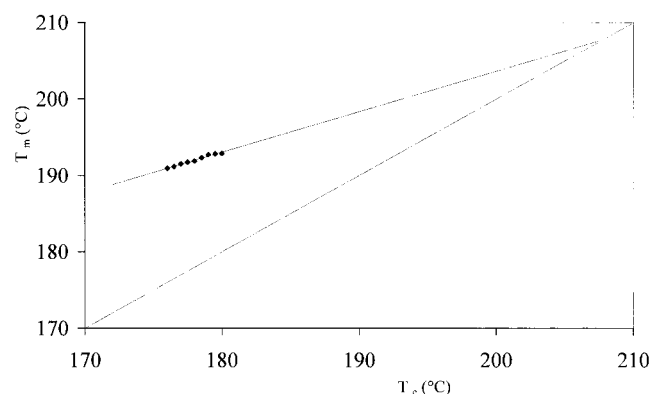
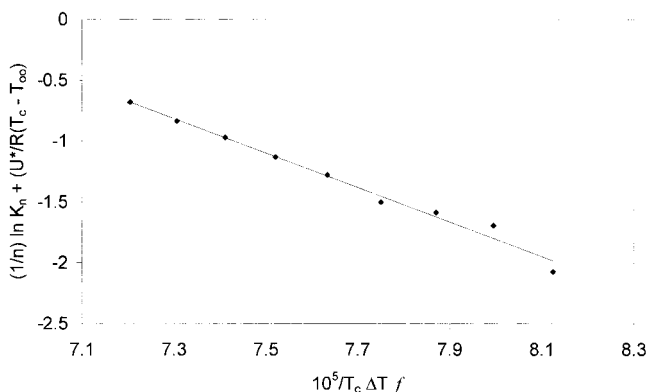


Figure 11 Hoffman-Weeks plot of apparent melting temperature versus crystallization temperature for determining the equilibrium melting temperature of 1,2-PB.



**Figure 12** Kinetic analysis of the overall crystallization rate according to the Lauritzen–Hoffman theory for 1,2-PB.

$K$ ),  $\Delta T$  is the undercooling ( $\Delta T = T_m^\circ - T_c$ ),  $R$  is the universal gas constant,  $A_0$  is a preexponential factor, and  $K_g$  is the nucleation rate parameter.  $f$  is a correction factor that takes into account the temperature dependency of the heat of fusion,  $f = 2T_c/(T_c + T_m^\circ)$ . In our calculation we used  $n$  and  $K_n$  values reported in Table I,  $T_m^\circ = 481$  K and  $T_g = 291$  K.<sup>10</sup>

By plotting  $(1/n)\ln K_n + [U^*/R(T_c - T_\infty)]$  versus  $1/(T_c \Delta T f)$ , a straight line was obtained, as shown in Figure 12. According to eq. (14), the slope corresponds to the  $K_g$  parameter, which takes the form<sup>36</sup>

$$K_g = (nb_0 \sigma \sigma_e T_m^\circ) / (2.3k \Delta H_m^0), \quad (15)$$

where  $b_0$  is the distance of two adjacent fold planes;  $\sigma$  and  $\sigma_e$  are the lateral and fold surface free energies of planar surface lamellae,  $k$  is the Boltzmann constant, and  $\Delta H_m^0$  is the enthalpy of fusion. The usual approach to calculate the  $\sigma$  value is the Thomas–Stavely relation:<sup>36</sup>

$$\sigma = \alpha b_0 \Delta H_0, \quad (16)$$

where the empirical constant  $\alpha$  assumes the value of 0.1 for polyolefins.<sup>37</sup> The  $n$  variable can assume values of 2 or 4 according to the regime of crystallization:  $n = 4$  when the crystallization conforms to regime I or III kinetics, whereas  $n = 2$  when the crystallization process occurs according to regime II.<sup>38</sup> In the present work we exclude, *a priori*, the crystallization process can occur according to the regime III because the 1,2-PB crystallization was observed at low undercoolings.<sup>39</sup> To investigate to which regime the data in the selected temperature region belong, the Lauritzen  $Z$ -test can be applied.<sup>40</sup>  $Z$  is a quantity defined as

$$Z = 10^3(L/2a_0)^2 \exp - (x/T_c \Delta T), \quad (17)$$

where  $L$  is the effective lamellar thickness and  $a_0$  is the width of the molecular chain in the crystal. According

to this test, if by substitution for  $x$  in eq. (17) of value of  $K_g$ , results in  $Z < 0.01$ , then crystallization conforms to regime I; on the contrary, if substitution of  $2K_g$  for  $x$  gives  $Z > 1$ , then crystallization follows regime II. Using the measured  $K_g$  value it is possible to estimate the range of  $L$  values consistent with regime I or regime II behavior. Assuming the  $K_g$  values refers to regime I kinetics, and using  $Z = 0.01$  we calculated that the  $L$  values must be lower than 0.04 nm for all  $T_c$  investigated; these values are too small to be acceptable. Assuming that the  $K_g$  values refer to regime II and using  $Z = 1$ , a value of  $L \geq 4.6$  nm was calculated. This value is more reasonable and indicates that 1,2-PB crystallizes according to regime II. This hypothesis was supported by an  $L$  value of 5.9 nm calculated for 1,2-PB crystallized at 179°C, by the relation

$$L = L_p \omega_c \quad (18)$$

where  $L_p$  is equal to 14.7 nm (by SAXS), and the crystallinity  $\omega_c$  is equal to 0.40 (by DSC).

Assuming  $n = 2$  and considering eqs. (15) and (16), the fold surface free energy can be calculated by

$$\sigma_e = (K_g k) / (2b_0^2 \alpha T_m^\circ). \quad (19)$$

The  $\sigma_e$  value for 1,2-syndiotactic polybutadiene was evaluated to be 48 erg/cm<sup>2</sup>.

According to the Lauritzen–Hoffman secondary nucleation theory, regime II is observed when, during the crystallization process, the rate of the deposition of the secondary nucleus on the growth face and the rate of the lateral spreading of polymer chain (or segments of the chain), across the growth face, are comparable.<sup>36</sup>

## CONCLUSION

1,2-PB was prepared at -30°C using the catalyst system  $\text{CrCl}_2(\text{dmppe})_2\text{-MAO}$ . The molar fraction of the syndiotactic pentads [rrrr], evaluated by <sup>13</sup>C-NMR measurements, indicated a highly syndiotactic structure. The lamellar structure for isothermal crystallized 1,2-PB was evidenced by SAXS investigation.

An extensive study on the thermal behavior of 1,2-PB was performed by DSC investigations. 1,2-PB crystallizes in a relative short range of temperatures and its crystallization speed is generally fast, as shown by the  $t_{0.5}$  values obtained from isothermal crystallization curves and by the  $t_{\text{max}}$  values calculated from the nonisothermal crystallization data. The attitude to a fast crystallization is well defined by the calculated CRC value of 203 h<sup>-1</sup>, the highest reported CRC for polyolefins. Very similar values of the activation energy of melt crystallization were calculated from isothermal and nonisothermal crystallization data. A three-dimensional growth of crystalline units, devel-

oped by heterogeneous nucleation, was observed when 1,2-PB crystallized from the melt under isothermal conditions. A secondary stage of crystallization was observed to develop when the fraction of crystallizable material reached the value of about 0.75, for all investigated  $T_c$ . According to the Lauritzen–Hoffman secondary nucleation theory, 1,2-PB crystallizes according to regime II; from the overall rate constant of crystallization, a fold surface free energy was calculated. The equilibrium melting temperature derived from the Hoffman–Weeks approach was equal to 208°C.

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