Characterization of Polypropylene–Poly(1-butene)–Hydrogenated Olygo(cyclopentadiene) Ternary Blends

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ABSTRACT: Ternary blends containing polypropylene (PP), poly(1-butene)(PB), and hydrogenated oligo(cyclopentadiene)(HOCP) have been studied using microscopic calorimetric and dynamic mechanical techniques, with no phase separation having been observed in the melt for all the considered compositions. The morphology of the crystallized blends and spherulite growth rate of the PP component appeared to be influenced by the blend composition. The presence of one or two T_gs revealed by dynamic mechanical thermal analysis (DMTA) on quenched or crystallized blends has suggested that demixing phenomena can occur during the crystallization of the components. The blend composition has been found to affect the overall crystallization rate and the equilibrium melting temperature of the PP component. A parameter describing the enthalpic interactions between the PP component and the diluent fraction evidenced that the addition of HOCP to PP and PB increases the stability of the ternary blend. The above results suggest that the three components can form a miscible blend in the melt. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 1659–1665, 1997

Key words: polymer blends; polypropylene; poly(1-butene); hydrogenated oligo-(cyclopentadiene); melting behavior; morphology

INTRODUCTION

Studies concerning the influence of the presence of hydrogenated oligo(cyclopentadiene) (HOCP) on the morphology, crystallization, and melting behavior of isotactic polypropylene (PP) and of isotactic poly(1-butene)(PB) have been reported in our previous articles.[1,2] The spherulitic growth rate, the overall crystallization rate, and the equilibrium melting temperature of the two polyolefins, PP and PB, were found to be depressed by the presence of HOCP. Moreover, both series of polyolefin–HOCP blends showed a single glass transition temperature depending on composi-

tion. In another article,[3] we studied the influence of the presence of HOCP on the kinetics of transformation of PB crystals from form II to form I. The presence of HOCP can produce, in the crystallized mixture, an amorphous phase characterized by a molecular mobility so reduced to lower the rate of the process. The above results suggest that both polyolefins, PP and PB, can form a homogeneous mixture in the melt with HOCP. Furthermore, studies on the thermal behavior of PP blended with PB revealed that these two compounds are compatible in the amorphous state.[4] The crystallization rate of PP appeared to be depressed by the presence of PB, even if such an interference was not as strong as that observed in the case of the PP/HOCP blends. Investigations on the morphology of the crystallized PP/PB blends revealed the presence of separate phases

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of the two components: the demixing phenomena occurred during the crystallization of the PB component.

In this context, it seemed interesting to look at ternary PP–PB–HOCP blends to investigate the possibility of improving the miscibility of the two polyolefins by the addition of HOCP. Some ternary blends with miscible components have been investigated in the literature. Kwei et al.[5] found that two incompatible polymers, poly(methyl methacrylate) and poly(ethyl methacrylate), can be brought together by poly(vinylidene fluoride) (PVF_2) to form ternary mixtures that are compatible. Miscibility was found in the amorphous phase with PVF_2 content between 30 and 70%. Ternary blends comprising poly(carbonate)(PC), poly(styrene-*co*-acrylonitrile)(SAN), and several polyesters were found to be miscible based on the presence of a single glass transition temperature at many compositions.[6] With poly(1,4-butylene adipate) and poly(1,4-cycloehexanedimethylene succinate), miscibility was generally found, except at very low polyester concentrations whatever the PC/SAN ratio; while with poly(caprolactone) (PCL), the miscibility was found at PCL concentrations larger than 29%. PCL was also used to solubilize PC and poly(hydroxy ether of bisphenol A)(phenoxy). Miscibility was found at PCL concentrations larger than 48%.[7] A single glass transition temperature was observed in ternary PCL/poly(vinyl chloride) (PVC)–chlorinated poly(vinylchloride) (CPVC) blends containing more than 40% of PCL. PVC and CPVC are immiscible, and their T_g values are too close to each other to conclude that PCL–PVC–CPVC can form a homogeneous ternary phase.[8] Poly-

(tetramethyl carbonate)(MPC) showed more affinity for PC than for poly(styrene)(PS) in ternary blends; while PS–MPC binary blends are fully miscible, and PC–MPC blends are only partially miscible.[9]

Two ternary blends involving poly(butylene terephthalate)(PBT) and phenoxy were also investigated. In a first case,[10] blends prepared with poly(arylate)(PAr) as the third component showed a single T_g value when the PBT content was 30% or more. PBT melting point depression was also observed, suggesting a significant interaction between polymers. In a second case,[11] PBT–phenoxy and PC were mixed attempting to improve the miscibility of the PC–phenoxy components. Two T_g values corresponding to a PC-rich phase and a phenoxy-rich phase appeared at all the blend compositions.

In the present work, the morphology and the thermal behavior of PP–PB–HOCP ternary blends have been investigated by using optical microscopy, dynamic mechanical thermal analysis (DMTA), and differential scanning calorimetry (DSC). Some preliminary results have been already given.[12]

EXPERIMENTAL

Materials

Ternary blends of isotactic PP (Moplen T 30-S; M_w 300,000; from Montedison), PB (PB 8340; M_w 700,000; from Shell), and HOCP (Escorez; M_w 630; from Esso Chemical) were prepared by melt-mixing the components at 195°C for 15 min in a Bra-bender electronic plasti-corder PLE 330 mixer, in the following weight ratios.

PP	80	70	70	60	60	60	50	50	50	50
PB	10	10	20	10	20	30	10	20	30	40
HOCP	10	20	10	30	20	10	40	30	20	10

Optical Microscopy

The morphology and the radial growth rate values of PP spherulites (G) were studied employing an optical polarizing Wild microscope with an automatic hot-stage Mettler model FP82 controlled by a Mettler FP80 Control Processor. Thin films of

blend samples, sandwiched between microscope cover glasses, were melted at 210°C for 10 min and then rapidly cooled to the crystallization temperature (T_c). During the isothermal crystallization process, the radii of the growing spherulites were measured as a function of time by taking photomicrographs at different intervals of time.

Figure 1 Avrami plot for the 70 : 10 : 20 PP–PB–HOCP ternary blend at various crystallization temperatures [X_t is the weight fraction of the material crystallized during the time t (s)].

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical measurements were performed with a DMTA MKIII apparatus (Polymer Laboratories, Ltd.) operating in the tensile mode at a frequency of 1 Hz and a strain × 1. The temperature range investigated was −140 to 90°C with a heating rate of 3°C min^{-1}. The measurements were carried out on film samples melted at 200°C for 5 min, then cooled to 120°C to allow the crystallization of PP component, and finally quenched in liquid nitrogen to avoid the crystallization of PB component. Film samples crystallized from the melt at room temperature were also analyzed.

Wide Angle X-ray Diffraction

The wide angle X-ray diffraction (WAXD) data were obtained at 6°C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10, 2000W Cu tube (CuKα radiation, λ = 1.54 Å). The operating voltage and current were 45 kV and 25 mA, respectively. The data were collected (0.02 2θ intervals) and treated by the Diffract-AT V 3.2 software controlling system. The degree of crystallinity of the blends prepared for the DMTA analysis (i.e., by inducing PP crystallization, followed by quenching) was calculated from diffracted intensity data in the range of 2θ 7.5–30.5 degrees by using the area integration method.[13]

Differential Scanning Calorimetry (DSC)

The kinetics of overall crystallization and the melting properties of pure and blended PP were analyzed by DSC using a Perkin-Elmer DSC-4 with a Perkin-Elmer 3600 Data Station (TADS System). About 7 mg of sample were melted at 200°C for 10 min, then cooled to the desired crystallization temperature (T_c); the heat that evolved during the isothermal crystallization was recorded as a function of time; and, after a complete crystallization, the samples were heated again to the melting point at a scanning rate of 20°C min^{-1}.

The weight fraction X_t of the material crystallized during the time t was calculated by the following relation:

Table I Spherulite Isothermal Radial Growth Rate (G, μ/s) as a Function of Crystallization Temperature (T_c) of Various PP/PB/HOCP Ternary Blends

T_c (°C)	PP/PB/HOCP										
	100/0/0	80/10/10	70/20/10	70/10/20	60/30/10	60/20/20	60/10/30	50/40/10	50/30/20	50/20/30	50/10/40
118											0.2678
120										0.2345	0.1863
122							0.1968		0.2826	0.1909	0.1341
123									0.2381	0.1671	0.1133
124						0.2262	0.1316		0.1972	0.1355	0.0866
125				0.1555		0.1739	0.1192				
126		0.2483	0.2436	0.1333		0.1448	0.0957		0.1335	0.0885	
127				0.1177		0.1271	0.0718	0.2599			
128	0.1894	0.1367	0.1289	0.0938	0.1485	0.0889		0.1432	0.0768		
129					0.1265			0.1346			
130	0.1639	0.0865	0.0971	0.0594	0.0989			0.0983			
131					0.0817			0.0744			
132	0.0926	0.0743	0.0599		0.0638						
133	0.0844	0.0539	0.0546								
134	0.0627										

Table II   Values of T_g of Various PP/PB/HOCP Ternary Blends Crystallized at Room Temperature from the Melt

PP/PB/HOCP[a]	PP/PB/HOCP[b]	T_g (K)[c]	T_g (K)[d]
80/10/10	65.6/19.9/14.5	256	293
70/20/10	58.2/27.2/14.6	260	290
70/10/20	56.5/14.2/29.3	257	302
60/30/10	49.5/36.7/13.8	266	284
60/20/20	47.0/25.5/27.5	262	298
60/10/30	48.0/13.0/39.0	259	310
50/40/10	43.0/44.4/12.6	277	283
50/30/20	41.4/33.5/25.1	271	298
50/20/30	40.3/23.0/36.7	267	314
50/10/40	39.9/11.7/48.4	265	318

[a] Nominal composition.

[b] Composition corrected on the basis of the PP and PB crystallization extent determined by WAXD.

[c] PB-rich phase.

[d] PP-rich phase.

$$X_t = \int_0^t (dH/dt)\cdot dt \bigg/ \int_0^\infty (dH/dt)\cdot dt$$

where the first integral is the heat generated during the time t, and the second is the total heat at complete crystallization.

The isotherms of crystallization of pure PP and of PP in the ternary blends allowed the determination of the overall PP crystallization rate constant (k_n), at the various T_c considered, using the Avrami equation[14], as follows

$$X_t = 1 - \exp(-k_n t^n)$$

where n is a parameter depending on the type of nucleation and on the geometry of the growing crystals. For each T_c, the values of n and k_n were determined from the slope and the intercept, respectively, of the straight lines obtained by plotting $\ln[-\ln(1 - X_t)]$ versus $\ln t$. An example of data elaboration is reported in Figure 1.

The observed melting temperature (T_m) was obtained from the maximum of the endothermic peak. Gallium and indium standard samples were employed to calibrate the temperature scale and the heat of transition.

RESULTS AND DISCUSSION

Morphology and Spherulite Growth Rate

Thin films of pure PP and blends, when observed under the optical polarizing microscope during the isothermal crystallization process, showed birefringent spherulitic structures. After crystallization, the samples appeared to be completely filled with impinged spherulites for all the blend compositions studied. The absence of separate domains in both the intraspherulitic regions and the interspherulitic contact zones suggests that PB and HOCP components are incorporated in the interlamellar or interfibrillar zones of PP spherulites. Considering the same T_c value, the spheru-
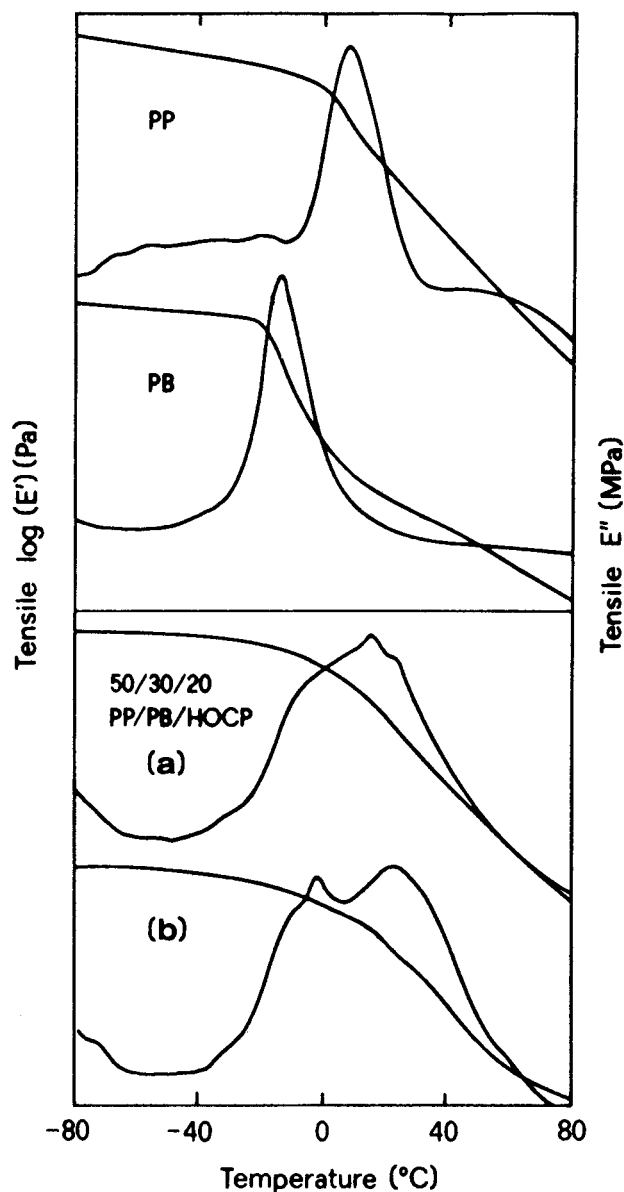

Figure 2 DMTA analysis of the single polymers PP and PB and of 50 : 30 : 20 PP–PB–HOCP ternary blends after PP crystallization from the melt and quenching (a) and after PP and PB crystallization from the melt at room temperature (b).

Table III   Comparison Between Experimental and Calculated T_g Values of Various PP/PB/HOCP Ternary Blends Quenched after PP Crystallization from the Melt

PP/PB/HOCP[a]	PP/PB/HOCP[b]	T_g (exptl) (K)	T_g (calcd) (K)[c]
100/0/0	100/0/0	281	—
0/100/0	0/100/0	258	—
0/0/100	0/0/100	355	—
80/10/10	65.3/17.3/17.4	288	287
70/20/10	57.4/28.3/14.3	286	282
70/10/20	56.2/14.6/29.2	295	295
60/30/10	47.3/39.5/13.2	282	279
60/20/20	46.2/26.9/26.9	292	290
60/10/30	47.8/13.0/39.2	300	302
50/40/10	40.0/48.0/12.0	281	276
50/30/20	39.0/36.5/24.5	289	286
50/20/30	39.5/24.2/36.3	299	297
50/10/40	40.0/12.0/48.0	313	309

[a] Nominal composition.
[b] Composition corrected on the basis of the PP crystallization extent determined by WAXD.
[c] Calculated by Fox equation.

lite dimension was found to increase with increasing concentration of the noncrystallizable component. For all the T_c values investigated, the spherulite radius R linearly increased with the crystallization time for pure and blended PP.

The isothermal radial growth rate $G = dR/dt$ of all the examined samples are reported in Table I. The G values appear to decrease with the increase of T_c for all the compositions. At a constant T_c value, the blends prepared with the same PP fraction exhibit G values that decrease with increasing HOCP fraction.

Glass Transition Temperature

The ternary blends, when crystallized at room temperature from the melt, showed two separate T_g values (Table II), as observed for other ternary blends.[11] This corresponds to the occurrence of a PP-rich and PB-rich phase, where all the HOCP component is dissolved. In fact, no change of E' and E'' moduli was observed in the zone where the T_g of HOCP (82°C) should have appeared. Figure 2 reports the DMTA scans of the 50 : 30 : 20 PP–PB–HOCP ternary blend, chosen as an

Table IV   Crystallization Rate Constant ($10^8 * k_n$ in s^{-3}) of Pure and Blended PP

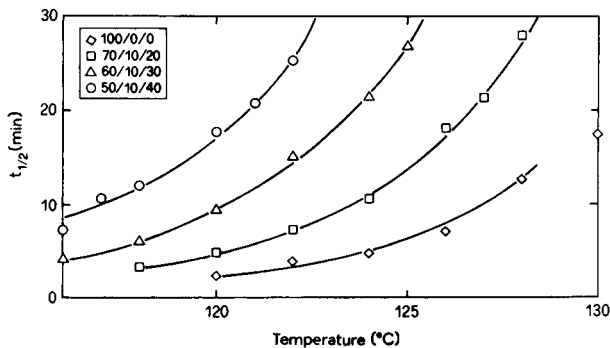|	PP/PB/HOCP										
T_c (°C)	100/0/0	80/10/10	70/20/10	70/10/20	60/30/10	60/20/20	60/10/30	50/40/10	50/30/20	50/20/30	50/10/40
116						42.900	4.600		21.600		0.845
117											0.263
118				9.340			1.410		8.380		0.182
119										0.592	
120	30.000	28.100	20.000	2.900		2.710	0.380		2.460		0.057
121							0.340			0.156	0.036
122	5.750		3.310	0.831		0.729	0.091	1.570	0.429		0.019
124	3.070	1.570	1.530	0.266		0.220	0.032	0.491	0.133	0.022	
125							0.016				
126	0.904	0.559	0.436	0.054	0.555	0.053		0.220	0.028		
127				0.033		0.039		0.109			
128	0.155	0.128	0.073	0.014	0.175			0.042			
129								0.016			
130	0.060	0.035	0.020		0.043						

Figure 3   Temperature dependence of the half-time of crystallization ($t_{1/2}$) of PP in various PP–PB–HOCP ternary blends.

example, quenched after PP crystallization from the melt (a) and crystallized at room temperature from the melt (b). In the first case, a single T_g value is shown (289 K) rather close to that calculated by Fox equation (286 K). This suggests that PP, PB, and HOCP are miscible in the amorphous phase of the blend. The same behavior has been observed for all the other ternary blends. In the calculation of the T_g values ($T_{g,b}$) by Fox equation:[15]

$$\frac{1}{T_{g,b}} = \frac{W_{PP}}{T_{g,PP}} + \frac{W_{PB}}{T_{g,PB}} + \frac{W_{HOCP}}{T_{g,HOCP}}$$

where $T_{g,PP}$, $T_{g,PB}$, $T_{g,HOCP}$, and W_{PP}, W_{PB}, and W_{HOCP} are the glass transition temperatures and the weight fractions, respectively, of the three polymer components, where weight fractions W have been obtained on the basis of the PP crystallization extent determined by WAXD. Such T_g values are reported in Table III. The slight differences between experimental and calculated values could be attributed to minor demixing effects
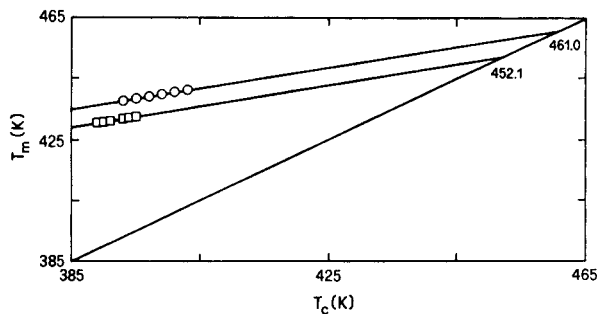
Figure 4   Hoffmann plot for pure PP (○) and a PP–PB–HOCP ternary blend chosen as an example [50 : 10 : 40 (□)].

Table V   Values of T_m^o of PP in Various PP/PB/ HOCP Ternary Blends

PP/PB/HOCP[a]	T_m^o (K)	PP/PB/HOCP[b]
100/0/0	461.0	100/0/0
80/10/10	460.1	0.822/0.097/0.081
70/20/10	459.4	0.723/0.195/0.082
70/10/20	458.3	0.735/0.099/0.0166
60/30/10	458.8	0.624/0.294/0.082
60/20/20	456.8	0.634/0.199/0.167
50/40/10	458.6	0.523/0.394/0.083
50/30/20	456.0	0.531/0.301/0.168
50/20/30	453.2	0.540/0.203/0.257
50/10/40	452.1	0.549/0.103/0.348

[a] Weight composition.
[b] Volume composition (for calculation, see text).

due to a not sufficient quenching. In the light of this fact, the shoulder at the left side of the main peak in Figure 2(a) (observed only for some PB-rich blends) can be justified.

Isothermal Bulk Crystallization Kinetics

The isotherms of crystallization of pure PP and of PP in the ternary blends, compared at the same T_c, evidenced that the crystallization rate constant increases in most cases with the increase of the amount of PP in the blend and that, with a constant fraction of PP, it decreases when the HOCP fraction increases (Table IV). In every case, the increase of T_c have led to decreasing values of k_n. In Figure 3, the half-time of crystallization, $t_{1/2}$ (defined as the time taken for half of the crystallinity to develop), is plotted versus T_c values for the same blend composition. For all the examined systems, values of the Avrami exponent close to 3 have been obtained, suggesting a three-dimensional growth of crystalline units, developed by heterogeneous nucleation.

Melting Behavior

The observed melting temperature of blended PP (T_m) appeared to linearly increase with its crystallization temperature. The experimental data could be fitted by the Hoffmann equation[16], as follows:

$$T_m = (1/\gamma)T_c + (1 - 1/\gamma)T_m^o$$

where γ is the morphological factor of the crystallite, and T_m^o is the equilibrium melting temper-
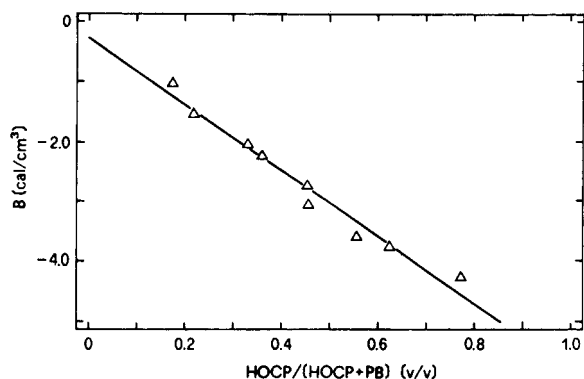
Figure 5 Dependence of the interaction parameter B on the composition of PB + HOCP system.

ature of blended PP. Examples are reported in Figure 4. The extrapolated T_m^o values were influenced by the blend composition (Table V), while the values of $1/\gamma$ were close to each other ($1/\gamma \approx 0.34$). The volume blend compositions in Table V have been calculated at the various T_m^o on the basis of reported[17] temperature dependences of the molar volumes of the considered components. Assuming the absence of annealing and morphological effects,[18] the values of T_m^o have been related to the melting temperature of the pure component ($T_{m,o}^o$) by the following equation:[19]

$$T_m^o = T_{m,o}^o + B(\nu_2/\Delta H_2)T_{m,o}^o(1 - \phi_2)^2$$

where $\Delta H_2/\nu_2$ is the heat of fusion per unit volume of the pure crystal, ϕ_2 is the volume fraction of PP in the blend, and B is the parameter describing the enthalpic interactions between PP and the diluent fraction consisting of PB and HOCP. In Figure 5, the B values are reported versus the HOCP volume fraction on the total volume of the diluent phase. For all the blend compositions considered, negative values of B were obtained that decreased with the increase of the HOCP fraction in the diluent phase, thus indicating that such an increase leads to a higher stability of the blend.

CONCLUSIONS

The miscibility in the melt of PP, PB, and HOCP has been evidenced by the presence of a single glass transition and, considering the spherulite growth rate, the overall crystallization rate and the melting equilibrium temperature of PP. The addition of HOCP component to PP and PB has been found to increase the stability of the blends.

Work is in progress with the aim of obtaining information about the thermal behavior of PB component and on the morphology and the supermolecular structure of the ternary blends.

REFERENCES

1. A. Martuscelli, C. Silvestre, M. Canetti, C. de Lalla, A. M. Bonfatti, and A. Seves, *Makromol. Chem.,* **190,** 2615 (1989).
2. A. M. Bonfatti, M. Canetti, P. Sadocco, A. Seves, and E. Martuscelli, *Polymer,* **34,** 990 (1993).
3. M. Canetti, M. Romanò, P. Sadocco, and A. Seves, *Makromol. Chem.,* **191,** 1589 (1990).
4. M. Canetti, A. M. Bonfatti, P. Sadocco, A. Seves, and M. Pracella, *Polym. Networks Blends,* **3,** 83 (1993).
5. T. K. Kwei, H. L. Frish, W. Radigan, and S. Vogel, *Macromolecules,* **10,** 157 (1977).
6. V. S. Shah, J. D. Keitz, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.,* **32,** 3863 (1986).
7. J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.,* **27,** 1482 (1987).
8. B. Ameduri and R. E. Prud'homme, *Polymer,* **29,** 1052 (1988).
9. C. Belaribi, G. Marin, and Ph. Monge, *Eur. Polym. J.,* **22,** 487 (1986).
10. J. I. Eguiazabal, J. J. Iruin, M. Cortazar, and G. M. Guzman, *J. Appl. Polym. Sci.,* **32,** 5945 (1986).
11. P. M. Remiro and J. Nazabal, *J. Appl. Polym. Sci.,* **42,** 1475 (1991).
12. A. Castelli, G. Munaretto, P. L. Beltrame, M. Canetti, and A. Seves, *4th Eur. Conf. on Advanced Materials and Processes,* Padua, Italy, September 25–28, 1995, p. 633.
13. L. E. Alexander, *X-Ray Diffraction Method in Polymer Science,* Wiley-Interscience, New York, 1969, p. 137.
14. M. Avrami, *J. Chem. Phys.,* **7,** 1103 (1939).
15. T. G. Fox, *Bull. Am. Phys. Soc.,* **2,** 123 (1956).
16. J. D. Hoffmann and J. J. Weeks, *J. Chem. Phys.,* **37,** 172 (1962).
17. D. W. Van Krevelen, *Properties of Polymers,* Elsevier, Amsterdam, 1972, p. 51.
18. J. Boon and J. M. Azcue, *J. Polym. Sci. A-2,* **6,** 885 (1968).
19. P. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, 1953.