Macromolecules **2002,** *35,* 9069−9073

Polymorphism of Isotactic Poly(1-butene) as Revealed by Microindentation Hardness. 1. Kinetics of the Transformation

F. Azzurri,[†] A. Flores,[‡] G. C. Alfonso,[†] and F. J. Baltá Calleja*[,‡]

Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy; and Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

Received June 26, 2002; Revised Manuscript Received September 5, 2002

ABSTRACT: The microindentation hardness technique has been employed to examine the II → I polymorphic transformation of *i*-PBu1 taking place upon aging at room temperature. The hardness values of form I are shown to be remarkably higher than those of form II due to the denser packing of chains in the hexagonal crystal modification. The kinetics of the II → I transformation has been followed by means of microindentation hardness measurements in real time. The influence of molar mass and crystallization temperature on the kinetics of the polymorphic transformation is examined. Results suggest that the rate of polymorphic transformation is independent of molecular weight. In addition, it is seen that increasing the crystallization temperature (up to 105 °C) notably reduces the time required for a full transformation of form II into form I. The influence of the fraction of amorphous material on the rate of polymorphic transformation is discussed.

Introduction

Isotactic poly(1-butene) (*i*-PBu1) is of great industrial interest due to the outstanding mechanical properties that this polymer exhibits in contrast to common polyolefins.[1,2] Isotactic poly(1-butene) presents five different crystal modifications.[3] Samples crystallized from the melt in quiescent conditions at atmospheric pressure generally exhibit the tetragonal form II which, upon aging at room temperature, is gradually transformed into the twinned hexagonal form I.[4] These two crystalline forms represent a paradigmatic example of conformational polymorphism, resulting from small variations in the sequences of nearly trans and nearly gauche dihedral angles along the main chain.[5] Four molecular chain stems with 11/3 helical conformation are packed in the unit cell of form II, while a slightly more extended 3/1 helix is found in the thermodynamically stable form I. The 11/3 helices are loosely packed, and the resulting crystal density ($\rho_{II} = 0.907$ g/cm^3) is only slightly higher than that of the amorphous state ($\rho_a = 0.868$ g/cm^3).[6] In addition, chain packing in the 3/1 helical conformation results in a denser crystalline phase ($\rho_I \approx 0.95$ g/cm^3), with a DSC melting temperature of ca. 125 °C (about 10−15 °C higher than that of the tetragonal crystals) and with enhanced elastic properties.[7]

The polymorphic behavior of *i*-PBu1 is unique due to its solid state spontaneous transformation from the kinetically favored form II into the thermodynamically stable form I. This transformation is completed after approximately 10 days storage at atmospheric pressure and room temperature; longer times are required upon aging, both at lower and higher temperatures.[2,8] This slow process is detrimental for industrial applications and is the main factor that has, so far, hindered the commercial relevance of this polymer. Kinetics of structural interconversion has been thoroughly investigated by means of various techniques, such as thermal analysis, infrared spectroscopy and X-ray diffraction.[9−11] It has been shown that, besides the aging temperature, the rate of transformation also depends on the presence of comonomeric or stereoirregular units along the chain[12] and on the inclusion of additives.[13] It has also been suggested that molar mass is another variable affecting the kinetics of the transformation;[1] a faster rate of transformation has been reported for oligomers of $M_w < 4000$ g/mol. Most important, it has been demonstrated that the transformation rate is largely enhanced by all kinds of mechanical stimuli (pressure, stress, orientation).[14−16]

Despite the extensive investigation on the kinetics of *i*-PBu1 polymorphic transformation, its mechanism is not yet fully understood. Apparently, the process is not accompanied by changes in the gross morphology and the overall crystallinity:[7] at most, an increase of the degree of crystallinity of about 5% has been reported for samples quenched from the melt. Electron microscopy studies suggest that the II → I transformation might produce fragmentation of lamellae into small blocks separated by cracks.[14] However, recent high-resolution transmission electron microscopy studies could not provide an evidence of such cracks in transformed solution grown lamellae.[17]

The microindentation hardness technique is based on the local deformation produced at a microscopic scale on a polymer surface. Microhardness has been shown to be intimately related to molecular and morphological parameters of polymer materials such as the average molar mass, the degree of crystallinity, the crystal thickness, and the surface free energy of lamellar crystals.[18−20] It is now widely accepted that the microhardness of an isotropic semicrystalline polymer, H, can be described in terms of an additive empirical relationship of the crystalline and amorphous regions following:[19]

$$H = H_c\alpha + H_a(1 - \alpha) \tag{1}$$

where H_c and H_a are the hardness values of the crystalline and amorphous phases, respectively, and α

[†] University of Genova.

[‡] Instituto de Estructura de la Materia, CSIC.

10.1021/ma021005e CCC: $22.00

Table 1. Weight-Average Molar Mass and Fraction of Isotactic Pentads of the *i*-PBu-1 Samples

sample code	M_w, 10^3 g/mol	fraction of isotactic pentads, %
PBu BR 200	850	83.1
PBu 200	525	82.7
PBu 300	400	81.7
PBu 800	200	79.5

is the degree of crystallinity. H_c is a function of the intermolecular forces holding the chains within the crystal lattice, and it has also been shown to depend on crystal thickness and surface free energy of the crystals.[21] The sensitivity of crystal hardness to chain packing makes the microhardness technique of great value to detect polymorphic changes in semicrystalline polymers. It has been shown that the amount of the α and β phases in an isotactic polypropylene (iPP) sample can be successfully distinguished using the microhardness technique.[22] Moreover, microindentation hardness has been applied with success to gain information on the stress-induced polymorphic transition in poly(butylene terephthalate), its block copolymers and blends, and iPP.[23−26]

This paper is the first of a series of two concerning the study of the polymorphic changes occurring in *i*-PBu1 upon aging at room temperature using the microhardness technique. In part 1, the micromechanical measurements are analyzed to gain a deeper understanding on the kinetics of the polymorphic transformation. In particular, the influence of molar mass and crystallization temperature on the kinetics of the transformation is examined. Part 2 deals with the correlation between microhardness and microstructure of both forms I and II.[27]

Experimental Section

Materials. Experiments were performed on four isotactic poly(1-butene) homopolymers with different molar mass kindly supplied by Basell Polyolefins, Louvain-la-Neuve, Belgium. Table 1 collects the available molecular characteristics for each *i*-PBu1 sample.

Quenched films, about 300 μm thick, were prepared by compression molding of the as received pellets at 180 °C under a pressure of 5 psi and subsequent cooling using circulating tap water within the platens. Samples prepared under these conditions crystallize at around 50 °C, as could be deduced from the temperature plateau detected in parallel experiments performed using a microthermocouple imbedded in the solidifying sample.

Isothermally crystallized samples were prepared by melting strips of the quenched films in a Mettler hot stage at 180 °C for 5 min. The samples were then quickly transferred to a second hot stage, set at a temperature in the range 80−110 °C, where they were kept until the field of observation was fully covered by spherulites.

Techniques. Calorimetric measurements were carried out using a DSC 7 Perkin-Elmer differential scanning calorimeter. Calibration was made by means of indium and benzoic acid. The scans were performed in the range 25−150 °C, at a heating rate of 20 °C/min, under a blanket of dry nitrogen. The degree of crystallinity, α, was derived from the ratio between the measured heat of fusion, ΔH_m, and the corresponding heat of fusion for ideal infinite crystals, ΔH°_m. In agreement with Rubin,[7] we have assumed a value of $\Delta H^\circ_{mII} = 62$ J/g and $\Delta H^\circ_{mI} = 141$ J/g for the crystal modifications corresponding to forms II and I, respectively.

Microindentation hardness measurements were carried out at room temperature using a Leitz microindenter equipped with a Vickers diamond pyramid (136° between nonadjacent faces). Microhardness values are calculated according to[19]

$$H = K\frac{P}{d^2} \tag{2}$$

where P is the applied load, d is the indentation diagonal, and K is a geometric factor equal to 1.854.

To minimize creep, an indentation time of 0.1 min was used. Three different loads were employed (49, 98, and 147 mN) to correct for the instant elastic recovery. Parts a and b of Figure 1 illustrate typical indentations produced on the surface of two *i*-PBu1 samples of different molar mass ($M_w = 200\,000$ and 850 000 g/mol, respectively) using a load of 98 mN. It is noteworthy that the indentation surface in both cases covers a number of spherulites. At least eight indentations were performed at each load at locations sufficiently apart from each other to be unaffected by the deformation fields of preceding sampling that might accelerate the rate of the II → I transformation. The indentations were performed in a rapid succession to provide hardness data corresponding to a constant degree of polymorphic transformation.

Table 2. Degree of Crystallinity Values and Microhardness Data for Quenched *i*-PBu1 Samples with Different Molar Mass, Immediately after Quenching (Form II) and after the Transformation Is Completed (Form I)

M_w, 10^3 g/mol	crystal form	α	H, MPa
850	II	0.44	5.4
525	II	0.40	5.2
400	II	0.40	4.75
200	II	0.41	4.2
850	I	0.43	34.3
525	I	0.40	22.4
400	I	0.38	21.4
200	I	0.40	26.4

Results and Discussion

Polymorphism As Revealed by Microhardness. (a) Quenched Samples. Table 2 collects the α and H values of the quenched samples with different molar mass, measured immediately after quenching (form II) and long after the transformation is completed (form I) (see Figure 2). It can be observed that the degree of crystallinity for each sample, as determined by DSC, remains nearly constant upon polymorphic transformation. Parallel wide-angle X-ray scattering measurements show similar crystallinity values and confirm that X-ray degree of crystallinity does not vary significantly after the polymorphic transformation. This result is in agreement with previous calorimetric measurements that suggest that the overall crystallinity does not substantially vary during the II → I transformation.[7,10]

Table 2 shows that the H values of form I ($H \approx 20-35$ MPa) are notably higher than those for form II ($H \approx 4-5$ MPa). The former values are in the range of those for LDPE and paraffins, hence, much lower than values characteristic of most common polymeric materials.[19] The finding that H for form I is much higher than for form II is related to the chain packing within the crystals. Indeed, the molecules in the hexagonal crystal modification (form I) are more densely packed than in the tetragonal crystal structure (form II). Table 2 also reveals the tendency of H to increase with increasing chain length. Parts a and b of Figure 1 illustrate that, for a given load, the area of deformation induced in the low molar mass material is slightly larger than that in the sample containing longer chains. This result is a consequence of the hardness dependence on the degree

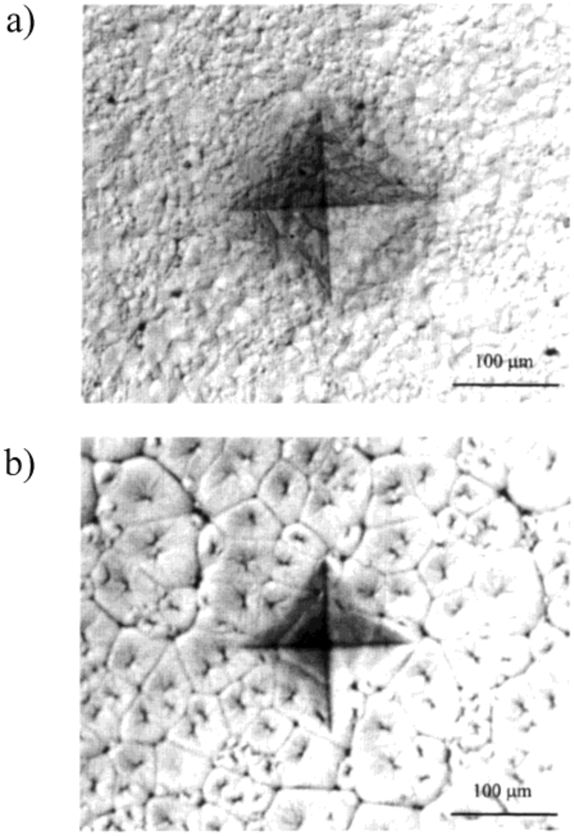

Figure 1. Vickers indentations produced on *i*-PBu1 nonaged samples (using a load of 98 mN for 0.1 min): (a) $M_w = 200\ 000$ g/mol, (b) $M_w = 850\ 000$ g/mol.

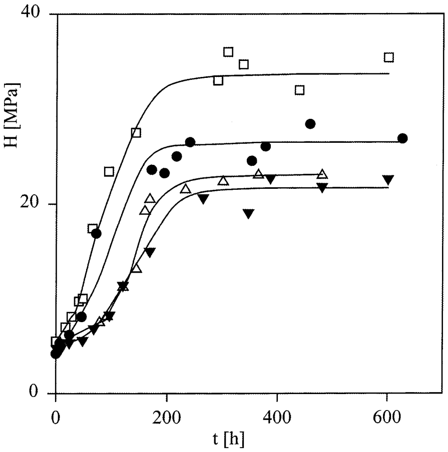

Figure 2. Hardness variation with aging time for *i*-PBu1 quenched samples with $M_w = 200\ 000$ g/mol (●), $M_w = 400\ 000$ g/mol (▼), $M_w = 525.000$ g/mol (△), and $M_w = 850\ 000$ g/mol (□).

of crystallinity (see eq 1) and on the crystal lamellar thickness as will be discussed in the second part of this series.

(b) Isothermally Crystallized Samples. Table 3 collects the α and *H* values of the highest molar mass sample crystallized in the range $T_c = 80-110$ °C. The α and *H* values of each sample were measured immediately after the end of the crystallization process (form II) and long after the transformation was completed (form I).

In all cases, one sees that *H* (form I) ≫ *H* (form II). As mentioned in the preceding section, this result is related to the fact that form I exhibits a much denser chain packing than form II. The remarkable hardness increase with increasing T_c (see Table 3) can be tentatively associated with the higher degree of crystallinity obtained with increasing T_c (see Table 3 and eq 1). A detailed analysis of the microhardness-microstructure correlation will be discussed in the second part of this series.

Table 3. Degree of Crystallinity and Microhardness Values as a Function of Crystallization Temperature for *i*-PBu BR 200, Measured Immediately after the End of the Crystallization Process (Form II) and after the Transformation Is Completed (Form I)

T_c, °C	crystal form	α	*H*, MPa
80	II	0.53	5.1
100	II	0.56	5.85
105	II	0.64	7.7
110	II	0.70	8.3
80	I	0.50	38.2
100	I	0.56	38.4
105	I	0.64	49.5
110	I	0.71	54.6

Kinetics of the II → I Transformation. (a) Quenched Samples. Figure 2 illustrates the hardness variation as a function of aging time, *t*, for rapidly cooled samples ($T_c \approx 50$ °C) with different molecular mass. Figure 2 reveals an initial steep increase of hardness with increasing t, associated with the gradual transformation from form II ($H = 4-5$ MPa) into form I ($H = 20-30$ MPa), followed by a plateau at which the polymorphic transformation can be considered to be completed.

Let us next define a time dependent degree of transformation $\epsilon_H(t)$ through:

$$\epsilon_H(t) = \frac{H(t) - H(t_0)}{H(t_\infty) - H(t_0)} \tag{3}$$

where $H(t)$ is the microhardness at a given aging time *t*, $H(t_0)$ is the hardness value of form II and $H(t_\infty)$ is the hardness value of form I; both limiting values depend on molecular characteristics and crystallization conditions. The $\epsilon_H(t)$ parameter is analogous to that employed in the study of the kinetics of the II → I transformation by means of DSC[10] and offers a measure of the degree of transformation, provided the overall crystallinity is constant during the polymorphic transformation.

Figure 3 shows the plot of $\epsilon_H(t)$ as a function of aging time for samples with different molar mass. The transformation rate does not seem to depend on the average chain length. Figure 3 reveals, in addition, that the room-temperature crystal−crystal transition is completed in about 300 h, in agreement with other data reported in the literature for unstressed samples.[7,9,10]

Figure 4 illustrates, for the highest and the lowest molar weight samples, the correlation between $\epsilon_H(t)$, derived from indentation hardness measurements, and $\epsilon_{DSC}(t)$, determined by means of calorimetric analysis as taken from ref 10. The plot shows a fairly good correlation between both quantities, $\epsilon_H(t)$ and $\epsilon_{DSC}(t)$, in support of the consistency of results from both techniques.

(b) Isothermally Crystallized Samples. Figure 5 illustrates the variation of microhardness with aging time for the highest molar mass sample crystallized at two relatively high temperatures: 80 and 105 °C. Data for the fast cooled sample ($T_c \approx 50$ °C) have also been included for comparison. One can observe that the rate

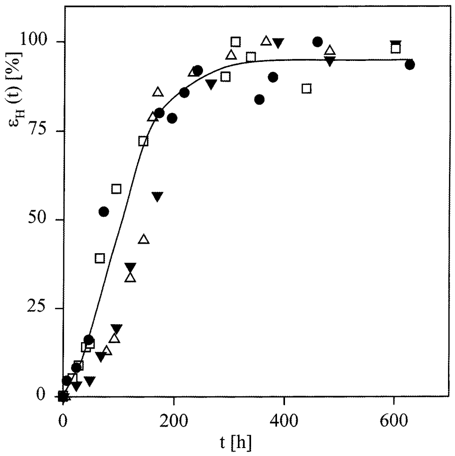

Figure 3. Degree of transformation $\epsilon_H(t)$ (see eq 3) vs aging time for quenched samples with different molar mass. Symbols are as in Figure 2.

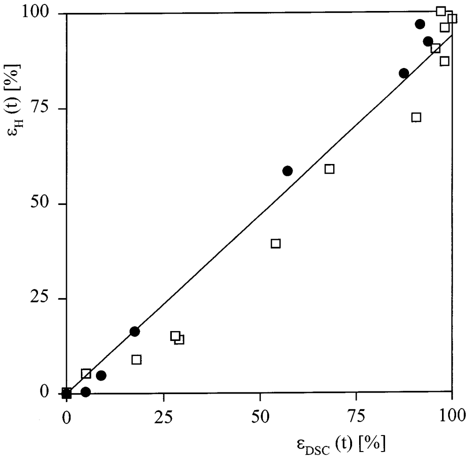

Figure 4. Plot of $\epsilon_H(t)$, derived from indentation hardness measurements, vs $\epsilon_{DSC}(t)$, determined from calorimetric analysis (as taken from reference 10) for quenched samples with M_w = 200 000 g/mol (●) and M_w = 850 000 g/mol (□).

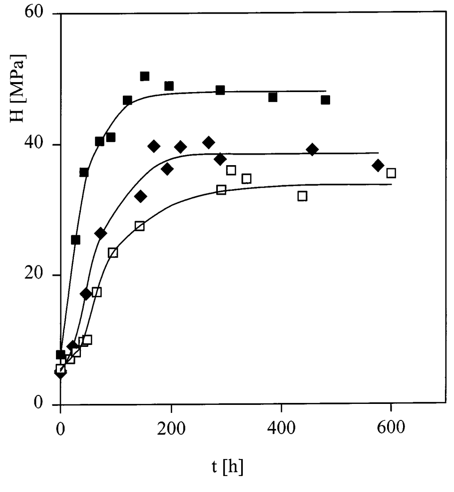

Figure 5. Microhardness variation with aging time for the highest molar mass sample crystallized at T_c = 80 °C (◆) and T_c = 105 °C (■). Data for the quenched sample ($T_c \approx$ 50 °C) have also been included for comparison (□).

of transformation increases with increasing crystallization temperature. While the time required for a complete conversion of form II into form I is about 300 h for the rapidly cooled sample (see Figures 2, 3, and 5), much shorter times (about 170 and 120 h for T_c = 80 and 105 °C, respectively) are needed for the samples isothermally crystallized. In addition, Figure 5 shows that the asymptotic hardness values of form I increase with increasing crystallization temperature; this is a consequence of a higher degree of crystallinity at higher T_c values (see Table 3). A parallel increase of crystallinity and hardness is also obtained for form II (see Table 3).

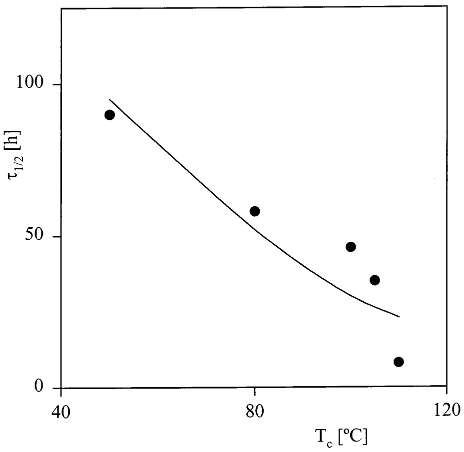

Figure 6. Plot of $\tau_{1/2}$ values vs T_c for the highest molar mass sample.

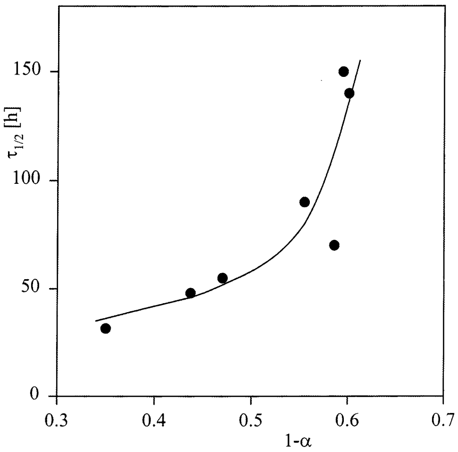

Figure 7. Variation of the half crystallization time with the fraction of amorphous material.

(c) Half-Transformation Time. Figure 6 shows the plot of the room-temperature half-transformation time, $\tau_{1/2} = t(\epsilon{=}0.5)$, as a function of T_c. Data for T_c = 100 and 110 °C have been determined from DSC measurements. The $\tau_{1/2}$ values are shown to be strongly dependent on crystallization temperature. For example, an increase of crystallization temperature of 10 °C reduces the half-transformation time in about 10 h.

Figure 7 illustrates the empirical relationship found between $\tau_{1/2}$ and the fraction of amorphous material, $1 - \alpha$, for the rapidly cooled samples (with different molar mass) and for the high molar mass sample isothermally crystallized at different temperatures (see Tables 2 and 3). The obtained dependence suggests that the rate of polymorphic transformation in unstressed poly(1-butene) might be related to the amount of amorphous material within the sample. The fact that the half-transformation time decreases with decreasing fraction of amorphous material might possibly be explained on the basis of the number of tie molecules connecting adjacent crystals. One may expect the occurrence of a large number of tight sequences between lamellae in samples exhibiting a high degree of crystallinity, as opposed to samples with low crystallinity in which tie chains would adopt a looser conformation. Indeed, Gohil et al. suggested that the tightening of tie molecules may induce additional tensile stress components acting on the chain segments through the crystal−amorphous interphase.[28] One may speculate that this additional tensile stress, which facilitates the local extension of the 11/3 into the 3/1 helical conformation, could enhance the formation of nuclei and, therefore, contribute to an increase in the overall rate of transformation.

Conclusions

1. The present results demonstrate that microindentation hardness allows one to easily distinguish between the kinetically favored form II and the thermodynamically stable form I of *i*-PBu1. The measured microhardness values of form I are shown to be notably higher than those of form II due to the higher chain packing density of the former.

2. The “in situ” microhardness variation at room temperature of *i*-PBu1 samples has been shown to provide a valuable information on the kinetics of the II → I transformation. A good agreement is found between the degree of transformation evaluated from microhardness data and the values obtained from melting enthalpy measurements.

3. The present data suggest that the rate of transformation does not depend on molecular mass, for the range of molecular weight samples studied.

4. High crystallization temperatures are shown to substantially reduce the rate of II → I transformation. It is found that the time required to complete the transformation is reduced from about 12 days, for rapidly cooled samples, to less than 1 week for samples isothermally crystallized in the range 80−105 °C.

5. An empirical relationship between the half-time of transformation and the degree of crystallinity for different poly(1-butene) grades crystallized, in a wide temperature range, has been found. The increase in the rate of the process with decreasing fraction of amorphous material is tentatively explained on the basis of the role played by taut tie molecules at the crystal−amorphous interphase eventually favoring the helix extension needed for the phase transformation.

Acknowledgment. This work was supported by the COST P1 “Soft Condensed Matter” program of the EU and by the MCYT of Spain (Grant No. BFM2000-1474). A.F. is also grateful to the Comunidad Autónoma de Madrid for the award of a postdoctoral grant.

References and Notes

(1) Foglia, A. J. *Appl. Polym. Symp.* **1969**, *11*, 1.
(2) Luciani, L.; Seppala, J.; Lofgren, B. *Prog. Polym. Sci.* **1988**, *13*, 37.
(3) Cojazzi, G.; Malta, V.; Celotti, G.; Zannetti, R. *Macromol. Chem.* **1976**, *177*, 915.
(4) Marigo, A.; Marega, C.; Cecchin, G.; Collina, G.; Ferrara, G. *Eur. Polym. J.* **2000**, *36*, 131.
(5) Corradini, P.; Guerra, G. *Adv. Polym. Sci.* **1991**, *100*, 185.
(6) Aronne, A.; Napolitano, R.; Pirozzi, B. *Eur. Polym. J.* **1986**, *9*, 703.
(7) Rubin I. D. *J. Polym. Sci.* **1964**, *B2*, 747.
(8) Armeniades, C.; Baer, E. *J. Macromol. Sci. Phys.* **1967**, *B1*, 309.
(9) Hong, K.; Spruiell, J. E. *J. Appl. Polym. Sci.* **1985**, *30*, 3163.
(10) Alfonso, G. C.; Azzurri, F.; Castellano, M. *J. Therm. Anal. Calorim.* **2001**, *66*, 197.
(11) Chau, K. W.; Yang, Y. C.; Geil, P. *J. Mater. Sci.* **1986**, *21*, 3002.
(12) Gianotti, G.; Capizzi, A. *Makromol. Chem.* **1969**, *124*, 152.
(13) Siegmann, A. *J. Appl. Polym. Sci.* **1982**, *27*, 1053.
(14) Hsu, T. C.; Geil, P. H. *J. Macromol. Sci.* **1989**, *B28*, 69.
(15) Nakamura, K.; Aoike, T.; Usaka, K.; Kanamoto, T. *Macromolecules* **1999**, *32*, 4975.
(16) Samon, J. M.; Schultz, J. M.; Hsiao, B. S.; Wu, J.; Khot, S. *J. Polym. Sci.* **2000**, *B38*, 1872.
(17) Tosaka, M.; Kamijo, T.; Tsuji, M.; Kohjiya, S.; Ogawa, T.; Isoda, S.; Kobayashi, T. *Macromolecules* **2000**, *33*, 9666.
(18) Deslandes, Y.; Alva Rosa, E.; Brisse, F.; Meneghini, T. *J. Mater. Sci.* **1991**, *26*, 2769.
(19) Baltá Calleja, F. J.; Flores, A. Hardness. In *Encyclopedia of Polymer Science and Technology*, 3rd ed.; John Wiley & Sons: New York, 2002.
(20) Flores, A.; Pietkiewicz, D.; Stribeck, N.; Roslaniec, Z.; Baltá Calleja, F. J. *Macromolecules* **2001**, *34*, 8094.
(21) Baltá Calleja, F. J.; Kilian, H. G. *Colloid Polym. Sci.* **1985**, *263*, 697.
(22) Baltá Calleja, F. J.; Martínez Salazar, J.; Asano, T. *J. Mater. Sci. Lett.* **1988**, *7*, 165.
(23) Fakirov, S.; Boneva, D.; Baltá Calleja, F. J.; Krumova, M.; Apostolov, A. A. *J. Mater. Sci. Lett.* **1998**, *17*, 453.
(24) Apostolov, A. A.; Boneva, D.; Baltá Calleja, F. J.; Krumova, M.; Fakirov, S. *J. Macromol. Sci. Phys.* **1998**, B37, 543.
(25) Boneva, D.; Baltá Calleja, F. J.; Fakirov, S.; Apostolov, A. A.; Krumova, M. *J. Appl. Polym. Sci.* **1998**, *69*, 2271.
(26) Krumova, M.; Karger-Kocsis, J.; Baltá Calleja, F. J.; Fakirov, S. *J. Mater. Sci.* **1999**, *34*, 2371.
(27) Azzurri, F.; Flores, A.; Alfonso, G. C.; Sics, I.; Hsiao, B. S.; Baltá Calleja, F. J. *Polymer*, in press.
(28) Gohil, R. M.; Miles, M. J.; Petermann, J. *J. Macromol. Sci.−Phys.* **1982**, *B21*, 189.

MA021005E