Annealing-Induced Enhancement of the Gas Diffusivity in Coextruded LLDPE Films Investigated by Positron Lifetime Spectroscopy

M. A. Monge,*,[†] J. P. G. Villaluenga,[‡] A. Muñoz,[†] T. Leguey,[†] and R. Pareja[†]

Departamento de Física, Universidad Carlos III de Madrid, 28911 Leganés, Spain, and Departamento de Física Aplicada I, Facultad de Ciencias Físicas, Universidad Complutense, 28040 Madrid, Spain

Received March 27, 2002

ABSTRACT: The annealing effect on coextruded linear low-density polyethylene (LLDPE) films has been investigated by positron annihilation lifetime spectroscopy (PALS). From the continuous positron lifetime distribution found for these films, the size distribution of the free-volume holes in the amorphous phase is calculated, as well as their fractional free volume. Also, diffusivity measurements at 298 K for He, O_2, and N_2 and X-ray diffraction measurements have been performed. The results reveal that annealing induces changes in the hole size distribution and in the amorphous fractional free volume of the films, along with an enhancement of the gas diffusivity. The correlation found between the amorphous fractional free volume and diffusion coefficients agrees with the free-volume model for diffusion in polymers. Moreover, the results show that the probability density function of the free-volume holes has certain influence on the diffusion coefficients, revealing that the impedance factors for diffusion would be controlled by the size distribution shape of the free-volume holes in the amorphous phase.

Introduction

Semicrystalline polymers are regarded as two-phase materials consisting of microcrystalline regions in a continuous amorphous medium. According to experimental studies, the diffusion coefficient of gas molecules in a polymer crystal is expected to be very small or negligible. The crystalline entities in semicrystalline polymers act as impenetrable barriers for gas diffusion. The presence of crystallites in a polymer matrix compels the diffusing molecules to surround those moving through the amorphous phase and reduces the mobility of the amorphous chain segments close to the crystalline regions, which gives rise to a decrease in the gas diffusivity. The effective diffusion coefficient of a gas molecule in a semicrystalline polymer can be described as[1]

$$D = \left(\frac{\psi}{B}\right) D^{a} \tag{1}$$

where D^a is the diffusivity in the amorphous phase, ψ a detour factor taking into account the lengthening of the diffusion pathway due to the impenetrability of the crystallites, and B a blocking factor accounting for the chain immobilization around the crystallites and the existence of amorphous regions with narrow cross sections which do not allow the passage of the gas molecules. Kreituss and Frisch also have treated the effect of crystallinity on gas diffusivity using the so-called free-volume theory.[2] The free volume can be defined as the difference between the total volume and the volume occupied by the polymer molecules. These authors considered that the presence of a crystalline phase in a polymer would reduce its free volume in direct proportion to the amount of crystalline material present. The free-volume approach assumes that both the motion of the diffusing gas and the mobility of the polymer segments are determined by the amount of free volume in the system. A model, based on the free-volume theory, yields an effective gas diffusion coefficient given by[3]

$$D = \left(\frac{\psi}{B}\right) RTA_{\mathrm{d}} \exp\left(-\frac{B_{\mathrm{d}}}{f_{\mathrm{v}}}\right) \tag{2}$$

where f_v is the fractional free volume in the amorphous phase of the polymer, R, the universal gas constant, T, absolute temperature, and A_{d} and B_{d}, temperature independent parameters related to the size and shape of the gas molecule. B_{d} also depends on the minimum size of hole required for a diffusive jump.

In polyethylene (PE), it has been found that the gas diffusivity depends on the volume fraction of the permeable amorphous phase as well as the morphology and size distribution of the crystallites. The results for PE with different grades of crystallinity indicate that the constraining effect of the crystallites may be neutralized by an enhancement of the permeability of the diffusing molecule in the amorphous phase.[3,4] Permeability measurements performed on biaxially stretched PET films have revealed that their diffusional characteristics depend on the hole size at a molecular level, as well as on the crystallinity and polymer chain alignment.[5−7] According to recent results, the diffusional characteristics exhibit a complex dependence on the above parameters.[7] This would explain some diverging results in LLDPE films. For instance, Compañ et al.[8,9] reported that annealing of these films induces an enhancement of the gas permeation accompanied by a slight decrease in the diffusion coefficient.

The interpretation of the experimental results in terms of the free-volume model requires the measurement of the fractional free volume in the material. However, problems arise when conventional methods are used to attempt to measure the local free volume because they estimate, or indirectly determine, the amount of free volume. Positron annihilation lifetime spectroscopy (PALS) has been revealed as a successful

---

* Corresponding author: E-mail: mmonge@fis.uc3m.es.

[†] Universidad Carlos III de Madrid.

[‡] Universidad Complutense.

10.1021/ma020484e CCC: $22.00

technique to determine the free volume hole characteristics. Positrons have the capability to probe the free volume in polymers because they can be localized in nanovoids as a positronium atom in an ortho state ($^3S_1$). The lifetime of the ortho positronium (o-Ps) localized in a free-volume hole, $\tau_{o-\mathrm{Ps}}$, is related to the hole radius R by[10−12]

$$\tau_{o-\mathrm{Ps}} = \frac{1}{2}\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \quad (3)$$

where $\tau_{o-\mathrm{Ps}}$ is given in ns, and ΔR is an adjustable parameter so that $R_0 = R + \Delta R$ is the radius of the spherical potential wells corresponding to the free-volume hole. A ΔR value of 0.166 nm is used for polymers according to experimental results. So, the $\tau_{o-\mathrm{Ps}}$ value gives us an indication of the free volume hole size. The spectral intensity associated with this lifetime component, $I_{o-\mathrm{Ps}}$, is related to the number of free volume hole sites yielding an o-Ps in the polymer.

The aim of the present work has been to investigate the origin of the diffusivity changes induced by isochronal annealing in coextruded LLDPE films using the positron annihilation lifetime spectroscopy.

Experimental Procedure

The films are made of 1-octene-*co*-ethylene copolymers with roughly 8% mol content of the first comonomer. The films are composed by two layers of Dowlex 2247 ($\rho = 0.917$ g cm^{-3}) with thicknesses of 3.5 and 16.0 μm, respectively, and a third layer of Dowlex 2291 ($\rho = 0.912$ g cm^{-3}) 3.5 μm thick. The thicker Dowlex 2247 layer is set between the other two layers. Both materials are additive-free. The extrusion rate was 88 rpm for the thinner layers and 29 rpm for the thicker one. The distance between the die exit and the chill roll was 15 mm, with the temperatures at these points being 543 and 293 K, respectively. More details about the films have been reported elsewhere.[9] Pieces of the film were isochronally annealed for 8 h at five different temperatures in the temperature range 300−383 K.

Measurements of the diffusion coefficient of He, N_2, and O_2 in the films at 298 K were carried out with the experimental setup described elsewhere.[8,13] The measurement technique adopted in the present work is the time-lag method. The polymeric film is used as a diaphragm to separate two chambers of a high-vacuum system. Then the gas is introduced at a known pressure on one side of the film, upstream side. The gas diffuses through the film into a constant sealed volume on the downstream side and is detected by the resulting change in the pressure. Once steady-state conditions are achieved, the amount of gas diffusing at time t is given by

$$Q(t) = \frac{DC_{\mathrm{o}}}{l}\left(t - \frac{l^2}{6D}\right) \quad (4)$$

where C_{o} is the gas concentration in the upstream chamber and l is the film thickness. The diffusion coefficient can be obtained from $Q(t)$ by using the following relationship:

$$D = \frac{l^2}{6\theta} \quad (5)$$

where θ, the time lag, can be determined from the intersection of $Q(t)$ on the time axis. Diffusion measurements were not performed on the samples annealed at 383 K because this heat treatment produced partial melting of the samples. This wrinkled the films, preventing the accurate measurement of their thickness.

X-ray diffraction measurements were carried out on an X-Pert Philips diffractometer using Cu Kα radiation. The crystalline fraction was determined from the ratio of the area of the crystalline peaks to the total area over the angular range 10−30° (2θ) following the procedure described elsewhere.[14] The apparent crystallite size L was determined using the Scherrer formula

$$L = \frac{0.94\,\lambda}{\Delta\cos\theta} \quad (6)$$

where $\lambda = 0.1542$ nm, and Δ is the peak width (fwhm) corrected for the instrumental broadening.

Positron annihilation experiments at room temperature were performed on as-received and annealed samples. A suitable number of pieces of films were stacked together on either side of a ^{22}Na positron source to ensure 100% positron absorption in the samples. The positron lifetime spectra were registered using a fast−fast coincidence system having a time resolution of 250 ps (fwhm). For each measurement a lifetime spectrum with a total of 10^7 counts was accumulated by addition of successive 10^6 count spectra. Assuming that the real positron lifetime spectrum in a polymer is a continuous distribution of lifetime values τ, the observed lifetime spectrum is described by

$$y(t) = R(t) \otimes [N_{\mathrm{t}}s(t) + B] \quad (7)$$

where $\otimes$ denotes the convolution of the resolution function of the spectrometer with the annihilation decay integral function $s(t)$, and N_{t} and B are the total counts and the background of the spectrum, respectively. The term $s(t)$ is given by

$$s(t) = \int_0^\infty \frac{I(\tau)}{\tau}\exp\left(-\frac{t}{\tau}\right)\mathrm{d}\tau = -\int_0^\infty \lambda\alpha(\lambda)\exp(-\lambda t)\,\mathrm{d}\lambda \quad (8)$$

where $\lambda = \tau^{-1}$ is the positron annihilation rate and $\int_0^\infty I(\tau)\,\mathrm{d}\tau = -\int_0^\infty \alpha(\lambda)\,\mathrm{d}\lambda = 1$, with $\alpha(\lambda)$ the annihilation rate probability density function. The spectra were analyzed with the MELT 4.0 routine[15] which yields a continuous lifetime distribution. Another routine used for continuous lifetime distribution analyses is CONTIN. The results obtained from both MELT and CONTIN are very similar, either of them proving reliable to analyze the positron lifetime spectra from polymers.[16,17] Although CONTIN could be more realistic in resolving the o-Ps lifetime distribution, the MELT routine is more simple to handle and sensitive to close distributed lifetimes than CONTIN. The analyses via CONTIN are very sensitive to experimental drifts and require the determination of the experimental time resolution of the spectrometer using reference samples. On the contrary, MELT uses a Gaussian resolution function, to which fwhm is an input parameter. Another input parameter required by MELT is the time zero value. Before applying the MELT routine, we have performed discrete term fits of the spectra using the routine PATFIT[18] in order to obtain accurate and reliable values for the above input parameters.

Results and Discussion

Table 1 summarizes the results obtained from X-ray diffraction, gas diffusion, and positron annihilation

Table 1. Results Obtained from X-ray Diffraction, Gas Diffusion, and Positron Annihilation Measurements in Coextruded LLDPE Films[a]

annealing temperature (K)	crystallinity (%)	crystallite size (nm)	D_{He} ($\times 10^{-6}$ cm^2/s)	D_{O2} ($\times 10^{-7}$ cm^2/s)	D_{N_2} ($\times 10^{-7}$ cm^2/s)	$\Delta\tau_4$ (ps)	$\Delta g(v_h)$ ($\times 10^{-3}$ nm^3)	f_v (%)
298 (as-received)	31.3 ± 1.5	14.2 ± 0.2	1.8	6.0	4.7	240	28.5	6.00
313	35.0 ± 1.5	11.8 ± 0.5	1.9	6.2	5.5	156	13.4	5.42
323	31.4 ± 1.5	13.8 ± 0.2	2.2	6.9	7.0	109	11.7	5.46
333	33.5 ± 1.5	12.4 ± 0.5	4.1	9.3	7.2	90	9.0	5.66
343	34.9 ± 1.5	12.8 ± 1.0	4.5	10.0	8.1	77	8.5	5.88
363	33.9 ± 1.5	13.0 ± 1.0	5.0	11.0	7.9	54	6.0	5.81
383	31.5 ± 1.5	12.7 ± 0.3	–	–	–	132	14.1	5.81

[a] $\Delta\tau_4$ and $\Delta g(v_h)$ are the fwhm values for the τ_4 distribution and the probability density function $g(v_h)$, and f_v is the fractional free volume.

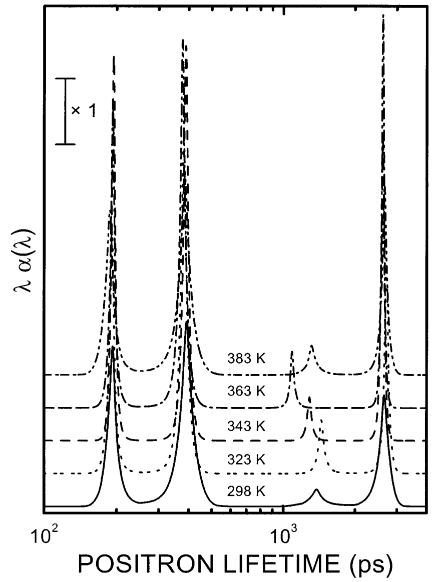

Figure 1. Annealing effect on the positron lifetime distribution function for coextruded LLDPE films.

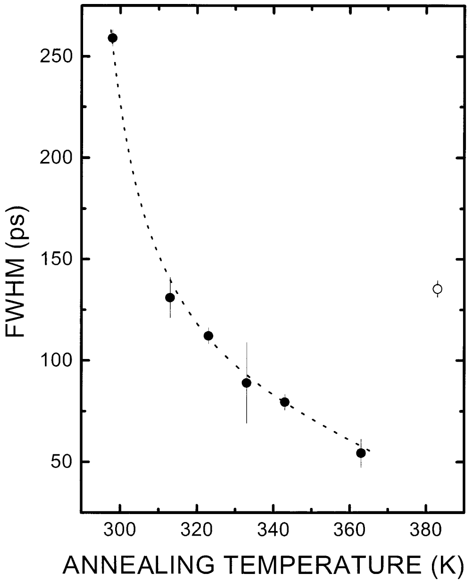

Figure 2. Full width at half-maximum of the *o*-Ps lifetime distribution τ_4 versus annealing temperature for coextruded LLDPE films. (○) films partly melted during annealing.

measurements. The results show a clear increase of the diffusion coefficients after annealing of the coextruded films. Annealing at increasing temperatures produces slight variations in the crystallinity grade of the films and in their crystallite sizes that do not reveal any significant trend correlated with the increase of the gas diffusion coefficients. This rules out that the annealing-induced changes in the crystalline regions, which most likely cause variations in the detour and blocking factors ψ and B, may be responsible for the observed increase of the diffusion coefficients.

The four discrete-term analyses performed on the spectra obtained in our experiments yield lifetime and intensity values in reasonable agreement with those obtained via the MELT routine. The discrepancies between the parameters obtained from MELT and those from a discrete-term analysis have been exhaustively investigated by Dublek et al.[17] It has been well established that the discrepancies found between the parameters obtained from the experimental spectra indicating the Ps formation, i.e., the τ_1 value and the ratio I_1/I_4, and the theoretically expected values for $\tau_{p-\mathrm{Ps}}$ and the ratio $I_{p-\mathrm{Ps}}/I_{o-\mathrm{Ps}}$, are larger in the case of the discrete-term analyses. Moreover, the discrepancies increase as the Ps yield in the polymers decreases.[17] On the basis of these results we discuss our experiments using the results obtained from MELT.

The annealing effect on the positron lifetime spectrum of the coextruded films is shown in Figure 1. The positron lifetime distribution exhibits four well-defined peaks centered around 190, 380, 1300, and 2630 ps, with intensities of about 28, 46, 5, and 21%, respectively. The shortest lifetime peak arises from *p*-Ps self-annihilation and free positron annihilation and it does not provide any relevant information in polymers.[19] The intermediate lifetime peak with lifetime around 380 ps is attributed to positrons localized at the crystalline/amorphous interface, i.e., at the interfacial phase, or at some defects in the crystalline regions. The intensity of this lifetime component remained inside the interval 44.5−47.0% over the annealing temperature range. It is found that a crystallinity variation between 31.3 and 35.0%, induced by annealing, results in no changes in this lifetime component peak. The third $\tau_3 \approx (1.1-1.4)$ ns and the fourth $\tau_4 \approx (2.6-2.7)$ ns are attributed to *o*-Ps pick-off annihilation in the crystalline phase and at the free-volume holes in the amorphous regions of the polymer, respectively.[20,21] The τ_3 value appears to be correlated with the crystal packing density in the crystalline regions, while τ_4 depends on the size of the free-volume holes in the amorphous regions through eq 3. Since the gas diffusion in semicrystalline polymers takes place through the amorphous regions, we are concerned about the evolution of the fourth lifetime peak.

Figure 2 shows the annealing effect on the full width at half-maximum (fwhm) of the distribution function for the four lifetime peak τ_4 distribution. The peak width goes continuously down for annealing up to 363 K going up after annealing at 383 K. It should be noted that at

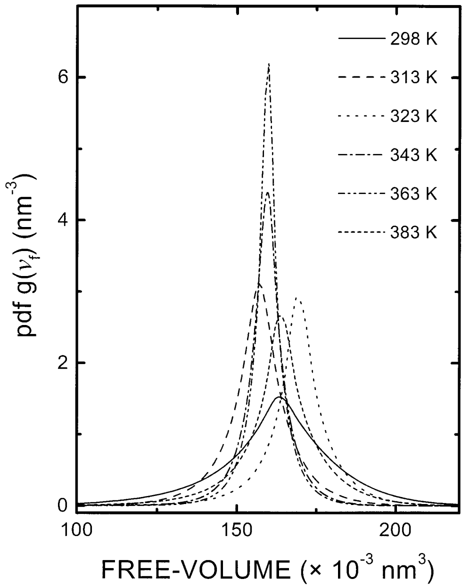

Figure 3. Annealing effect on the free-volume hole distribution in the amorphous phase of coextruded LLDPE films.

a temperature as high as 383 K extensive melting of crystalline regions in these films occurs. This behavior found for the lifetime τ_4 distribution appears to be due to relaxation processes and changes in the amorphous regions rather than changes in the crystallinity of the films. It is observed from the results in Table 1 that the crystallinity of the annealed films and the τ_4 width are not correlated.

Using eq 3 and the probability density function $\alpha(\lambda_4)$ obtained by the MELT-4 code, a probability density function for the free-volume hole radius, $f(R)$, can be obtained. Following Jean and Deng,[22,23] a linear hole radius dependence has been considered for the Ps trapping rate in the free volume. Assuming a spherical approximation for the free-volume holes, from $f(R)$ we have obtained a probability density function for the free volume hole sizes $g(v_h)$. It is given by

$$g(v_h) = \frac{f(R)}{4\pi R^2} = -2\Delta R \frac{\cos\left(\dfrac{2\pi R}{R + \Delta R}\right) - 1}{4\pi R^2 (R + \Delta R)^2 K(R)} \alpha(\lambda_4) \tag{10}$$

where $K(R) = 1 + 8R$ is the correction factor for the Ps trapping rate used by Jean and Deng;[22,23] here the hole radius R is given in Å.

Figure 3 shows the annealing effect on the free volume hole size distribution in the amorphous phase of the films. Annealing produces remarkable changes in the fwhm value of $g(v_h)$, $\Delta g(v_h)$, but meaningless shifts of its maximum. An unambiguous correlation is found between the diffusion coefficient and the width $\Delta g(v_h)$ as shown in Figure 4.

Following Dlubek et al.,[21] we assumed that the amorphous fractional free volume in the samples, f_v, is equivalent to the fractional hole volume f_h determined from the positron lifetime distributions, i.e., $f_v \equiv f_h$. This fractional hole volume can be obtained by integration of

$$f_h = \int_0^\infty g(v_h)\, dv_h \tag{11}$$

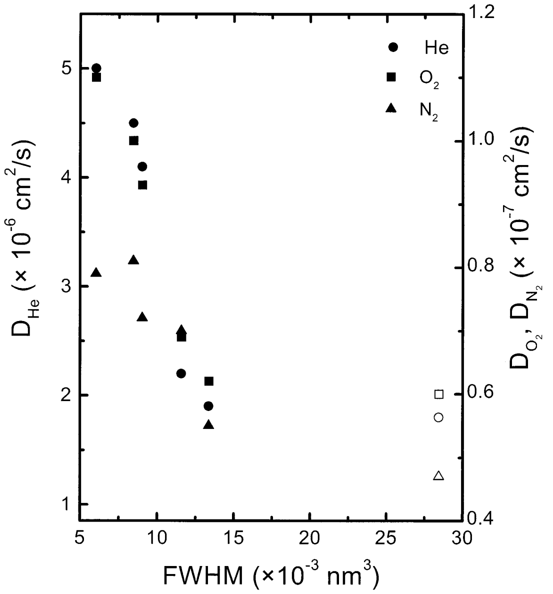

Figure 4. Gas diffusion coefficients versus the full width at half-maximum of the probability density function $g(v_h)$ of free-volume hole sizes in the amorphous phase of annealed coextruded LLDPE films. The open symbols correspond to as-received films.

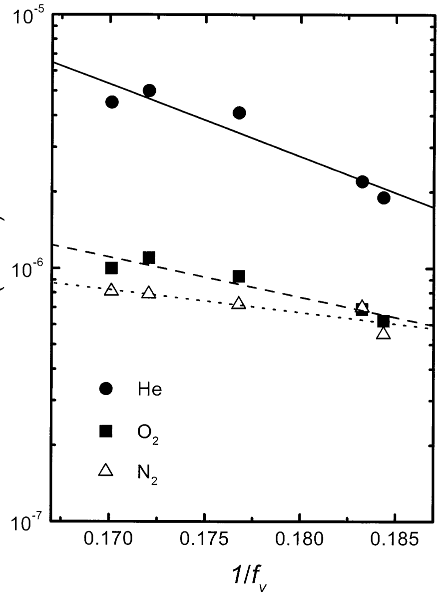

Figure 5. Arrhenius plots for gas diffusion coefficients versus fractional free volume in annealed coextruded LLDPE films.

The obtained fractional free-volume values are given in Table 1. No correlation seems to exist between fractional free volume f_v and the fwhm values of the τ_4 distribution and the probability density function $g(v_h)$. The Arrhenius plots of D versus the fractional free volume f_v, excluding the data points for the as-received films, are shown in Figure 5. The results indicate that the diffusion coefficients for He, O_2, and N_2 scale with f_v according to the free-volume model. The fitting of the gas diffusion data to eq 2, with $(\psi/B)A_d$ and B_d as adjustable parameters, can be considered satisfactory. The values found for these parameters are given in Table 2. It should be noted that the values for O_2 and N_2 are in good agreement with those previously reported for similar types of LLDPE films.[13]

The data points for the as-received films do not follow the above Arrhenius plot. These films have the lowest diffusion coefficients although their fractional free volume f_v is the highest. Nevertheless, their hole-volume

Table 2. $(\psi/B)A_d$ and B_d Values Obtained from the Fits of the Diffusion Data to Eq 2

	B_d	$(\psi/B)A_d$ kmol m^2/(J s)
He	0.66	1.5×10^{-11}
O_2	0.37	2.3×10^{-14}
N_2	0.21	1.1×10^{-15}

distribution is much wider than those for the annealed films. This shows that the values of the parameters $(\Psi/B)A_d$ and B_d are governed by the width of the hole-volume distribution. This result can be interpreted as evidence for a correlation between the shape of the hole-volume distribution and the detour and blocking factors, Ψ and B. One can envisage an alternative, though equivalent, interpretation. According to eq 5, lower D values mean that the time lag θ for the gas flowing through the films increases. Our results also indicate that the width of the hole-volume distribution $\Delta g(v_h)$ governs this time lag. This would implicate the lengthening of the diffusion pathway. On the other hand, the wider the hole-volume distribution, the higher the number of possible diffusion pathways for the gas through the amorphous regions of the film. This would result in an increase of the tortuosity in the diffusion pathway. Then, the annealed films with less fractional free volume and having a narrower hole volume distribution can exhibit higher diffusion coefficients. This suggests that the structural relaxation induced by annealing in as-received coextruded LLDPE films produces a qualitative change in some of the impedance factors, (ψ/B) or B_d.

Finally, it should be noted that it would be very difficult to quantify or determine the dependence of the diffusion coefficients on the width $\Delta g(v_h)$, because changes in $\Delta g(v_h)$ can also induce changes in the fractional free volume f_v.

Conclusions

In annealed coextruded LLPDE films, PALS results obtained from a continuous data analysis using the routine MELT appear to be well correlated with the diffusion coefficient increase induced by annealing. The results reveal that annealing produces changes in the size distribution of the free-volume holes, as well as in the fractional free volume. In addition, they evidence that the impedance factors, or tortuosity, for the gas diffusion pathway can be controlled by the size distribution shape of the free-volume holes in the amorphous phase of the polymers.

Acknowledgment. The research carried out at Universidad Carlos III de Madrid was supported by Consejería de Educación de la Comunidad Autónoma de Madrid (Spain) under the auspices of the Financing Program for Strategic Research Groups. The authors are grateful to Dr. B. Seoane for useful discussions.

References and Notes

(1) Peterlin, A. *J. Macromol. Sci. Phys. B* **1975**, *28*, 57.

(2) Kreituss, A.; Frisch, H. L. *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 889.

(3) Hedenqvist, M.; Angelstok, A.; Edsberg, L.; Larsson, P. T.; Gedde, U. W. *Polymer* **1996**, *37*, 2887.

(4) Gohil, R. M. *J. Appl. Polym. Sci.* **1993**, *48*, 1649.

(5) Sha, H.; Harrison, I. R. *J. Polym. Sci. B: Polym. Phys.* **1992**, *30*, 915.

(6) Sodaye, H. S.; Pujari, P. K.; Goswami, A.; Monohar, S. B. *J. Polym. Sci. B: Polym. Phys.* **1998**, *36*, 983.

(7) McGonigle, E. A.; Liggat, J. J.; Pethrick, R. A.; Jenkins, S. D.; Daly, J. H.; Hayward, D. *Polymer* **2001**, *42*, 2413.

(8) Compañ, V.; Andrio, A.; López, M. L.; Riande, E. *Polymer* **1996**, *37*, 5831.

(9) Compañ, V.; Andrio, A.; López, M. L.; Álvarez, C.; Riande, E. *Macromolecules* **1997**, *30*, 3317.

(10) Nakanishi, H.; Jean, Y. C. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier: Amsterdam, 1988; p 159.

(11) Jean, Y. C. In *Positron Annihilation, Proceedings of the 10th International Conference on Positron Annihilation*; He, Y. J., Cao, B. S., Jean, Y. C., Eds.; *Mater. Sci. Forum* 1995; Vol. 175−178, p 599.

(12) Pethrick, R. A. *Prog. Polym. Sci.* **1997**, *22*, 1.

(13) Villaluenga, J. P. G.; Seoane, B.; Compañ, V. *J. Appl. Polym. Sci.* **1998**, *70*, 23.

(14) Murthy, N. S.; Minor, H. *Polymer* **1990**, *31*, 996.

(15) Shukla, A.; Hoffmann, L.; Manuel, A. A.; Peter, M. In *Positron Annihilation, Proceedings of the 11th International Conference on Positron Annihilation*; Jean, Y. C., Eldrup, M., Schrader, D. M., West, R. N., Eds.; *Mater. Sci. Forum* 1997; Vol. 255−257, p 233.

(16) Cao, H.; Dai, G. H.; Yuan, J. P.; Jean, Y. C. In *Positron Annihilation, Proceedings of the 11th International Conference on Positron Annihilation*; Jean, Y. C., Eldrup, M., Schrader, D. M., West, R. N., Eds.; *Mater. Sci. Forum* 1997; Vol. 255−257, p 238.

(17) Dlubek, G.; Hübner, C.; Eichler, S. *Nucl. Instrum. Methods B* **1998**, *142*, 191. Dlubek, G.; Eichler, S.; Hübner, C.; Nagel, C. *Nucl. Instrum. Methods B* **1999**, *149*, 501.

(18) Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. *PATFIT-88*; 1989; Risø-M-2740.

(19) Mogensen, O. E. In *Positron Annihilation in Chemistry*; Springer-Verlag: Berlin, 1995.

(20) Dlubek, G.; Saarinen, K.; Fretwell, H. M. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 1513.

(21) Dlubek, G.; Bamford, D.; Henschke, O.; Knorr, J.; Alam, M. A.; Arnold, M.; Lüpke, T. *Polymer* **2001**, *42*, 5381.

(22) Jean, Y. C.; Deng, Q. *J. Polym. Sci. Part B: Polym. Phys.* **1992**, *30*, 1359.

(23) Deng, Q.; Jean, Y. C. *Macromolecules* **1993**, *26*, 30.

MA020484E