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Determination of the Binodal and Spinodal Phase Separation Temperatures in the Blend System PαMS$_{0.5}$-*co*-AN$_{0.5}$ (Luran)/PMMA$_{0.95}$MA$_{0.05}$ (Lucryl) with Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: The temperature dependence of free volume in the blend system of commercial PαMS$_{0.5}$-*co*-AN$_{0.5}$ (Luran KR 2556)/PMMA$_{0.95}$MA$_{0.05}$ (Lucryl G77) has been investigated by means of positron annihilation lifetime spectroscopy (PALS). The PALS measurements show characteristic changes in free volume parameters at temperatures that coincide with the cloud point and spinodal temperatures of the system. Hence, PALS seems to be a powerful method to detect in-situ both binodal (cloud point) and spinodal phase separation temperatures in polymers. The binodal can be detected at a very early stage.

Introduction

Luran KR 2556 (PαMS$_{0.5}$-*co*-AN$_{0.5}$) is a statistical copolymer made up of equal parts of α-methylstyrene and acrylonitrile. Lucryl G77 (PMMA$_{0.95}$MA$_{0.05}$) is a PMMA with 5 wt % MA methylacrylate. Blends of Luran KR 2556 and Lucryl G77 exhibit an upper miscibility gap (LCST)[1−4] and are a topic within the IUPAC Working Party "Structure and Properties of Commertial Polymers". The most important use for blends are construction parts, which need low weight but a high impact strength. Blends are often easier to process in contrast to pure polymers, which have to be formed first and impact strengthened afterward. This advantage can only be profited if a homogeneous mixture is obtained. Hence, studies on separation behavior are important to investigate thermal stability.[5,6]

Positron annihilation lifetime spectroscopy (PALS) is sensitive to small changes in free volume in polymers[7] resulting from temperature changes, e.g., near the glass transition temperature. The pick-off lifetime of the $^3S_1$ state of positronium (orthopositronium, termed o-Ps) is correlated to the free volume hole sizes in polymers. The corresponding intensity has to be investigated carefully, because it could be influenced by many factors, e.g., radiation effects,[8] exposure to light,[9] or an electrical field.[10]

The importance of blends has stimulated many groups to do PALS studies.[11−18] Most of these studies were done to investigate the free volume related lifetime as a function of composition and the glass transition behavior of homogeneous and phase-separated samples. In this work the time dependence of the annihilation parameters at increasing temperatures was investigated. We observed characteristical changes in o-Ps intensity at temperatures which were identified to the binodal (cloud point) and spinodal phase separation temperatures. In contrast to most of the common methods (cloud point experiments, TEM, DSC), we were able to detect both phase separation temperatures with one method—PALS—making in-situ measurements at increasing temperature. Measuring different compositions as well as pure Luran KR 2556 and Lucryl G77 the phase separation temperatures determined by other methods (optical cloud point experiments, TEM)[1,2,19] could be confirmed. Homogeneous mixing before the temperature treatment and the separation afterward were verified by means of differential scanning calorimetry (DSC) and optical microscopy.

Experimental Section

The experiments were done on solvent-casted and hot-pressed samples. For the solvent-casted samples the commercial polymer Luran KR 2556 (statistical copolymer made up of equal parts of αMS and AN) and Lucryl G77 (statistical copolymer of MMA with 5% MA, methacrylate) from BASF AG Ludwigshafen were dissolved in acetone. The solvent was evaporated for 1 week at normal conditions. Residual solvents were expelled afterward in a vacuum furnace (10^{-8} mbar) by annealing up to the glass transition temperature at a rate of 5 K/day. Faster evaporation results in bubbles. The samples had a thickness of 0.25 mm and were stacked to 1 mm for the PALS measurements. The hot-pressed samples were blended in an extruder and hot-pressed to plates. These samples were cut to $1 \times 6 \times 6$ mm^3 for the PALS measurements. The absence of solvent residues was checked with thermal gravimetric analysis (TGA 7 by Perkin-Elmer) using 1 and 20 K/min and 5 ± 1 mg. Homogeneous mixing was verified with optical microscopy and with DSC (differential scanning calorimetry). The measurements were done with a DSC PYRIS 1 by Perkin-Elmer with 20 K/min using 10 ± 0.5 mg. The DSC curves showed one glass transition temperature before decomposition and two close to the pure polymers of the blend afterward.

The PALS measurements were carried out under vacuum conditions (10^{-6} mbar) in-situ at 30−190 °C in 5 K steps. At each temperature the samples were held for at least 1 day. The positron lifetime spectra were measured using a fast−fast coincidence setup with Hamamatsu photomultipliers, Ortec electronic components, and Bicron BC420 scintillator material. The full width at half-maximum (fwhm) of the time resolution function was 227.5−229 ps. The sample holder was in the horizontal position. We used encapsulated Kapton foils (30HN, Du Pont) with activities of $\cong$30 μCi as well as directly

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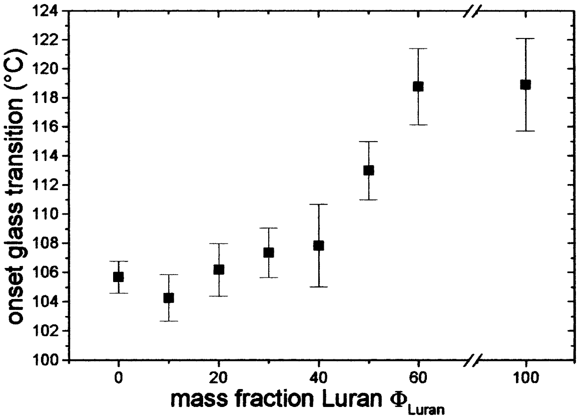

Figure 1. Onset glass transition temperatures as a function of composition measured with DSC.

deposited sources of the same activity. The counting rates was ≅250 s^{-1}. For each temperature 4−6 spectra containing total counts of 3 × 10^6 and 6 × 10^6 were counted automatically. The spectra were separated in three discrete lifetimes using the Patfit88 package.[20] The longest lifetime τ_3 is the o-Ps lifetime is well correlated to the average free volume of polymers.[7] Since only this long lifetime component and relative changes in the related intensity (I_3) were considered, no source correction was needed. (The source parameters were 365 ps, 2% for directly deposited sources, and 372 ps, 15% for Kapton foils.) To rule out influences of the intensity caused by radiation effects, we also measured with doubled source activity (counting rate ≅ 500 s^{-1}).

Results and Discussion

Figure 1 shows the onset glass transition temperatures measured with DSC as a function of the mass fraction Φ_{Luran} of Luran KR 2556. For $\Phi_{Luran} < 0.6$ they obey the Gordon−Taylor equation[21]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

where w_i is the weight fraction and T_{gi} the glass transition temperatures of components i and $k = 4$. For $\Phi_{Luran} > 0.6$ the glass transition temperatures are equal to that of pure Luran KR 2556 (119 ± 3 °C).

The orthopositronium lifetimes show the expected temperature dependence. They increase with increasing temperature and show one kink at the glass transition temperature in the blended samples (Figure 2). Since PALS is an isochronal experiment, the resulting glass transition temperature is well below that measured with DSC. The absolute lifetime of Luran (1927 ± 6 ps) is comparable to the values reported by Wästlund et al.[15,22] and Čižek et al.[18] for SAN. For pure polystyrene they found an intensity of 39.9%, but the o-Ps yield decreased dramatically with increasing AN content (down to 9.3%). A good interpretation of the intensity decrease in copolymers is that the o-Ps formation probability depends on the concentration of electron-scavenging groups, which applies to our blends due to the presence of acrylonitrile.[22] An equation describing the partial inhibition was given by Eldrup et al.:[23]

$$I_3 = I_3^0\left[A + \frac{1 - A}{1 + \sigma C}\right] \qquad (2)$$

Here, I_3^0 is the o-Ps yield at $C = 0$, C is the concentration of scavenger in mol/L, A is a constant related to the saturation value of I_3, and σ is a fitting parameter called the inhibition constant. The inhibition constant is related to the efficienty of the scavenger relative to the formation efficienty.

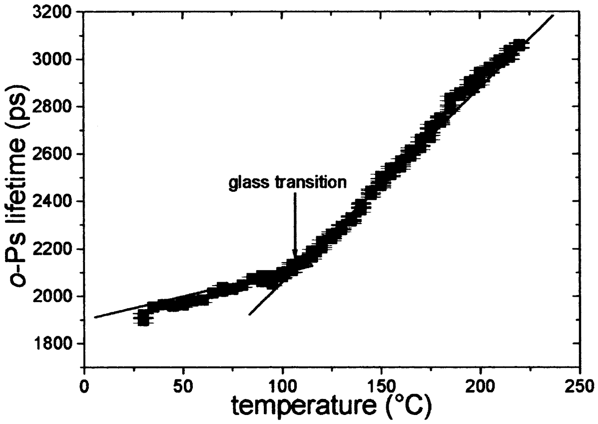

Figure 2. Typical plot of o-Ps lifetime as a function of temperature shown for a Luran fraction of $\Phi_{Luran} = 0.6$. The o-Ps lifetime correlates with the average hole size of the free volume. The change in slope at 105−120 °C is caused by the glass transitions. The glass transition temperature T_g is obtained from the crossing of linear fits as shown.

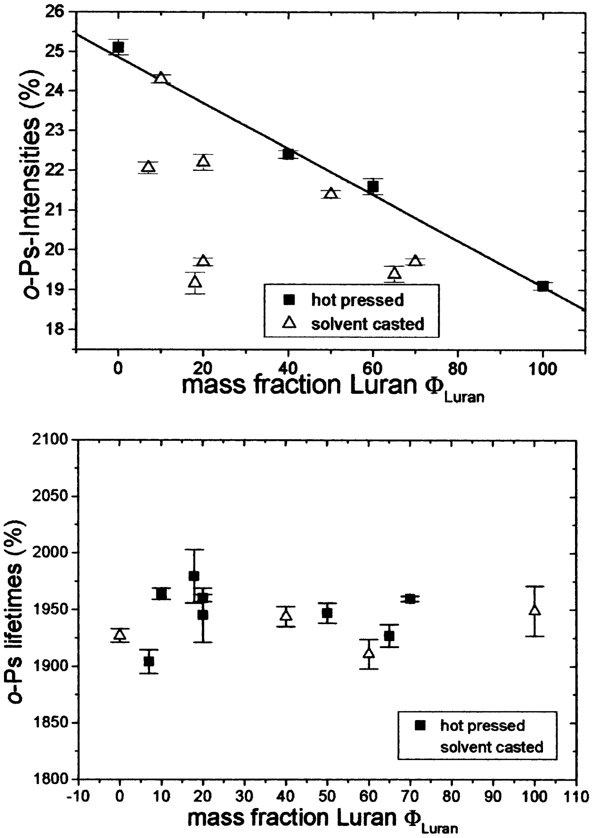

Figure 3. (a) o-Ps intensity at 30 °C vs composition. (b) o-Ps lifetime vs composition.

In Lucryl we measured a lifetime of 1940 ± 20 ps with an intensity of 19.1 ± 0.1%. Literature data for pure PMMA are between 1650 ps (21.5%) and ~2000 ps (~14%).[24,25] For the hot-pressed samples we found a linear dependence of o-Ps intensity on the Luran KR 2556/Lucryl G77 composition (Figure 3). The intensities for the solvent-casted samples are lower. This may be caused by partial annihilation at external surfaces due

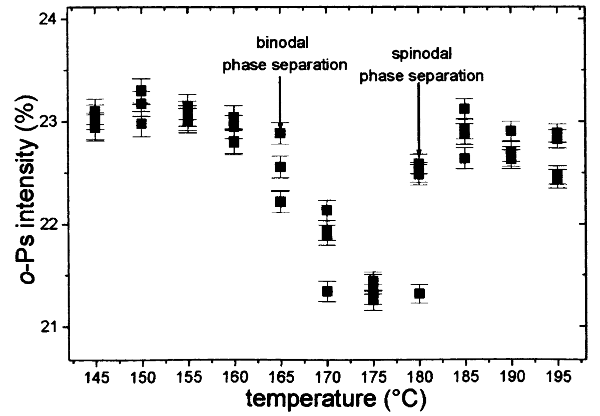

Figure 4. o-Ps intensity vs temperature at $\Phi_{\mathrm{Luran}} = 0.6$. At the binodal decomposition temperature the annihilation parameters change continuously and at the spinodal separation temperature steplike.

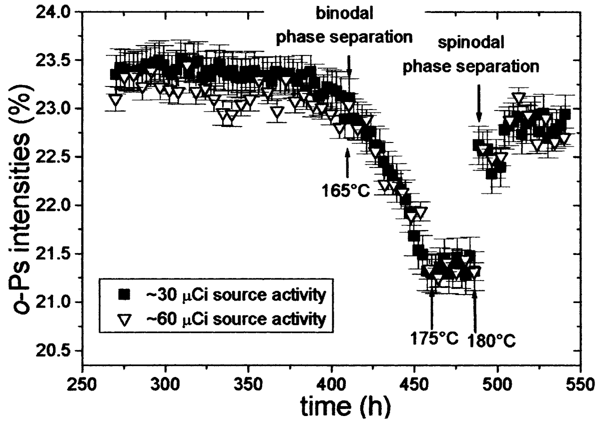

Figure 5. Measurements with different source activities showing that there is no influence on the relative o-Ps intensity. The time scale of the *x*-axis represents a temperature scale. The corresponding temperatures are indicated at relevant points.

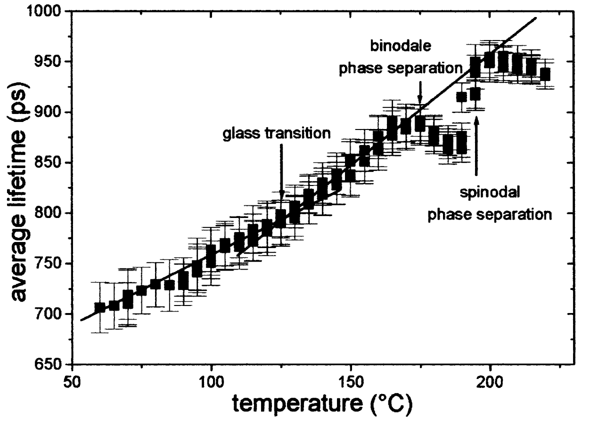

Figure 6. Temperature dependence of the average lifetime τ_{av}. It reflects changes in both intensity and lifetime. Because of the relation $\tau_{\mathrm{av}} = \sum I_i\tau_i$ the changes of the o-Ps component are amplified.

to stacking or at resulting bubbles from solvent evaporation.

Above the glass transition temperature there are additional kinks in o-Ps intensity I_3 in the case of phase separation. Comparison with other experiments (cloud point, TEM, and DSC)[4,19] shows that the kink temperatures are very close to experimental cloud points and calculated spinodal temperatures.[19] The o-Ps intensity changes continuously at the binodal (cloud point) and steplike at the spinodal separation temperature (Figure 4). This is a good indication that the kinks are caused by structural changes resulting from the phase separation. The steplike change at the spinodal composition temperature can be attributed to the absence of an incubation time. Measurements with higher activity demonstrate that the results are not effected by radiation behavior (Figure 5). Figure 6 shows the course at the average lifetime τ_{av} at a Luran fraction of $\Phi_{\mathrm{Luran}} = 0.6$. The average lifetime reflects changes in both intensity and lifetime. The longest o-Ps component is amplied by the definition $\tau_{\mathrm{av}} = \sum I_i\tau_i$.

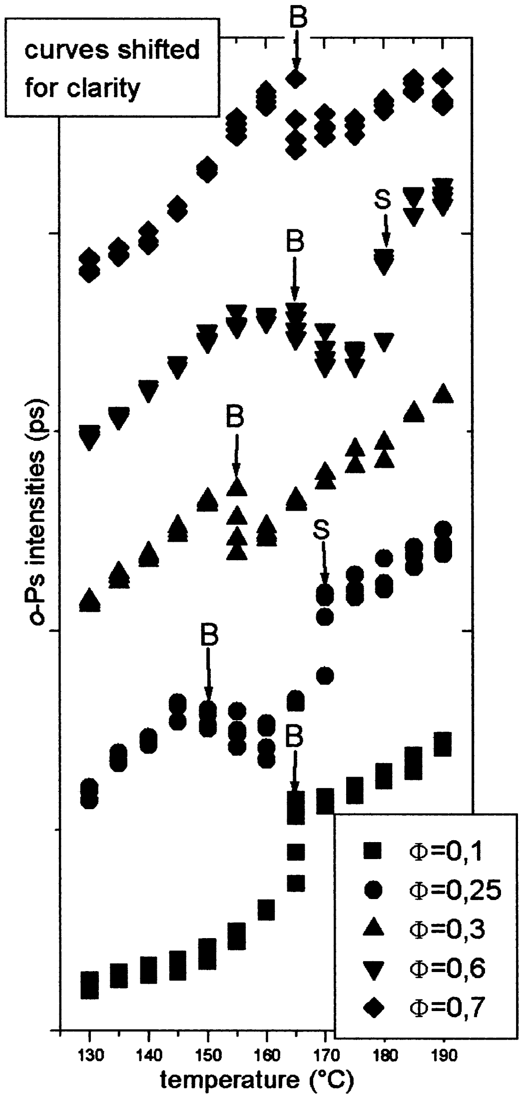

Figure 7. Typical o-Ps intensity curves for different concentrations of the blend system. The curves are shifted in the *y*-axis for clarity (B indicates the binodal phase separation; S indicates the spinodal).

Changes in o-Ps intensity should always be investigated carefully, as they could be caused by chemical reactions, but also by exposure to light, humidity, changes in the fwhm of the spectrometer, or vacuum conditions, and by the radiation effect.[26] In our case the measurements were done in a dark vacuum system with a constant vacuum of $(1.1 \pm 0.1) \times 10^{-6}$ mbar. The stability of the fwhm was controlled before and after each measurement with an aluminum reference sample. The radiation effect could be excluded from the measurements with doubled activity. Hence, the o-Ps in-

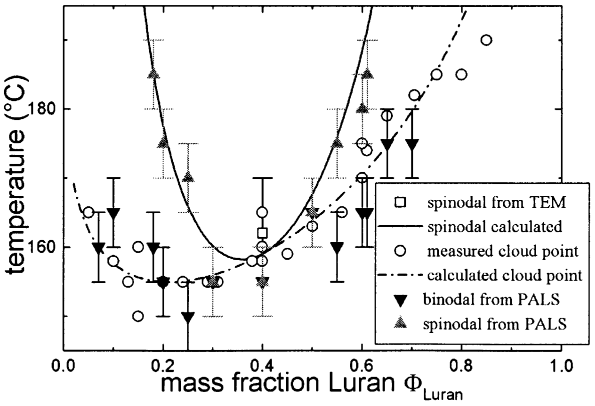

Figure 8. Phase diagram of Luran KR 2556/Lucryl G77, including results from PALS, cloud point, and TEM measurements as well as corresponding calculated cloud point and spinodal curves. (Constraints for the spinodal at temperatures between 200 and 220 °C, revealed by TEM studies[19] are accounted by the calculated spinodal.)

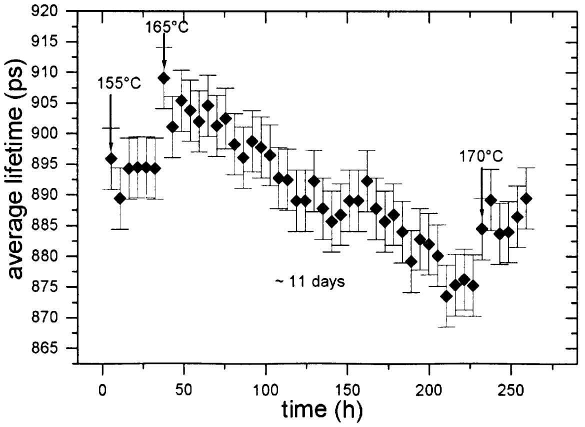

Figure 9. Time dependence of binodal decomposition for $\Phi_{\mathrm{Luran}} = 0.6$. The temperature was changed steplike at the temperatures investigated and then kept constant. The drop of τ_{av} at 165 °C is due to binodal decomposition.

tensity changes can only be related to changes in the positronium building probability. Possible reasons are different distributions of the acrylonitrile groups before and after phase separation and the resulting changes in the positronium building probability or varying mobilities of positronium precursors and/or trapping/detrapping reaction of electrons or positrons with scavengers, here the AN and MA units. In this connection it is interesting to note that the o-Ps lifetime and hence the average free volume sizes do not change during phase separation. We attribute this to the almost identical lifetimes of the pure components.

The o-Ps intensity curves for different compositions are shown in Figure 7. The kinks were identified as binodal separation temperatures, while steps were attributed to spinodal decomposition. For undercritical compositions the intensity increases at the binodal, and for overcritical compositions it decreases. The reason for this behavior might be that the system decomposes in phases with different o-Ps formation probabilities. Spinodal decomposition always results in an o-Ps intensity increase. The resulting separation temperatures are compared in Figure 8 with cloud point and TEM data and the calculated cloud point and spinodal curves.[19] The temperatures are in good agreement and confirm the phase diagram. So PALS seems to be the first method that can detect directly both separation temperatures simultaneously. One important advantage of PALS compared to cloud point and DSC is that the binodal can be detected at the very beginning after a few hours annealing. Additionally, the whole time dependence can be followed in-situ. An example for $\Phi_{\mathrm{Luran}} = 0.6$ is given in Figure 9.

Conclusions

$\mathrm{P\alpha MS_{0.5}}$-*co*-$\mathrm{AN_{0.5}}$ (Luran KR 2556)/$\mathrm{PMMA_{0.95}MA_{0.05}}$ (Lucryl G77) samples of different geometries, produced by hot-pressing and solvent-casting, were investigated in-situ as a function of temperature and composition with PALS. Blending during preparation and phase separation upon heating was also verified optically and with DSC.

At the binodal and spinodal separation temperatures the samples show continuous and steplike changes in the intensity of the longest lifetime, respectively, which are attributed to changes in the positronium building probability due to structural changes in the blend system during decomposition of the blend system. The decomposition temperatures from PALS are in good agreement with those from other experiments (morphology studies from TEM, optical cloud point, DSC).[19]

The changes of the annihilation parameters are continuous at the binodal and steplike at the spinodal separation temperature, in agreement with the expected kinetics. Hence, we conclude that it is possible to detect the separation temperatures with PALS in polymer blends. PALS seems to be the first method that is able to detect directly both separation temperatures. In contrast to ordinary optical cloud point experiments, using PALS, the binodal can be seen in the very beginning.

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References and Notes

(1) Laun, H. M. *Pure Appl. Chem.* **1998**, *70*, 1547−1566.
(2) Schytt, V.; Lyngaae-Joergensen, J. *J. Polym. Networks Blends* **1997**, *8* (2), 77−86.
(3) Schubert, D. W. *Mater. Res. Innovations* **2001**, *4*, 353−359.
(4) Koster, C. Diploma Thesis, Untersuchungen zum Ermüdungsverhalten von Polymerblends (LURAN und LUCRYL), BASF, Ludwigshafen and EPFL, Lausanne, 1994.
(5) Oswald, T. A.; Menges, G. *Materials Science of Polymers for Engineers*; Hanser: Cincinnati, OH, 1995; p 139 ff.
(6) Utracki, L. *Polymer Alloys and Blends*; Hauser Verlag: Berlin, 1989.
(7) Jean, Y. C. *Microchem. J.* **1990**, *42*, 72−102.
(8) Dlubek, G.; Clarke, A. P.; Fretwell, H. M.; Dugdale, S. B.; Alam, M. A. *Phys. Status Solidi A* **1996**, *157*, 351−364.
(9) Zrubcová, J.; Krištiak, J.; Pedersen, W. B.; Pedersen, N. J.; Eldrup, M. *Mater. Sci. Forum* **2001**, *363−365*, 359−361.
(10) Kobayashi, Y.; Wang, C. L.; Hirata, K.; Zheng, W.; Zhang, C. *Phys. Rev. B* **1998**, *58*, 5384−5389.
(11) Hill, A. J.; Zipper, M. D.; Tant, M. R.; Stack, G. M.; Jordan, T. C.; Shultz, A. R. *J. Phys.: Condens. Matter* **1996**, *8*, 3811−3827.
(12) Li, H.-L.; Ujihira, Y.; Nanasawa, A.; Jean, Y. C. *Polymer* **1999**, *40*, 349−355.
(13) McCullagh, C. M.; Yu, Z.; Jamieson, A. M.; Blackwell, J.; McGervey, J. D. *Macromolecules* **1995**, *28*, 6100−6107.
(14) Wang, C. L.; Kobayashi. Y.; Zheng, W.; Zhang, C.; Nagai, Y.; Hasegawa, M. *Phys. Rev. B* **2001**, *63*, 064204/1-9.
(15) Wästlund, C.; Berndtsson, H.; Maurer, F. H. J. *Macromolecules* **1998**, *31*, 3322−3327.
(16) Čižek, J.; Motycka, V.; Procházka, I.; Ilavsky, M.; Kolarik, J. *Mater. Sci. Forum* **2001**, *363−365*, 340−342.
(17) Dlubek, G.; Pionteck, J.; Bondarenko, V.; Pompe, G.; Taesler, C.; Petters, K.; Krause-Rehberg, R. *Macromolecules* **2002**, *35*, 6313−6323.

(18) Dlubek, G.; Taesler, C.; Pompe, G.; Petters, K.; Redmann, F.; Krause-Rehberg, R. *J. Appl. Polym. Sci.* **2002**, *84*, 654−664.
(19) Havermeyer, F.; Schubert, D. W. *Mater. Res. Innovations*, in press.
(20) Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. Risø-M-2740, Risø National Laboratory, Denmark, 1989.
(21) Gedde, U. W. *Polymer Physics*; Chapman & Hall: London, 1995.
(22) Wästlund, C.; Maurer, F. H. J. *Polymer* **1998**, *39*, 2897−2902.
(23) Eldrup, M.; Shantarovich, V. P.; Mogensen, O. E. *Chem. Phys.* **1975**, *11*, 129−142.
(24) Li, H. L.; Ujihira, Y.; Tanaka, S.; Yamashita, T.; Horie, K. *Ronbunshu* **1997**, *54*, 391−400.
(25) Pujari, P. K.; Tashiro, M.; Tseng, C. Y.; Honda, Y.; Nishijima, S.; Tagwa, S. *Mater. Sci. Forum*. **2001**, *363*−*365*, 275−277.
(26) Positron Annihilation ICPA-12; Triftshäuser, W., Kögel, F., Sperr, P., Eds.; *Mater. Sci. Forum* **2001**, *363*−*365*.

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