

# Interdiffusion in a Particle Matrix System of Two Miscible Polymers: An Investigation by Positron Annihilation Lifetime Spectroscopy and Differential Scanning Calorimetry

G. DLUBEK,<sup>1</sup> C. TAESLER,<sup>2</sup> G. POMPE,<sup>2</sup> J. PIONTECK,<sup>2</sup> K. PETTERS,<sup>3</sup> F. REDMANN,<sup>3</sup> R. KRAUSE-REHBERG<sup>3</sup>

<sup>1</sup> ITA Institute for Innovative Technologies, Köthen, Branch Office Halle, Wiesenring 4, D-06120 Lieskau, Germany

<sup>2</sup> Institute of Polymer Research, Hohe Strasse 6, D-01069 Dresden, Germany

<sup>3</sup> Martin Luther University, Department of Physics, D-06099 Halle/S., Germany

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**ABSTRACT:** Positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC) were used to study the interdiffusion in a particle matrix system consisting of (styrene-maleic anhydride) copolymer containing 24% maleic anhydride (SMA) and poly(methyl methacrylate) (50:50). Starting from the phase separated state of the miscible components, the transition to the mixed state due to interdiffusion during annealing at 160 and 180 °C was investigated. The diffused mass fractions of both components were estimated by DSC; they increase linearly with the logarithm of the annealing time. Both components show the same behavior, suggesting an average interphase composition of 50:50. For subsequent annealing, the kinetic behavior differs from the earlier behavior, probably because of the different diffusion coefficients of the two components. Experimental evidence is presented that the *ortho*-positronium (o-Ps) intensity correlates to the interdiffusion process. The response is due to the diffusion of inhibitors for Ps formation from one phase into the other. A semi-quantitative model is developed that allows the estimation of the interphase volume fraction from the relative change of the annihilation parameters. The PALS results are discussed in relation to those obtained by DSC. The results show that PALS is a useful tool to study mixing and demixing processes in polymer blends with a three-dimensional morphology. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 654–664, 2002; DOI 10.1002/app.10362

**Key words:** diffusion; blend; positron annihilation lifetime spectroscopy; differential scanning calorimetry; (styrene-maleic anhydride) copolymer; poly(methyl methacrylate)

## INTRODUCTION

During the last two decades, the phenomenon of interdiffusion in miscible or immiscible polymer

blends has been the subject of many investigations and is of interest for several applications, such as welding and blending of polymers.<sup>1</sup> When two miscible polymers come into contact with each other, mutual diffusion across the interface between the two polymers may occur. The composition inhomogeneities decrease, due to the interdiffusion, theoretically until a homogeneous mo-

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Correspondence to: G. Dlubek (gdlubek@aol.com).

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lecular mixture of both components is reached. The kinetics of such processes have been investigated in model systems of planar double layer films using neutron reflectometry, ellipsometry, and small-angle X-ray and neutron scattering.<sup>2-5</sup>

Real polymer blends are to a greater or lesser extent dispersed systems with a complex interface structure. The dispersed structure of the blends and the nonplanar interfaces lead to diffusion properties that may deviate from the planar layer model systems. For this reason, we have investigated a particle-matrix system with a three-dimensional morphology that describes the structure of engineering polymer blends better than planar model systems. The system under investigation consists of the two miscible polymers styrene-maleic anhydride copolymer (SMA), with maleic anhydride content of 24 wt %, and poly(methyl methacrylate) (PMMA). The particle matrix morphology was prepared by mixing fine powders of the respective polymers below their glass transition temperatures ( $T_g$ ). The PMMA powder of the polymer was converted into the matrix by annealing the powder mixture at a temperature situated between the  $T_g$ s of the two components.

The interdiffusion process occurring during annealing of the particle matrix system at temperatures near to the  $T_g$  of the polymer with the highest  $T_g$  was first examined by differential scanning calorimetry (DSC). From the change in the  $T_g$  behavior with the annealing time, as indicated in the DSC traces, we estimated semi quantitatively the decrease of the mass fraction of the pure SMA and PMMA phases and decided on the corresponding growth of the interdiffused phase.

As a second and novel technique we used positron annihilation lifetime spectroscopy (PALS) and tested its suitability for studying interdiffusion phenomena. Nowadays, PALS is an established technique for studying the local free volumes in polymers.<sup>6, 7</sup> Positrons emitted from radioactive sources, like  $^{22}\text{Na}$ , into the polymeric solid become thermalized and may annihilate with an electron or form positronium (Ps) — a hydrogen-like bound state.<sup>8</sup> Ps is the result of the combination of a thermalized positron with one of the available free electrons. The Ps formation is affected by a large variety of processes, such as mobility of electrons and positrons and the appearance of scavengers for electrons or positrons.<sup>8</sup> One quarter of the formed Ps appear as *para*-positronium (p-Ps). The electron and positron spins are anti-parallel in p-Ps, which decays

quickly via self-annihilation with a lifetime of  $\sim 150$  ps. Three quarters of the formed Ps appear as *ortho*-positronium (o-Ps), with the electron and positron spins parallel. In a vacuum, o-Ps has a lifetime of 142 ns.<sup>8</sup> In matter, the positron in o-Ps may annihilate during collision with molecules with an electron of opposite spin. This process, called pick-off annihilation, reduces the o-Ps lifetime in polymers to  $\sim 1-5$  ns. From this lifetime, the size of local free volumes in which the o-Ps is trapped can be calculated.<sup>6-10</sup> These holes have typical dimensions of between 0.3 and 1 nm and appear as a consequence of the structural disorder in amorphous polymers.

Employing the PALS technique, the sizes of local free volumes in homo- and co-polymers have been widely investigated.<sup>6-10</sup> Recently, the variation of hole sizes in polymer blends as a function of the composition or heat treatment has also been studied.<sup>11-20</sup> As already mentioned, the microstructure of polymers is usually concluded from the variation of the o-Ps lifetime  $\tau_3$ .

In the current work we will show that, under certain circumstances, the o-Ps intensity  $I_3$  may contain information on the compositional inhomogeneities in miscible polymer blends and their subsequent evolution during annealing. Using a number of assumptions and simplifications, we develop a model for a quantitative estimation of the fractional interdiffusion volume from the variation of  $I_3$  or other suitable annihilation parameters. The result obtained from the PALS experiments will be discussed in relation to those obtained from DSC.

## EXPERIMENTAL

### Sample Preparation

Styrene-maleic anhydride copolymer (SMA), containing 24 wt % maleic anhydride, was kindly supplied by DSM, Inc. The density of the copolymer was  $1.174 \text{ g/cm}^3$ , and its weight average molecular weight,  $M_w$ , was estimated by gel permeation chromatography (GPC) to be 95,000 g/mol (polydispersity PD = 2.9, PS standard with corrected Mark Houwing constants for SMA copolymers<sup>21</sup>). The  $T_g$  was determined by DSC to be 158 °C. Fine powders of SMA were prepared by precipitating a 5% solution of the polymer in tetrahydrofuran (THF) into excess *n*-heptane under vigorous stirring. The powder was filtered off,

washed with *n*-heptane, and finally dried at 90 °C in vacuum for 12 h.

A commercial grade poly(methyl methacrylate) (PMMA) containing very small amounts of an acrylic comonomer (<2%) and with a  $T_g$  of 94 °C and a density of 1.19 g/cm<sup>3</sup> was kindly supplied by BASF AG. The  $M_w$  was estimated by GPC to 82,000 g/mol (PD = 2.4, PS standard). Fine powders of the polymer were made following the same procedure as already described. The powder was dried in vacuum at 60 °C for 12 h.

For the preparation of the SMA/PMMA particle matrix system with a composition of 50:50 (v/v) a powder mixture of the two polymers was made by suspending the polymer powders together in *n*-heptane followed by a subsequent treatment with an ultrasonic finger for 30 min while cooling the suspension in ice water. *n*-Heptane was then evaporated at room temperature, and the remaining powder mixture was dried in vacuum at 50 °C for 12 h. Samples were made by pressing the powder mixture, with a pressure of 700 MPa for 30 min at room temperature, into pills with a thickness of 1.1–1.5 mm and a diameter of 12 mm. Subsequently, the material was annealed at  $T > T_g$  (PMMA) to transform the PMMA powder into a matrix by coalescence of the PMMA powder particles.

For investigation of the interdiffusion process with PALS, the samples were annealed in an external furnace under an argon atmosphere for different times at a temperature of 160 °C (Table I). The influence of annealing on the glass transitions was measured by DSC; the annealing was carried out at 160 and 180 °C.

A molecularly mixed blend of SMA and PMMA with the same composition as the re-

spective particle matrix system was prepared by coprecipitating the polymers from a common solution in THF into *n*-heptane with subsequent drying in vacuum at 90 °C for 16 h. From this material, pills were pressed and annealed for 10 min at 170 °C.

### Scanning Electron Microscopy (SEM)

SEM pictures of the powder materials and of the cryo-fractures of the SMA/PMMA particle matrix system were taken at 10 kV with a LEO 435 VP (Leo Elektronenmikroskopie). Samples were covered with a 25-nm gold layer by sputtering.

### Differential Scanning Calorimetry (DSC)

DSC measurements were performed with a DSC 7 (Perkin Elmer) in the temperature range 40–180 °C. The DSC traces were analyzed with Pyris software, version 3.51. The temperature scale was calibrated by In and Pb standards at a heating rate of 10 K/min. The glass transition behavior of the SMA and PMMA homopolymers, of the SMA/PMMA particle matrix system subjected to different heat treatments, and of the molecularly mixed SMA/PMMA blend were investigated using the following cycles: heat – cool – heat, with rates of +40 and –80 K/min. The  $T_g$  of the sample was determined from the second heating scan. The high heating rate was chosen to keep the thermal annealing during the DSC scan as small as possible. By using the Pyris software, the sample temperature is recorded, so the thermal lag at 40 K/min is small (~1.5 K). This small effect was not corrected because only the change of the glass transition

**Table I** Investigated Samples, Thermal Treatment, Glass Transition Temperatures, and PALS Results

Sample	Treatment	$T_g$ (°C) (DSC)	$\tau_3$ (ps) $\pm 3$	$\tau_{av}$ (ps) $\pm 0.5$	$I_3$ (%) $\pm 0.05$
PMMA, pure	Annealed at 120°C, 10 min	94	1791	769.6	30.33
SMA, pure	Annealed at 170°C, 10 min	158	1936	735.7	23.81
(50 : 50) SMA/PMMA particle particle system	Initial state	158/94	1868	749.0	26.84
(50 : 50) SMA/PMMA particle matrix system	Annealed at 160°C, 2 min	—	1860	745.0	26.58
(50 : 50) SMA/PMMA particle matrix system	Annealed at 160°C, 300 min	—	1866	738.5	26.28
(50 : 50) SMA/PMMA molecularly mixed blend	Annealed at 170°C, 10 min	128	1859	728.2	25.91

behavior with respect to different annealing times was of interest.

Sample states with different thermal treatment were investigated. The annealing of the SMA/PMMA system at 160 °C for 15 and 35 min was done inside the DSC device. The sample annealed at 160 °C for 300 min was identical to that investigated by PALS. For additional studies, the SMA/PMMA system was annealed at 180 °C inside the DSC device. The cumulative annealing time,  $t_a$ , was increased in a stepwise manner from 0.1 to 235 min. Each annealing was followed by rapid cooling and subsequent recording of the respective DSC heating scan. This heating scan was used to characterize the dependence of the degree of mixing of the blend on the thermal treatment.

### Positron Annihilation Lifetime Spectroscopy (PALS)

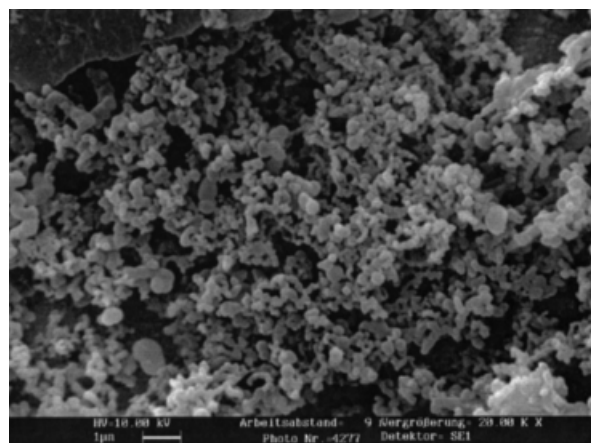
Positron annihilation lifetime experiments were carried out at room temperature using a fast-fast coincidence system<sup>8</sup> with a time resolution of 260 ps [full width at half maximum (fwhm)], a channel width of 25.32 ps, and a  $1 \times 10^6$  Bq  $^{22}\text{NaCl}$  positron source sandwiched between two Al foils of 2 mg/cm<sup>2</sup> thickness. Only small variations of the lifetime parameters were expected, so eight 1-h measurements were performed for each of the specimens. Each of the 1-h spectra was analyzed using the routine LIFSPECFIT (Helsinki University of Technology, 1992). The lifetime parameters and the time-zero channel of the different runs for one specimen always agreed with each other within the statistical error limits of the experiment. In this way, the reproducibility of the results was confirmed. For the analysis of the spectra, the content of each two channels were summed up to obtain the coincidence count for one 50.64 ps channel. The lifetime parameters analyzed from the eight spectra were averaged to obtain the final results. These results agreed with those analyzed from a spectrum that was obtained by summing the counts of the eight individual spectra ( $\sim 25 \times 10^6$  coincidence counts in total).

The lifetime spectra were decomposed into three discrete exponentials  $s(t) = \sum(I_i/\tau_i)\exp(-t/\tau_i)$  ( $i = 1..3$ : p-Ps, free positrons, and o-Ps annihilation, respectively) with lifetimes  $\tau_i$  and intensities  $I_i$ . During the fitting we constrained the p-Ps lifetime to its average of  $\tau_1 = 150$  ps and the ratio  $I_1/I_3$  to its theoretical value<sup>8</sup> of 1/3. Following our previous works,<sup>22, 23</sup> this procedure delivers the most accurate lifetime parameters.

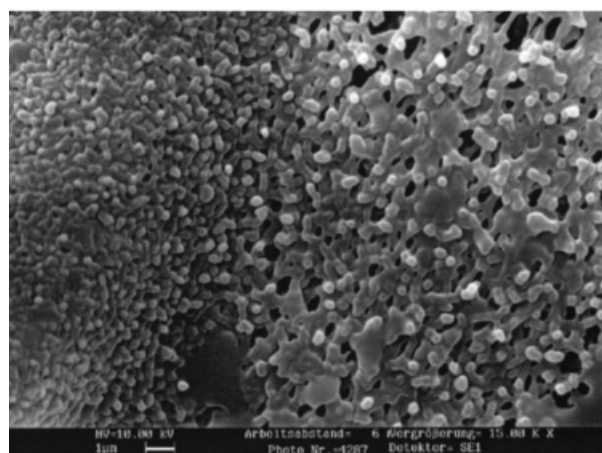
## RESULTS AND DISCUSSION

### Scanning Electron Microscopy

The morphology of the SMA/PMMA powder mixture can be seen in Figure 1a. The grain sizes of the powder particles range between 100 and 600 nm. To transform the PMMA powder to the matrix, an annealing at  $T \geq T_g(\text{PMMA})$  was necessary. We chose for the SEM investigation plotted in Figure 1b an annealing at 120 °C for 30 min. The result confirms the formation of a matrix particle structure, even if the homogenization of the PMMA matrix is not finished under these conditions. At higher annealing temperatures or longer times, the PMMA matrix will wet the SMA



(a)



(b)

**Figure 1** SEM micrographs of the (50:50) SMA/PMMA system. The bars correspond to 1  $\mu\text{m}$ : (a) initial state as powder/powder mixture; (b) initial state as particle matrix system (see text).

particles completely. However, due to the miscibility of both phases and the beginning of interdiffusion, this state of the particle matrix structure can not be detected by SEM or cryofractures.

The morphology development during the single annealing steps is sketched in Figure 2. The mor-

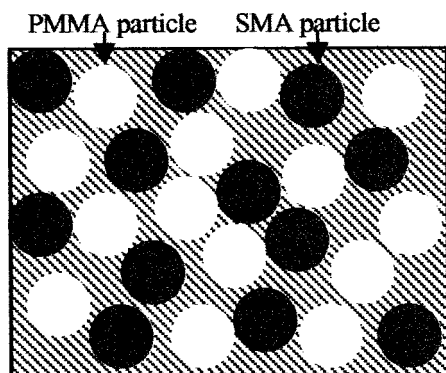


Figure 2a:  $T < T_g(\text{PMMA})$

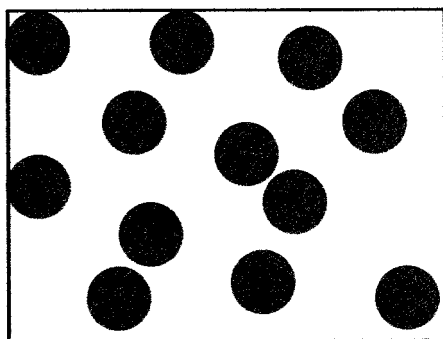


Figure 2b:  $T_g(\text{PMMA}) < T < T_g(\text{SMA})$

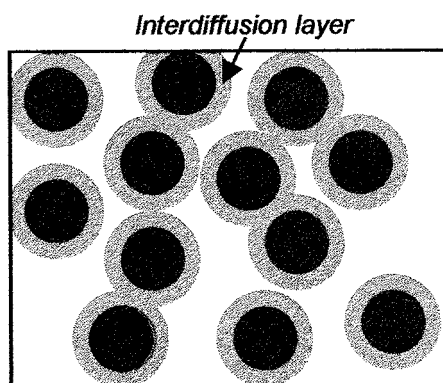


Figure 2c:  $T > T_g(\text{SMA})$

**Figure 2** Sketches of the morphology development in the SMA/PMMA particle matrix system: (a) initial state as powder/powder mixture; (b) initial state as particle matrix system; (c) intermediate interdiffused blend state.

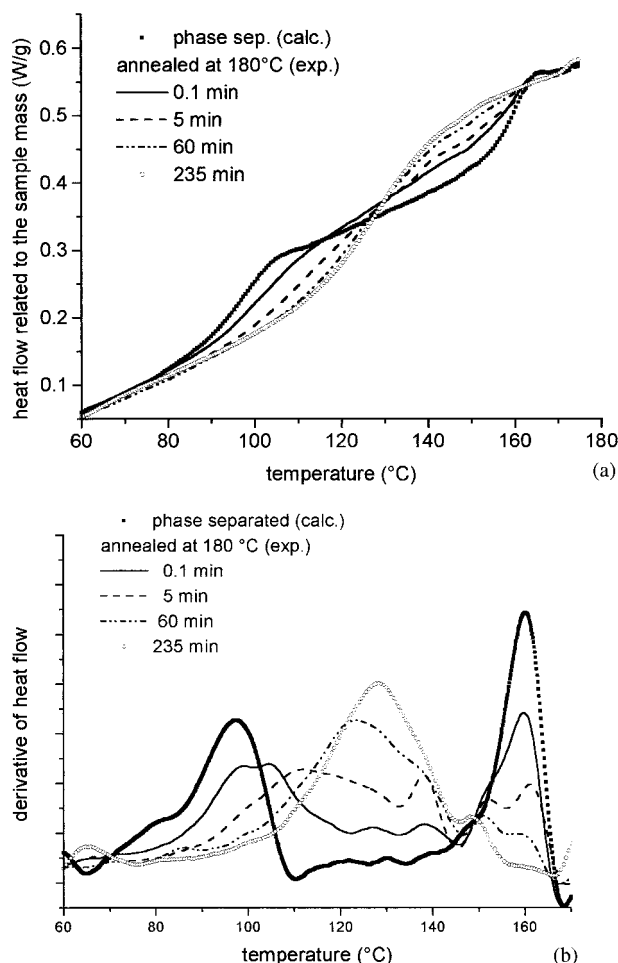
phology imaged by SEM in Figure 1a and the idealized initial state for the interdiffusion studies are shown in Figures 2a and 2b, respectively. The intermediate stage of the morphology development caused by mutual diffusion is shown in Figure 2c. In this state, the sample contains pure matrix, pure dispersed particles, and an interlayer consisting of an interphase made from both types of macromolecules and formed by interdiffusion.

### Differential Scanning Calorimetry

The initial materials and the molecularly mixed blend were investigated by DSC using the half-step method to determine the  $T_g$  from the second heating scan. The results are given in Table I. For the molecularly mixed blend,  $T_g = 128\text{ }^\circ\text{C}$  was obtained. This value is in good agreement with the value of  $124\text{ }^\circ\text{C}$  calculated using the Fox relation.<sup>24</sup>

The DSC heating scans measured after annealing the SMA/PMMA particle matrix system at  $180\text{ }^\circ\text{C}$  for different annealing times  $t_a$  are shown in Figure 3a. Additionally, the DSC scans of the initial, demixed state of the 50:50 blend, the latter obtained by linear combination of the scans of the pure components, were plotted. The characterization of the initial state can not be realized experimentally, because interdiffusion has already started during the first heating of the sample.

For further analysis of the change of the glass transitions, the first derivation of the heat flow was calculated, as shown in Figure 3b. One can clearly observe that for the particle matrix system, the height  $h$  of the peaks representing the glass transition of pure PMMA ( $T_g = 94\text{ }^\circ\text{C}$ ) and SMA ( $T_g = 158\text{ }^\circ\text{C}$ ) decrease distinctly with increasing annealing time. This result indicates a decreasing mass fraction of the phases made from pure components. At the same time, a broad transition peak with a maximum at  $\sim 128\text{ }^\circ\text{C}$  develops, which narrows with increasing annealing time. The interphase formed due to interdiffusion has a composition gradient ranging from almost pure SMA to almost pure PMMA. The broad transition peak is the sum of the different glass transitions corresponding to each composition across the interlayer. During further annealing, the peak grows because of the increasing volume fraction of the interphase. In addition, the concentration gradient between particles and matrix tends to disappear and a more uniform composition is formed in the interphase region, leading to a nar-



**Figure 3** DSC measurements of the SMA/PMMA particle matrix system subjected to different annealing treatments showing (a) the heat flow and (b) the derivative of heat flow. The phase-separated state was calculated from the DSC traces of the pure components.

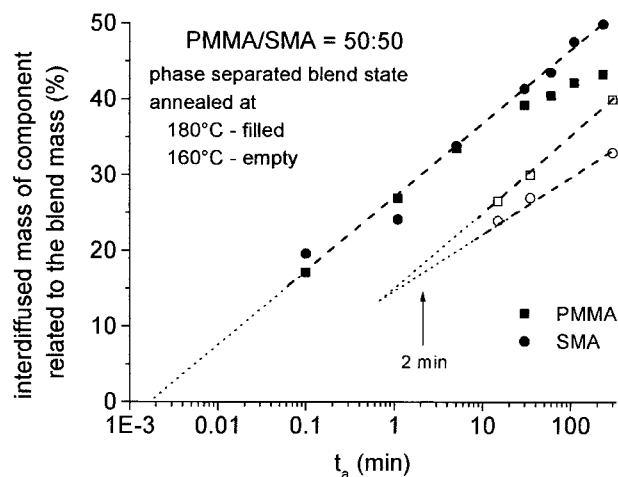
rowing of the glass transition. In the late annealing stage, the peak at  $\sim 128$  °C becomes similar to the molecularly mixed SMA/PMMA blend.

The height  $h$  of the peaks at  $T_g$  of the pure PMMA and SMA in the plots of the derivative heat flow relates to the mass fraction of the residual pure component in the system and can be used for a rough estimation of their change as a function of the progressive interdiffusion. The fraction of the components diffused into the interphase can be calculated according to  $(h(t_a = 0) - h(t_a))/h(t_a = 0)$  determined at the corresponding  $T_g$  of the pure component. These values, related to the mass fractions of the components in the blend, are plotted as a semi-log plot in Figure 4 as a function of the annealing time  $t_a$ . A linear relation was found for SMA. At the beginning, the values

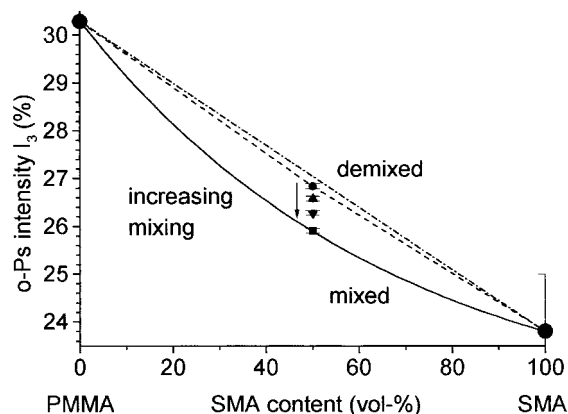
of PMMA show the same dependence, which means that almost a symmetrical concentration gradient in the interphase regions is formed with an average composition of 50:50. With further increasing  $t_a$ , the amount of interdiffused PMMA increases more slowly and shows a saturation behavior, which indicates that PMMA chains migrate faster into the SMA phase than the SMA chains into the PMMA matrix. This result is due to the higher mobility of the PMMA chains compared with that of the SMA chains at 180 °C. Therefore, the SMA phase is penetrated by PMMA chains after shorter times than PMMA by SMA chains.

When annealing at 160 °C instead of 180 °C, the behavior of both components is different: PMMA is completely in the amorphous liquid state, whereas SMA is partially in the rigid amorphous state, which is hardly accessible to interpenetration with PMMA. Consequently, the amount of the residual pure SMA is higher than that of pure PMMA after annealing at 160 °C.

In the following section we will estimate the thickness of the interphase layer and the growth rate of the interphase thickness. For this discussion, we assume that the volume fraction and the mass fraction are about the same because the difference between the densities of both constituents is small ( $\pm 1.3\%$  to the average value). By combining the interphase volume fraction  $v_{ip}$  with the interfacial area, one obtains information about the thickness  $\delta_{ip}$  of the interphase. The particle matrix system of composition 50:50 (V/V) will be considered as spherical SMA particles of



**Figure 4** Interdiffused mass content of SMA and PMMA as a function of the annealing time  $t_a$  at 180 and 160 °C obtained from the DSC measurements.



**Figure 5** o-Ps annihilation intensity  $I_3$  in SMA/PMMA system (50:50 v/v). Key: (○) demixed initial state and pure components; (△) annealing for 2 min at 160 °C; (▽) annealing for 300 min at 160 °C; (□) molecularly mixed blend.  $I_3 = f(\text{SMA content})$ : dash-dotted line, completely demixed calculated from (eq. 1); dashed line, completely demixed, corresponding the experimental spectrum; solid line, molecular mixed system, corresponding the experimental spectrum.

diameter  $d_p$  embedded in the PMMA matrix. For early interdiffusion states ( $\delta_{ip} \ll d_p$ ), the fractional interdiffused volume is described by  $v_{ip} \sim 3 \delta_{ip}/d_p$ . Because the size distribution of particles in the particle matrix system is not known quantitatively, one can make only a rough estimation about the interphase thickness; for example, the DSC investigations after annealing at 180 °C for 2 min indicate that the whole interphase volume fraction (i.e., the sum of interdiffused PMMA and SMA) is 0.54 (Figure 4). Assuming a mean particle diameter of 400 nm, the interphase thickness  $\delta_{ip}$  can be estimated to be  $\sim 70$  nm. These values mean that the interphase thickness increases with a velocity of  $\sim 35$  nm/min at the beginning of the interdiffusion process.

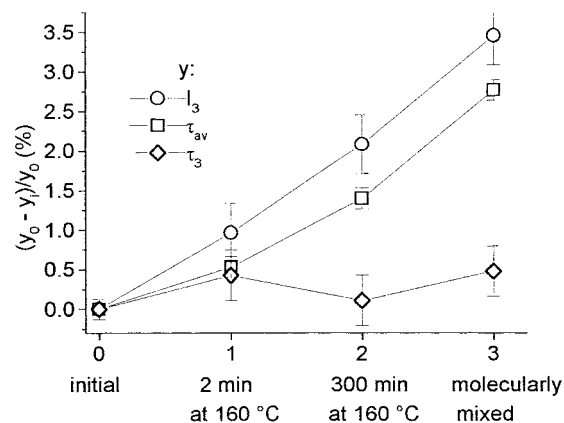
Sauer and Walsh<sup>25</sup> observed that in a planar PS–PVME double-layer film annealed at 120 °C, the interphase thickness grows at  $\sim 3$  nm/min. This annealing temperature, which is  $\sim 20$  degrees above the higher  $T_g$ , is similar to the annealing at 180 °C of the SMA/PMMA system. The different results of the growth rate can only be understood in connection with a second experiment. Sauer and Walsh also observed that the growth in the same system is up to 10 times faster than 3 nm/min when the PS films were not annealed before the interdiffusion experiment. This result was explained by a lack of entanglements by spin coating from solutions at temperatures

below the  $T_g$  of PS. Therefore, the intermingling between PS and PVME chains is much easier than starting the interdiffusion between polymers with a high entanglement density. Simultaneously, relaxation of the non-annealed PS occurs, which additionally favors the interdiffusion process.

The SMA and PMMA powder particles used in our studies also have a strongly reduced entanglement density because they are prepared by precipitation from solution into a coagulating agent. This process is similar to the process of spin coating. Consequently, the mobility of the chains is high at the beginning of the interdiffusion process in the particle matrix system. This early high mobility may explain the unexpectedly fast growth of the interphase thickness.

### Positron Annihilation Lifetime Spectroscopy

The three-component analysis of lifetime spectra delivered lifetimes  $\tau_i$  and relative intensities  $I_i$  of  $\sim 150$  ps/9%,  $\sim 360$  ps/65%, and (1791–1936) ps/(30.3–23.8)%. These lifetimes are due to annihilation of p-Ps, free positrons, and o-Ps,<sup>6–19</sup> respectively. The long-lived o-Ps responds most to changes in the sample. The lifetime  $\tau_3$  and intensity  $I_3$  of o-Ps annihilation, as well as the average positron lifetime  $\tau_{av}$  are summarized in Table I together with the  $T_g$  and the sample treatments. The average positron lifetime, defined as the mass center of the lifetime spectrum  $s(t)$  ( $\tau_{av} = \int ts(t)dt$ ) is a model-independent parameter that is related to the parameters of the individual components via  $\tau_{av} = \sum \tau_i \times I_i$  ( $i = 1 \dots 3$ ). In Figure 5, the o-Ps intensities  $I_3$  of the samples under investigation are shown. The relative change of  $I_3$ ,  $\tau_3$ ,



**Figure 6** Relative change of the annihilation parameters as a function of the sample state.

and  $\tau_{av}$  as a function of the sample treatment is plotted in Figure 6.

The o-Ps lifetimes  $\tau_3$  of PMMA and SMA are 1791 ps and 1936 ( $\pm 3$ ) ps, respectively.  $\tau_3$  correlates with the volume of subnanometer-size holes that form the free volume in amorphous polymers. Assuming spherical holes, their average radius can be calculated according to a semi-empirical model.<sup>6, 9, 10</sup> The average hole radius was estimated to be 0.266 nm for PMMA and 0.280 nm for SMA, which corresponds to hole volumes of 0.079 and 0.092 nm<sup>3</sup>, respectively.

For the unannealed SMA/PMMA system, an o-Ps lifetime of  $\tau_3 = 1868$  ps was found. The  $\tau_3$  values for the system subjected to the different annealing treatments as well as the molecularly mixed SMA/PMMA blend do not differ from each other within the error limits of the experiment (Table I, Figure 6). This behavior may be attributed to the miscible nature of both components. Because of the good mixing on a molecular scale, the o-Ps lifetime (mean hole size) of the mixed system corresponds well to the average of o-Ps lifetimes of the two constituents. Possible changes in free volume by repulsive or attractive interactions between the PMMA and the SMA chains may be too small to be detected. In immiscible blends, changes of o-Ps lifetime have been observed and attributed to extra free volumes occurring at incoherent interfaces.<sup>13, 26</sup>

The o-Ps intensities  $I_3$  of PMMA (30.3 %) and SMA (23.81%) clearly differ. The o-Ps intensity of the completely demixed, phase-separated system may be calculated by the relation<sup>11</sup>

$$I_{3,\text{demix}} = \nu_{\text{SMA}}I_{3,\text{SMA}} + (1 - \nu_{\text{SMA}})I_{3,\text{PMMA}} \quad (1)$$

where  $\nu_{\text{SMA}}$  is the volume fraction of the SMA component. This linear relation is plotted in Figure 5 as a dash-dotted line together with the experimental data. Equation 1 is only valid when a net flow of Ps from one phase into the other does not occur. This situation can be assumed for our system because the mean diffusion length of o-Ps in amorphous polymers is 1–2 nm,<sup>27</sup> whereas the particle sizes in the SMA/PMMA particle matrix system range from 100 to 600 nm. The value for  $I_{3,\text{demix}}$  calculated from eq. 1 is 27.07%. This value is somewhat larger than the experimental value of  $I_3 = 26.84$  ( $\pm 0.05$ )%. The cause of this small discrepancy is that the experimental lifetime spectrum of the demixed system contains two long-lived exponential components of different

lifetimes, which will be fitted by a single-exponential function with the mean values of  $\tau_3$  (1868 ps) and  $I_3$  (26.84%). Therefore, this analyzed intensity deviates slightly from the theoretical value given by eq. 1 (see also Figure 5). The deviation occurs in all of the experimental spectra. We found that the experimental intensity agrees within the error limits with the  $I_3$  that was analyzed from a synthetic spectrum generated by a linear combination of the spectra of the pure components weighted to their composition. For more details of this problem, see our previous paper.<sup>26</sup>

Because of the heat treatments, the o-Ps intensity of the particle matrix system varies outside of the statistical errors of  $\pm 0.05\%$  (Table 1, Figures 5 and 6).  $I_3$  decrease from 26.84% in the demixed particle matrix system to 25.91% in the molecularly mixed blend. The decreases in the o-Ps yield  $I_3$  may be caused by an inhibition<sup>8</sup> of the Ps formation caused by diffusion of SMA molecules into the PMMA matrix. It is known that this inhibition effect occurs in SMA<sup>12, 13</sup> due to the electron affinity of the carbonyl groups of the MA units. The carbonyl groups are scavengers<sup>8</sup> for spur electrons that become trapped and in this way escape from Ps formation. The spur electrons are created as a consequence of the ionization of molecules by the fast positrons emitted from the <sup>22</sup>Na source. The value of  $I_3$ , which in pure polystyrene is 40%, decreases to 9% in an SMA copolymer with 50 wt % MA.<sup>12, 13</sup> Inhibition is typically observed in polymers containing chlorine, nitrogen, and oxygen groups.<sup>28–30</sup> This interpretation permits the description of the o-Ps intensity in a molecularly mixed blend by the well-known inhibition relation.<sup>8, 30</sup>

$$I_{3,\text{mix}} = I_{3,\text{m}}[A + (1 - A)/(1 + \sigma C)] \quad (2)$$

where  $I_{3,\text{m}}$  is the o-Ps yield of the matrix ( $C = 0$ ),  $A < 1$  is a constant related to the saturation value of  $I_3$ ,  $C$  is the concentration of SMA scavengers (typically given in mol/unit volume<sup>8</sup>), and  $\sigma$  is the inhibition constant (or cross section) that describes the increased interaction of electrons with scavengers compared with other molecular groups of the polymer. This increased interaction is the physical reason for the nonlinear behavior of  $I_{3,\text{mix}}$ . Equation 2 is used to describe the variation of  $I_3$  with composition in liquid solutions,<sup>8</sup> halogenated polymers,<sup>27, 28</sup> copolymers,<sup>17</sup> and miscible blends.<sup>18</sup> The qualitative behavior of  $I_{3,\text{mix}}$  is shown in Figure 5 as solid line created



considering the experimental value  $I_{3,\text{mix}}$  of the 50:50 mixture and the pure components.

During annealing of the particle matrix system, the sample state changes from the phase-separated state towards a molecularly mixed state as a consequence of the mutual diffusion of molecules from the particles into the matrix and vice versa. A three-phase system is formed, consisting of pure SMA, pure PMMA, and the interphase. During interdiffusion, the o-Ps intensity changes from  $I_{3,\text{demix}}$  towards  $I_{3,\text{mix}}$ . Analogously, the average positron lifetime  $\tau_{\text{av}}$ , dominated by the term  $I_3\tau_3$ , changes from the value of the demixed sample towards the molecular mixture.

From our results we conclude that interdiffusion influences the o-Ps intensity  $I_3$  (or another suitable annihilation parameter such as  $\tau_{\text{av}}$ ) when one component of the disperse system causes inhibition of Ps formation in the other component. Recently, Wästlund et al.<sup>13</sup> observed that miscible blends of SMA and styrene-acrylonitrile copolymers (SAN) have smaller  $I_3$  values than immiscible SMA-SAN blends of comparable composition. This experimental result supports our conclusion; that is, the larger the difference in  $I_3$  and the larger the inhibition constant  $\sigma$  (eq. 2), the more sensitive is the PALS method for studying the interdiffusion process.

### Evaluation of the Interphase Volume in the Particle Matrix System

In the following section, relations will be developed that allow us to estimate the volume fraction of the interphase from the variation in the annihilation parameters. We focus our attention on the behavior of the o-Ps intensity  $I_3$ . For an exact estimation of the o-Ps intensity in the particle (p) matrix (m) system subjected to the annealing,  $I_{3,\text{a}}$ , the knowledge of the morphology of the system, the concentration-distance profile across the particle matrix interphase, and the inhibition function eq. 2 is required. Because these quantities are typically not well known, one has to introduce some assumptions and simplifications. First of all, we assume that the concentration profile of the interphase is symmetric with respect to the particle matrix interface of the initial system. The layer inside the particles affected by indiffusion of molecules from the matrix (volume fraction  $v_i$ ) is assumed to have the same volume as the layer in the matrix affected by out diffusion of molecules from the particles (volume fraction  $v_o$ ). Both layers form the interphase with the volume fraction

$v_{\text{ip}} = v_i + v_o$ , where  $v_o = v_i$  is assumed. A linear superposition of the o-Ps intensities  $I_3$  describing the o-Ps annihilation in the different phases will be assumed:

$$I_{3,\text{a}} = (1 - \nu_p - \nu_o)I_{3,\text{m}} + (\nu_p - \nu_i)I_{3,\text{p}} + (\nu_o + \nu_i)I_{3,\text{ip}} \quad (3)$$

As already mentioned,  $\nu_p$  is the fractional volume of the dispersed (particle) phase in the initial state of the system, and  $I_{3,\text{m}}$  and  $I_{3,\text{p}}$  denote the o-Ps intensity for the pure matrix and for the pure particles. The o-Ps intensity  $I_{3,\text{ip}}$  is an average value that characterizes the interphase. For the initial state of the system ( $t_{\text{a}} = 0$ ,  $v_o = v_i = 0$ ), eq. 3 is identical to eq. 1. Rearrangement of eq. 3 and  $v_i = v_o = v_{\text{ip}}/2$  leads to

$$\nu_{\text{ip}} = \{I_{3,\text{a}} - [(1 - \nu_p)I_{3,\text{m}} + \nu_p I_{3,\text{p}}]/[I_{3,\text{ip}} - (I_{3,\text{p}} + I_{3,\text{m}})/2]\} \quad (4)$$

If  $I_{\text{ip}}$  is known,  $\nu_{\text{ip}}$  can be estimated from this equation. For obtaining an estimate, we approximate the concentration-distance profile in the interphase by a constant average composition and assume that this average composition corresponds to that obtained after complete mixing of the particle and matrix phases. The o-Ps intensity of this state,  $I_{3,\text{mix}}$ , can be analyzed from the lifetime spectrum of the molecularly mixed sample. This simplification allows us to estimate  $\nu_{\text{ip}}$  for systems for which the inhibition function is not known. With this assumption and introducing  $I_{3,\text{demix}}$  according to eq. 1, we obtain the following formula for a 50:50 composition ( $\nu_p = 0.5$ ) of the particle matrix system:

$$\nu_{\text{ip}} = (I_{3,\text{a}} - I_{3,\text{demix}})/(I_{3,\text{mix}} - I_{3,\text{demix}}) \quad (5)$$

Within the approximations made in developing eq. 5, the fractional volume of the interphase  $\nu_{\text{ip}}$  corresponds to the relative change of the o-Ps intensity  $I_3$  caused by interdiffusion in the particle matrix system. It can easily be shown that for  $\nu_p \neq 0.5$ , eq. 5 is also valid when  $v_o/v_i = (1 - \nu_p)/\nu_p$  is applied, which is a realistic approximation for the later annealing stages. For early annealing states, when  $v_o = v_i$  is valid, eq. 4 has to be used for estimating  $\nu_{\text{ip}}$ . Analogous relations to eqs. 4 and 5 may be also valid for other annihilation parameters, such as the average positron lifetime

**Table II Interphase Volume Fraction  $\nu_{ip}$  after Thermal Annealing at 160°C for Different Times of the (50 : 50) SMA/PMMA System Obtained from PALS and DSC**

Annealed Time at 160°C, min	$\nu_{ip}$ from PALS	$\nu_{ip}$ from DSC
2	0.28	≈0.36
300	0.60	0.73

$\tau_{av}$  and the curve-shape parameter  $S$  of the Doppler-broadened annihilation line.<sup>8</sup>

The fractional volume of the interphase estimated from eq. 5 for the heat treatments at 160 °C are shown in Table II. The  $\nu_{ip}$  values are 0.28 for 2 min and 0.60 ( $\pm 0.10$ ) for 300 min. The results using the average positron lifetime agree within the error limits with those from  $I_3$ . These results may be compared with the data obtained from the DSC measurements. The volume fraction  $\nu_{ip}$  after annealing for 300 min at 160 °C is  $0.33 + 0.40 = 0.73$ . The value for 2 min of 0.36 can only be estimated by extrapolation of the linear relation obtained in Figure 4. These values agree sufficiently well with the PALS results considering the strong approximations made in the models and taking into account the systematical errors in the different techniques.

The correlation of both methods shows that positron annihilation is an additional, new method to investigate quantitatively the interdiffusion processes in chemically inhomogeneous polymer systems. For the same reasons as for mixing, the opposite process, the demixing in polymer blends, may also be studied by this technique.

## CONCLUSION

The interdiffusion process at different thermal treatment in a SMA/PMMA particle matrix system has been investigated by DSC and for the first time by PALS. The DSC investigations at 180 °C indicate that the interdiffusion process generates interphases with a concentration gradient that is symmetrical during the first 10 min of interdiffusion. In later stages of interdiffusion, the PMMA chains tend to diffuse faster into the SMA phase than vice versa because of the higher mobility of the PMMA chains. The high growth rate of the interphase thickness can be explained

by the low entanglement density in SMA caused by the processing of the initial, phase-separated state, which is lower than the entanglement densities in the fully relaxed, thermodynamic equilibrium state, reachable by long-time annealing at  $T > T_g$ .

Experimental evidence was presented that the intensity of the o-Ps annihilation  $I_3$  in the SMA/PMMA particle matrix system responds clearly to the interdiffusion process. The response is due to the diffusion of inhibitors for Ps formation from one phase into the other, which lowers  $I_3$  compared with the totally demixed state of the system. The SMA molecules act as scavenger for free electrons that in this way are removed from the Ps formation process. A simple semi-quantitative model was developed that allows the estimation of the interphase volume fraction from the relative change of  $I_3$  without knowing the inhibition function. This method can be applied for the investigation of engineering polymer blends with a three-dimensional morphology.

The sensitivity of the PALS technique for mutual diffusion will be higher when the inhibition cross section of one of the components of the system is larger than in the current work. In this case, a more qualified model for analyzing the PALS data than the simple one developed in the current study may be tested. These models may involve a realistic concentration–distance profile and the inhibition function of the system investigated. The inhibition function may be determined by measuring molecularly mixed blends of different composition. We remember also that with a monoenergetic slow positron beam,<sup>31, 32</sup> the penetration depth of positrons may be varied from some tenth of a nanometer to  $\sim 20 \mu\text{m}$ . With the monoenergetic positrons, the concentration–distance profiles in a planar double-layer film may be scanned systematically. Both of these advanced studies are now in progress.

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