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Free-volume properties of styrene–maleic anhydride and styrene–acrylonitrile copolymers

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Positron annihilation lifetime measurements were performed on amorphous styrene–maleic anhydride and styrene–acrylonitrile copolymers of different compositions. Glass transition temperatures of the copolymers were determined by differential scanning calorimetry and densities and specific volumes were obtained with a gas pycnometer. The average free-volume hole size measured by the positron lifetime technique was almost constant with composition in styrene–acrylonitrile, whereas in styrene–maleic anhydride it first increased up to 28% maleic anhydride content and then decreased at higher concentrations. This is caused by differences in copolymer constitution, which changes from random to alternating with increasing concentration of maleic anhydride, leading to differences in the packing of the polymer chains. The results also show a clear decrease in the ortho-positronium yield (I_3) with increasing maleic anhydride or acrylonitrile content of the copolymer, which is interpreted as inhibition of positronium formation by these components. An equation previously used to describe the inhibiting effect of scavengers in non-polar solvents and of halogenated compounds added to polycarbonate could be fitted to the experimental values. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: positron annihilation; ortho-positronium inhibition; styrene copolymers)

INTRODUCTION

When a positron emitted from a radioactive source enters a polymer, it has a kinetic energy of up to 0.54 MeV, which means that it will travel a short distance in the material before being thermalized. The positron can then annihilate as a 'free' positron together with an electron in ~0.4 ns. It can also form a metastable state with a free electron, which is called positronium (Ps). Depending on the spins of the positron and electron in the positronium, para- or ortho-positronium is formed. In para-positronium (p-Ps), the spins are antiparallel, giving a short lifetime of 0.125 ns, whereas the lifetime of ortho-positronium (o-Ps), in which the spins are parallel, is 142 ns in vacuum. In polymers, the o-Ps lifetime is found to be 1–5 ns, because the positron in o-Ps annihilates with one of the surrounding electrons of opposite spin. This is called pick-off annihilation. The pick-off annihilation lifetime is inversely proportional to the overlap of the positron and electron wave functions, and can thus be related to the size of the low-electron-density site at which the annihilation takes place. A technique that makes use of this fact is positron annihilation lifetime spectroscopy (PALS), with which it is possible to measure lifetimes and intensities of the above-mentioned species. A semi-empirical equation is used to calculate the average hole radius from the measured average o-Ps lifetime (τ_3)[1,2]:

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+\Delta R}\right)^{-1} \qquad (1)$$

This model assumes that the free-volume holes are infinite spherical potential wells of radius R_0 and that there is an electron layer in the region $R < r < R_0$, where $R_0 = R + \Delta R$. Nakanishi *et al.*[3] showed that a ΔR value of 1.66 Å is valid for materials, such as polymers, containing simple covalent bonds.

The formation of positronium in liquids and solids can be explained by the spur model[4,5], in which a positron spur in the last part of the positron track is created as a result of the slowing of the positron. In the spur, reactive species such as cations and free electrons are formed. Positronium is the result of a combination of the thermalized positron with one of the available free electrons. The formation of positronium must compete with other processes, such as electron–cation recombination, the diffusion of positrons and electrons out of the spur, and electron or positron scavenging. According to Mogensen[5], the spur processes influence the o-Ps yield in polymers.

Inhibition and anti-inhibition of positronium formation by different molecular liquids with and without additives have been described in a number of papers[6–9] and an extensive collection of data can be found in ref.5. For example, Eldrup *et al.*[6] studied the inhibition and quenching of o-Ps by strong Ps quenchers in aqueous solutions. When inhibition of positronium formation occurs, it is seen as a decrease in the o-Ps intensity, while quenching of o-Ps as a result of chemical reactions will shorten its lifetime (τ_3). Positronium formation in benzene solutions containing halogenated compounds has been studied in the presence and absence of C_6F_6 additive[7]. The o-Ps intensity is dramatically reduced when halogenated molecules are added to the solvent. With increasing concentration of halogen-containing compounds, the o-Ps yield reaches a saturation level above zero (at a concentration > 10 mol%). The addition of C_6F_6 increases the o-Ps yield, but does not completely restore the I_3 value. In this case C_6F_6 acts as an 'anti-inhibitor'. Hirata *et al.*[10,11] found that the addition of a nitro compound and also of halogenated compounds to some amorphous polymers resulted in a pronounced reduction of the o-Ps intensity.

Spur reactions in styrene–maleic anhydride (SMA) and styrene–acrylonitrile (SAN) copolymers containing maleic

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anhydride (MA) and acrylonitrile (AN) in the polymer chains are expected to be strongly composition-dependent.

EXPERIMENTAL

Materials and sample preparation

The materials used in this study are listed in *Table 1*. The percentages by weight signify the amount of maleic anhydride or acrylonitrile in the copolymer. The polymers were supplied in the form of pellets or powder. To obtain samples suitable for PALS measurements and other analyses, the polymers were compression-moulded into a cylindrical shape with a thickness of 2 mm. The styrene–maleic anhydride copolymers were all moulded at 210°C, whereas the pure polystyrene and the styrene–acrylonitrile copolymers were treated at 190°C. The polymers were preheated for 7 min and then exposed to increasing pressure over a period of 5 min. The samples were allowed to cool between aluminium plates. Polyacrylic acid was used instead of poly(maleic anhydride), because it is very difficult to homopolymerize the monomer to high molecular masses. The polyacrylic acid and polyacrylonitrile could not be melted, so the powders were cold-pressed into the same shape as the other samples. All the specimens were kept in a desiccator after pressing, to prevent moisture uptake.

Differential scanning calorimetry

A Perkin-Elmer DSC-7 instrument was used to measure the glass transition temperatures (T_g) of the melt-pressed samples. All measurements were calibrated against indium, and the sample mass was ~6 mg. The samples were annealed ~40°C above T_g for 4 min before 20°C min^{-1} cooling to 40°C. The glass transition temperatures were determined in the second heating run, which was made at a heating rate of 10°C min^{-1}.

Density measurement

Densities and specific volumes of the compression-moulded samples were measured at room temperature with a Micromeritics Multivolume Pycnometer 1305 using helium gas. Melt-pressed samples of ~1 g that did not contain visible bubbles or pores were examined. The accuracy of the measurements is estimated to be ± 0.2%.

PALS measurements and data analysis

A fast–fast coincidence system with CsF crystals was used to measure positron lifetimes in the samples. The ^{22}Na source, which was sandwiched between two 8 μm thick Kapton foils, had an activity of 1.7 MBq, which gave a count rate of ~650 s^{-1}. The time resolution of the spectrometer was 280 ps, full width at half-maximum, as measured with a ^{60}Co source. Identical polymer samples were placed on both sides of the source. Five spectra containing 3×10^6 counts each were measured for every polymer composition. During the short measurement time (five spectra in 6–7 h), no effect of radiation could be observed on o-Ps lifetimes or intensities. The measurements were performed in air at room temperature.

The spectra were analysed with the MELT program (version 3.0)[12], which gives lifetime distributions in addition to average lifetimes and intensities. The evaluations were performed without using any source correction or constraints, but the number of lifetimes cannot be fixed by this method. A constant value of the entropy weight, α, equal to 10^{-6} was used for all evaluations. The criteria described by Wästlund and Maurer[13] were used to choose the best fit.

RESULTS AND DISCUSSION

Physical properties of the copolymers

Differential scanning calorimetry of all the amorphous copolymers and polystyrene gave the glass transition temperatures (T_g) shown in *Figure 1a*. The T_g of the SAN copolymers is only weakly dependent on acrylonitrile content, whereas that of SMA increases considerably with increasing maleic anhydride content. *Figure 1b* and *c* show the copolymer densities and specific volumes as a function of composition. Here also, the SMA copolymers exhibit a pronounced composition dependence. The density shows a large increase with MA content and accordingly the specific volume decreases. The density of the SAN copolymers increases only slightly with AN content.

Free-volume hole sizes in styrene–maleic anhydride and styrene–acrylonitrile

Figure 2a and *b* show the average ortho-positronium lifetime and the corresponding average free-volume hole radii of SMA as a function of copolymer composition. The radii were calculated from the measured average o-Ps lifetimes (τ_3) listed in *Table 2* by using equation (1). The radius has a tendency to increase up to an MA content of

Table 1 Molecular weights and suppliers of the polymers used

Polymer	M_w (kg mol^{-1})	Source	Supplied as
Polystyrene	210[a]	Scientific Polymer Products	pellets
SMA 8 wt%	224	Monomer-Polymer Dajac Labs	pellets
SMA 14 wt%	50	Monomer-Polymer Dajac Labs	pellets
SMA 22 wt%	110	DSM Research	pellets
SMA 24 wt%	110	DSM Research	pellets
SMA 28 wt%	110	DSM Research	powder
SMA 32 wt%	110	DSM Research	pellets
SMA 50 wt%	50	Scientific Polymer Products	pellets
SAN 22 wt% (Luran 368R)	210[a]	BASF	pellets
SAN 25 wt% (Luran 358N)	170[a]	BASF	pellets
SAN 33 wt% (Luran 378P)	150[a]	BASF	pellets
Polyacrylic acid	450	Scientific Polymer Products	powder
Polyacrylonitrile	—	Scientific Polymer Products	powder

[a] Measured by size exclusion chromatography, calibration with narrow polystyrene standards. Other molecular weights are values according to the supplier

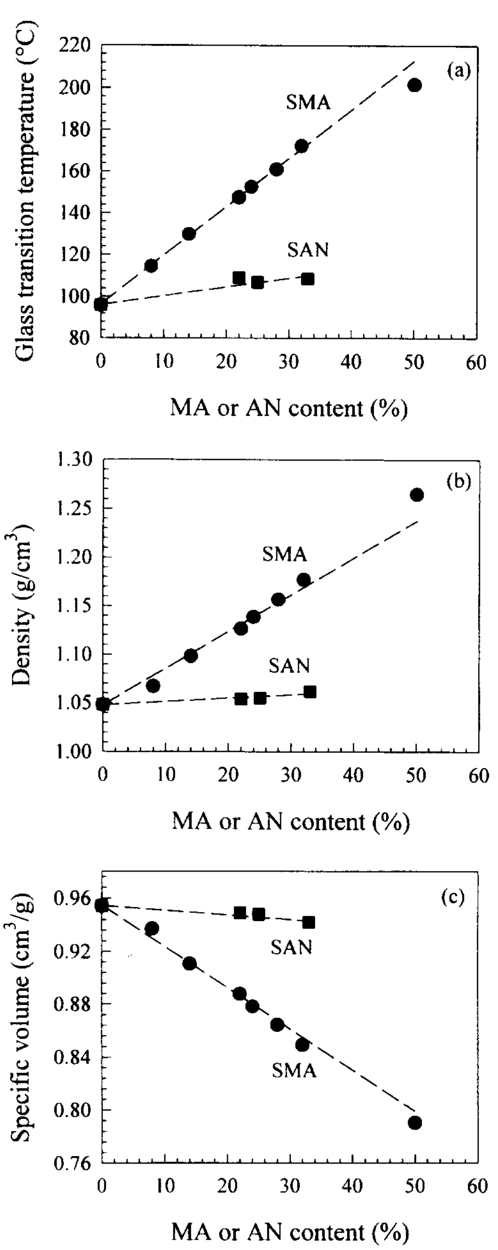

Figure 1 (a) Glass transition temperatures of SMA and SAN copolymers measured by d.s.c. (b) Densities of SMA and SAN copolymers. (c) Specific volume of SMA and SAN copolymers. The broken lines are for guidance only

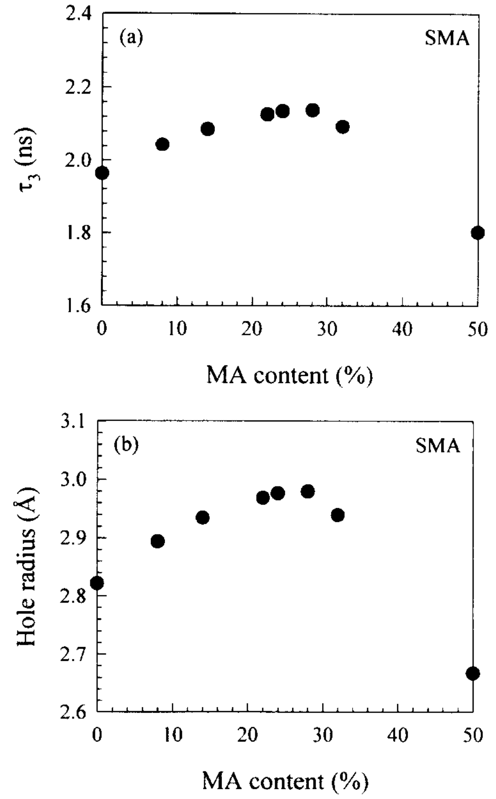

Figure 2 Ortho-positronium lifetime (a) and positronium free-volume hole radius (b) as a function of maleic anhydride content in SMA copolymers

Table 2 Average ortho-positronium lifetimes obtained with MELT and breadths (full width at half-maximum, FWHM) of the o-Ps lifetime distributions

Polymer	τ_3 (ns)	FWHM (ps)
Polystyrene	1.964	670
SMA 8 wt%	2.043	350
SMA 14 wt%	2.087	380
SMA 22 wt%	2.127	440
SMA 24 wt%	2.136	450
SMA 28 wt%	2.139	270
SMA 32 wt%	2.094	250
SMA 50 wt%	1.803	270
SAN 22 wt%	1.938	400
SAN 25 wt%	1.937	490
SAN 33 wt%	1.948	450
Polyacrylic acid	1.171	[a]
Polyacrylonitrile	1.565	[a]

[a] Difficult to determine a trustworthy value because of the low o-Ps intensity

28 wt%, but the hole size decreases at higher MA contents. The decrease could be attributed to the change in polymer structure, since the 50/50 composition corresponds to a completely alternating copolymer[14], which is probably able to pack in a more efficient way than the more random copolymers of lower MA content. It can also be seen in *Figure 1a* and *c* that the 50/50 SMA sample shows a slight deviation from a straight line. The sample seems to be denser than a linear relation between density and composition would suggest.

As mentioned above, evaluations with the MELT program also give lifetime distributions as a complement to average lifetimes and intensities. The breadths of the o-Ps lifetime distributions can be found in *Table 2*, where they are given as full width at half-maximum (FWHM) values. The styrene homopolymer used for all comparisons in this study has the broadest distribution of all samples investigated. An interesting observation is that, in the SMA copolymers, the breadth of the distribution increases up to an MA content of 24 wt%, but the distribution is much sharper at 28 wt% and higher concentrations of MA. This may once again be explained by the random and alternating constitution of the copolymers. When maleic anhydride is introduced into the styrene chains, the packing of the molecules is disturbed and the hole size is increased. The distribution of hole sizes is also gradually broadened, since the MA is randomly distributed in the chains, disturbing the packing more in some parts than in others. With increasing amount of MA, the sequence length distribution changes, leading to a more alternating structure of the copolymer chains. Better packing of the macromolecular chains gives smaller hole sizes, but also a narrower hole size distribution, because the chain structure is more homogeneous, reducing the differences in packing efficiency.

Average o-Ps lifetimes and free-volume hole radii of the SAN copolymers are shown in *Figure 3a* and *b*. In polystyrene and the copolymers, the hole size is almost constant, whereas the acrylonitrile homopolymer (not shown in the figure) has a structure in which the holes are smaller: the average radius is 2.42 Å. Breadths of the ortho-positronium lifetime distribution for the SAN copolymers obtained with the MELT program are given in *Table 2*. All the samples show a similar distribution width, smaller than that of polystyrene.

Inhibition of positronium formation by maleic anhydride and acrylonitrile

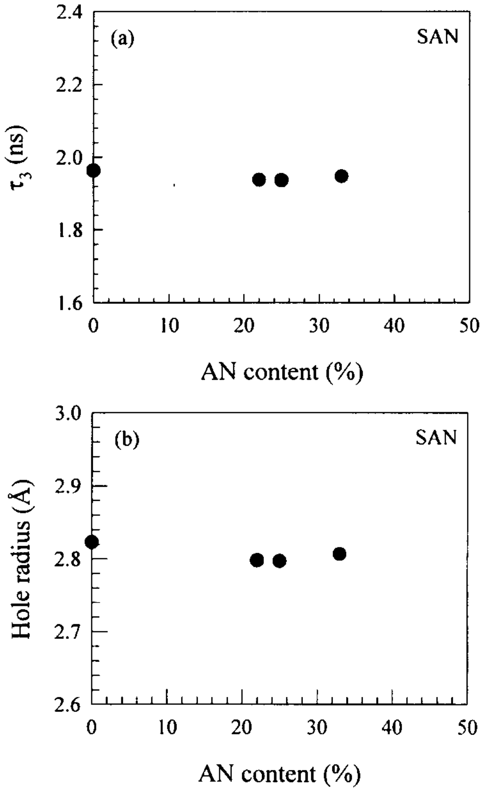

Figure 3 Ortho-positronium lifetime (a) and positronium free-volume hole radius (b) as a function of acrylonitrile content in SAN copolymers

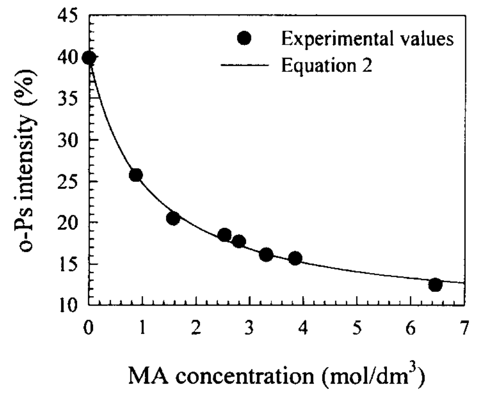

Figure 4 Ortho-positronium intensity as a function of maleic anhydride content in SMA copolymers. The curve represents the best fit of equation (2) to the experimental values

Figure 4 shows the o-Ps intensity as a function of SMA composition. The I_3 value of polystyrene is close to 40%, but the o-Ps yield decreases dramatically with increasing amount of maleic anhydride in the copolymer. The large change in I_3 shows that the o-Ps yield is strongly dependent on the MA content, which seems to inhibit Ps formation. A simple model of what might happen in the positron spur can be suggested. The maleic anhydride acts as an electron scavenger, whereas the styrene parts have a much lower probability of recombining with free electrons, which can be demonstrated by the high o-Ps intensity (~40%) in pure polystyrene. This means that Ps formation is strongly inhibited in the parts of the spur where MA is situated, whereas the Ps formation probability is much higher in the styrene-rich parts of the spur. The o-Ps formation probability will then obviously depend on the concentration of the electron-scavenging groups, which in this case are represented by the maleic anhydride. An equation describing partial inhibition can be fitted to the decrease in I_3 with increasing MA concentration:

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

where I_3^0 is the o-Ps yield at $C = 0$, C is the concentration of scavenger in mol dm^{-3}, 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 efficiency of the scavenger relative to the Ps formation efficiency. The above equation was used by Eldrup *et al.*[6] to describe the inhibiting effect of a few compounds known to be strong Ps quenchers. Alfassi and Ache[15] also used the equation for the introduction of a 'two-precursor' model used mainly for solvents containing scavengers. This model is based on the assumption that two types of precursors of thermalized o-Ps are initially formed. One can react with the solute and annihilate as such, or form the thermalized o-Ps. The other precursor will be directly transformed to thermalized o-Ps and annihilate as such. The total yield of Ps precursors is assumed to be I_3^0, which is the intensity of the long-lived component in the absence of solute.

Best-fit values of the constants, when fitting the equation to the experimental data in *Figure 4*, can be found in *Table 3*. The continuous curve in *Figure 4* represents the best fit of equation (2). The saturation value of I_3, denoted I_3^{sat}, is equal to $A \times I_3^0$. In this case, I_3^{sat} equals 9%, agreeing very well with the o-Ps yield of polyacrylic acid, which could be compared with poly(maleic anhydride), and is ~10% in our measurements.

Figure 5 shows the o-Ps intensity as a function of AN content. The basis here is also polystyrene, which has a high I_3 value. The o-Ps yield decreases dramatically with AN content, indicating that acrylonitrile, similarly to maleic anhydride, also has a strong inhibiting effect on o-Ps formation. equation (2) was fitted to the experimental results, and although there are only four points, a good indication of the scavenger efficiency is given. Best-fit

Table 3 Best-fit values of parameters σ and A in equation (2), and saturation values of I_3

Copolymer	I_3^0 (%)	σ (dm^3 mol^{-1})	A	I_3^{sat} (%)	
				Theoretical	Experimental
SMA	39.9	0.94	0.22	9	10
SAN	39.9	0.54	0.29	11.5	9.3

values of A and σ can be seen in *Table 3*. The saturation value of I_3 in this case is 11.5%, while pure polyacrylonitrile has an o-Ps intensity of 9% when evaluated with MELT.

Both SMA and SAN copolymers show a strong dependence of the o-Ps yield on composition. It could be argued that this effect is caused by a decreasing fractional free volume or a decreasing number of holes in the copolymers, but this is unlikely in SAN since the specific volume changes only slightly with composition and the glass transition temperature is almost constant. Instead, it seems to be the properties of the acrylonitrile and maleic anhydride as such that are the factors that primarily influence I_3. Shantarovich[16] recently reported that maleic anhydride in benzene solution has a quenching effect on the o-Ps lifetime. In that case, the o-Ps lifetime would be expected to decrease steadily with MA content, which is not observed here. The MA and AN parts of the macromolecular chains might act by forming complexes with positrons or by using their electron affinity to combine with free electrons appearing in the positron spur:

$$\mathrm{RA} \rightarrow \mathrm{RA}^+ + e^- \qquad \text{(ionization)} \qquad (3)$$

$$\mathrm{RA}^+ + e^- \rightarrow \mathrm{RA} \qquad \text{(recombination)} \qquad (4)$$

$$\mathrm{RA} + e^- \rightarrow \mathrm{RA}^- \qquad \text{(anionformation)} \qquad (5)$$

$$\mathrm{RA}^- + e^+ \rightarrow [\mathrm{RA}^-, e^+] \qquad \text{(positron capture)} \qquad (6)$$

Maleic anhydride has two carbonyl groups that are known to be electron-attracting because of the electronegativity of the oxygen atoms. The nitrile group is also known to be electron-attracting. The chemical structures of the two copolymers are depicted schematically in *Figure 6*. The large effect on I_3 could be explained by considering that the electrons belonging to maleic anhydride and acrylonitrile are so strongly bound that the positron creating the spur cannot ionize these parts of the polymer chain. Or, if electrons could be removed, a very fast recombination would take place, leaving the positron no chance to form positronium. In the styrene parts of the spur, however, free electrons are formed and some of these electrons can still be available to form Ps. Since the copolymer chains consist of a part of styrene monomer residues as well as of methylene ($-CH_2-$) groups (in the case of polyacrylonitrile), free electrons can always be produced to some extent in the positron spur and lead to the formation of Ps. This would explain the saturation values of I_3, which are close to 10% for the copolymers examined.

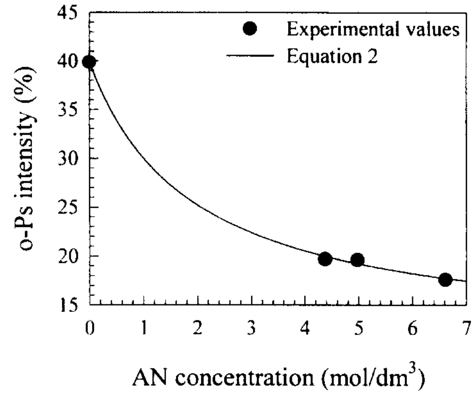

Figure 5 Ortho-positronium intensity as a function of acrylonitrile content in SAN copolymers. The curve represents the best fit of equation (2) to the experimental values

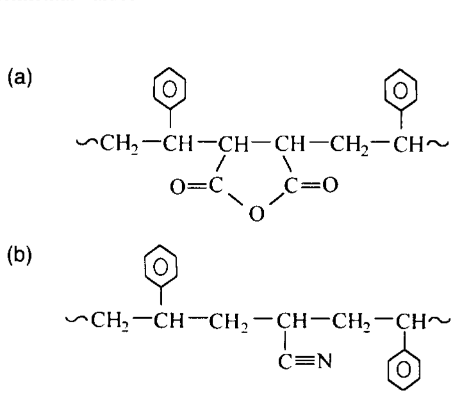

Figure 6 Simple sketch of the chemical structure of styrene-maleic anhydride (a) and styrene-acrylonitrile (b) copolymers

Positronium inhibition in polymers

Alfassi and Ache[17] used equation (2) to evaluate the scavenging effect of nitro and chlorinated compounds as additives in the non-polar solvents toluene and decane. Later, Hirata *et al.*[10] used the same equation to describe the effect of halogenated compounds added to polycarbonate. Some of the additives were found to act as partial inhibitors, since the o-Ps yield did not reach zero even at very high concentrations of the scavenger. A similar behaviour was also found for $CuCl_2$ in poly(vinyl alcohol)[18]. In the present study, the equation describing partial inhibition is also shown to be useful for copolymers with no added scavengers; here also, a saturation level of I_3 above zero is found.

In polymers, it has been proposed that the o-Ps intensity is proportional to the number of free-volume holes[19,20], which in turn is related to the total free-volume fraction of the polymer. This could be a valid assumption in situations in which the positronium formation probability is independent of spur reaction processes.

A few examples in which polymer chemistry can explain the unusually low o-Ps intensity results are as follows. PALS measurements of poly(vinyl chloride) are found to give an o-Ps yield of ~5–6%[21]. The inhibition by chlorine is often explained by the possibility of formation of a $[Cl^-, e^+]$ bound state, which would not contribute to the long-lifetime component. Chlorine anions can be formed because of the high electron affinity of the chlorine atom. A large number of polyimides has been examined with respect to positronium inhibition and quenching[22]. It was found that the Ps formation probability is largely controlled by the electron acceptability of the acid anhydride moieties. The positronium formation in chloropolystyrenes has also been found to be strongly inhibited[23]. The inhibiting effect seems to depend on the chlorine position in the polymer structure. Poly(chlorotrifluoroethylene) has been studied as a function of temperature by the PALS technique[24]. The o-Ps intensity was found to be 4–5%, but the authors did not explain this very low value, despite their later use of it to calculate a 'fractional free volume'. High-density polyethylene (HDPE) that had been heat-treated in an atmosphere containing oxygen has been found to give an o-Ps yield half of that measured in untreated samples[25]. It was suggested that carbonyl groups formed by thermal oxidation inhibit Ps formation.

CONCLUSIONS

The change in free-volume hole size in styrene–maleic anhydride copolymers of different composition could be followed by using the PALS technique. A change in hole size distribution with changing sequence length distribution was also found. The styrene–acrylonitrile copolymers showed an almost constant hole size and hole size distribution with composition. It has been shown that maleic anhydride and acrylonitrile have a strong inhibiting effect on positronium formation when they are part of a macromolecular chain, and that this effect is probably related to electron- or positron-scavenging in the positron spur. This means that the electron and positron affinities of constituents in the polymer chains, and their reaction products, are the most important factor influencing the ortho-positronium yield. It is therefore not always appropriate to use the measured o-Ps yield (I_3) as a measure of the fractional free volume of a polymer.

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