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Positronium inhibition and free volume in chloropolystyrenes studied by positron annihilation

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Abstract

Positron annihilation phenomenon has been studied in chloropolystyrenes. PAL and ACAR measurements have been performed in air and at room temperature for amorphous samples of different chlorine content. The increase in the latter is followed by the decrease in both the intensity of the narrow component of ACAR curves and the intensity of the longest-lived component (I_3) in PAL spectra. The latter one, related to the ortho-positronium intensity in polystyrene I_3^0 , changes according to the formula: $I_3/I_3^0 = [1 + (19.93 \cdot C)^{0.56}]^{-1}$ where C denotes the number of Cl atoms per unit of the polymer.

The inductive effect produced by the chlorine in chloropolystyrenes is assumed to be the reason of the inhibition of the positronium formation in them. In general the chlorine reactivity towards positrons seems to depend on its position in the polymer structure.

The numerical Laplace inversion technique /1/ has been applied to PAL data to recover the radius distribution of free volumes for each sample of the second series. A tendency towards decrease in mean radius of free volumes is seen when chlorine content increases in studied samples. The only exception is the sample in which the highest amount of chlorine atoms has been substituted at α -carbons in the aliphatic chain.

Introduction

The positron annihilation phenomenon has been studied in polystyrene from the very beginning of the development of positron annihilation spectroscopy (PAS) /2,3,4,5/up to nowadays /6,7/. Positronium (Ps) formation has been confirmed in this polymer by the existence of the long-lived component in positron lifetime spectra ($\tau \approx 2$ ns) and its magnetic quenching /8/ as well as by the appearance of the narrow component in ACAR curves /5/ and the abundance of the three-quantum annihilation events /9/. It is supposed that the formation of positronium in polystyrene takes place mainly in the

benzene rings /10/. The relaxation parameter (i.e. the electron density at the position of the positron forming Ps in polystyrene related to that of free Ps) was estimated in /8/ as equal to 0.80 ± 0.06 indicating the relaxation of the Ps. It has been established /11/ that:

- 1/ introduction of chlorine into polystyrene changes thermal stability of samples according to the position of chlorine atoms in polymer structure
- 2/ the highest thermal stability has been observed for samples with chlorine substituted to benzene rings
- 3/ in chloropolystyrene with chlorine atoms introduced into the aliphatic parts of its structure the dehydrochlorination takes place easily
- 4/ the chlorine atoms added to benzene rings are more easily detachable than the ones being in aliphatic chain.

Experimental

Samples. Polystyrene and chloropolystyrenes

Two series of samples were studied. The first one included polystyrene (PSP-the raw material and PSB) and one chloropolystyrene (PO7), while the second-the commercial polystyrene (AOP-the raw material) and five chloropolystyrene samples (AOW, AO3, AO4, AO6, AO48). Further characteristics of samples as chlorine content and its distribution are given in Table I. All the studied samples were amorphous as it was proved by X-ray diffraction studies. Powders of each sample, except PSB which was in bulk form, were formed into discs, of diameter equal to 20 mm and of thickness equal to 3 mm, under the pressure of 3 tons.

Polymer preparation and characterization

Table I. Chlorine content in studied samples.

SAMPLE		CHLORINE CONTENT			
		[wt. %]	[Cl atom/unit]		
			aliphatic chain	ring	
				aromatic	aliphatic
1st series	PSP	-	-	-	-
	PSB	-	-	-	-
	PO7	36.1	1.3	-	0.3
2nd series	AOP	-	y values	-	-
	AOW	1.1	0.03	-	-
	AO3	3.6	0.1	-	-
	AO4	15.3	0.5	-	-
	AO6	30.8	1.3	-	-
	AO48	66.0	0.6	4.9	-

The polystyrene samples (PSP and PSB) were obtained by the radical polymerization of styrene in benzene solutions, the procedure described in /12/. The chlorination of polystyrene was carried out with sulphuryl chloride in two ways: a) radical-initiation (samples PO7, AOW, AO3, AO4, AO6) /13/ and b) ionic catalysis (sample AO48) /14/. The chlorine content was determined using the Schöniger method /15/.

The positions of the chlorine atoms in the chlorinated polystyrenes depend on the mechanism of chlorination. In the chloropolystyrenes obtained in radical-initiated reactions, the chlorine atoms were substituted on the aliphatic part of the polymer (samples AOW, AO3, AO4, AO6) and as in case of the sample PO7 added to the cyclic aliphatic ring and substituted on the chain.

The general formula of samples AOW-A06 is

with values of y given in Table I while the formula of the sample PO7 is

In the chloropolystyrene A048, obtained by the ionic chlorination of polystyrene, the chlorine atoms were substituted on the aromatic rings of the polystyrene and on the aliphatic chain. The formula of the sample A048 is

All structures of the chloropolystyrenes were established with use of the $^1\text{H-NMR}$, IR spectroscopy techniques and elementary analysis /13/.

Measurements

ACAR and PAL techniques were used in our studies of polystyrene and chloropolystyrene samples. The two kinds of measurements were performed in air at R.T.

ACAR measurements

ACAR measurements were performed from -29 to $+29$ mrad with use of the LS spectrometer of angular resolution with FWHM equal to 0.8 mrad, described in details in /16/. Data were accumulated with the step of 0.5 mrad for the period of $2 \cdot 10^3$ s at each point resulting in about $8 \cdot 10^4$ counts at the peak of each distribution with background intensity reaching 3% of the peak value. The positrons were produced upon desintegration of ^{22}Na nuclei in the source of 15 mCi activity.

PAL measurements

A conventional fast-slow coincidence system with plastic, cylindrical scintillators NE 111 ($20\text{mm} \times 20\text{mm}$) was used for measuring the lifetime spectra. The positron source, ^{22}Na of activity 15 μCi was deposited between two identical thin Hostaphan foils (0.8 $\text{mg} \cdot \text{cm}^{-2}$ each) and then sandwiched between the samples under investigation. A typical decay curve contained about $1 \cdot 10^6$ counts and had the peak to background ratio of 2500.

Results

Table II. Results of ACAR measurements.

SAM- PLE	FWHM [mrad]				INTENSITIES [%]				variance of the fit
	G_1	G_2	G_3	F	$I(G_1)$	$I(G_2)$	$I(G_3)$	$I(F)$	
PSP	3.0(0.1)	8.8(0.1)	18.6(2.1)	-	6.9(0.1)	88.5(0.3)	4.6(0.3)	-	1.41
PSB	3.0(0.1)	8.7(0.1)	17.7(1.9)	-	6.9(0.1)	88.3(0.3)	4.8(0.3)	-	1.19
PO7	-	-	17.2(1.5)	9.4(0.1)	-	-	6.0(0.3)	94.0(0.3)	1.34
AOP	3.1(0.2)	8.6(0.1)	15.6(1.7)	-	8.9(0.2)	85.4(0.3)	5.7(0.3)	-	1.18
AOW	2.8(0.2)	8.8(0.1)	17.9(2.1)	-	3.9(0.1)	92.0(0.3)	4.1(0.3)	-	1.07
AO3	2.5(0.3)	8.8(0.1)	21.8(3.6)	-	2.3(0.1)	94.6(0.3)	3.2(0.3)	-	1.53
AO4	-	-	15.3(1.1)	8.7(0.2)	-	-	9.2(0.3)	90.8(0.3)	1.62
AO6	-	-	18.0(1.6)	9.2(0.1)	-	-	5.0(0.2)	95.0(0.2)	1.29
AO48	-	-	16.8(1.1)	9.3(0.1)	-	-	7.7(0.3)	92.3(0.3)	1.51

The ACAR curves were fitted with a sum of gaussians (for samples PSP, PSB, AOP, AOW and AO3) or the sum of the one very broad gaussian and a Ferrell function /17/ (samples PO7, AO48, AO4 and AO6) simultaneously together with a background represented as a sloped straight line, using the computer program FER /18/. The results of the analysis, i.e. the FWHM and the intensity of each component are given in Table II.

Table III. Results of PAL measurements.

The PAL spectra corrected for positron annihilation in the source (3%) were fitted with a sum of three exponentials convoluted with the resolution function of the lifetime spectrometer (a sum of two gaussians) plus a constant background, using the program POSITRONFIT /19/. The results of the analysis i.e. the lifetimes and the intensities are given in Table III. The analysis of the PAL spectra with use of a method employing numerical Laplace inversion technique /20/ was performed for the samples of the second series. Further details concerning the method are given in /21/. A modified version of Provencher program CONTIN was used to obtain the radius (R) and volume (V) distributions of free-volume cavities. A reference spectrum of 6N polycrystalline Ni was used ($\tau_{Ni}=110$ ps, $I_{Ni}=96\%$). The radius distributions are given

SAM- PLE	LIFETIMES [ps]			INTENSITIES [%]			Variance of the fit
	τ_1	τ_2	τ_3	I_1	I_2	I_3	
PSP	122 (5)*	418 (10)	2059 (13)	27.9 (1.1)	36.0 (0.9)	36.6 (0.3)	1.08
PSB	134 (5)	407 (8)	2005 (8)	27.1 (1.0)	34.9 (0.9)	38.1 (0.2)	0.92
PO7	158 (15)	389 (4)	2174 (120)	14.6 (1.8)	83.6 (1.7)	1.8 (0.1)	0.92
AOP	128 (7)	411 (17)	2012 (15)	31.8 (1.6)	28.6 (1.4)	39.6 (0.4)	1.08
AOW	132 (6)	382 (5)	2005 (11)	21.3 (1.0)	56.7 (1.0)	22.0 (0.2)	0.95
AO3	148 (10)	374 (5)	2003 (15)	17.4 (1.6)	63.9 (1.5)	16.7 (0.2)	1.03
AO4	165 (12)	379 (5)	2064 (24)	18.5 (2.1)	72.0 (1.9)	9.5 (0.2)	1.03
AO6	210 (12)	403 (7)	2359 (65)	25.3 (3.4)	71.3 (3.3)	3.4 (0.1)	0.96
AO48	213 (14)	403 (8)	1897 (34)	25.7 (4.1)	70.5 (4.0)	3.8 (0.2)	1.04

* Standard deviations of measured quantities are given in round brackets.

in Fig. 1.

Discussion

Comparison of the results for PSP and PSB samples indicates that there is no essential difference in positron annihilation characteristics for powder and bulk polystyrene. The lifetimes for raw samples in both series (PSP and AOP) are very close to those known from literature /6/ and being the results of the high precision measurements.

Assuming that in polystyrene the longest-lived component in the lifetime spectra (τ_3, I_3) comes from the ortho-positronium atoms decaying via the pickoff process one can conclude that the positronium formation in chloropolystyrenes is strongly inhibited. The inhibition reveals even at the low content of Cl atoms (the large decrease in I_3 follows the little increase in the chlorine content).

Fig. 1. Free-volume radius distribution functions, $f(R)$. Smooth lines were drawn through the data points for eye-guide purposes only.

In Fig.2 the decrease in I_3 is given vs. Cl content for samples of both series. Using the values of $\Delta I_3/I_3^0$ obtained for the sample A06 of the second series as reflecting the inhibition possibility of Cl atoms in the aliphatic chain, one can count the additional relative decrease in I_3 which takes place in the sample P07 and is caused by the chlorine atoms attached to the cyclic aliphatic rings. The value of $\Delta I_3/I_3^0$ equal about 12% per one Cl atom situated as mentioned above in the polymer structure in P07 is obtained. The similar comparison between samples A04 and A048 shows that the chlorine atoms substituted in the aromatic rings of the sample A048 don't give any contribution to the inhibition of the positronium. It seems that the Cl atoms attached to aliphatic carbons are the active ones in the inhibition of Ps formation.

Fig.2. The decrease in I_3 vs. Cl content.

The general conclusion is that the chlorine inhibits the positronium formation but its reactivity towards positrons depends on its position in the polymer structure, it means on the kind of bond between the halogen and carbon. The intensities I_3 vs. chlorine content (C) for the samples of the second series are well fitted with the equation: $I_3 = I_3^0 [1 + (\alpha * C)^\beta]^{-1}$ where I_3^0 denotes the o-Ps yield in the polystyrene sample (AOP), while α and β are the fitting parameters equal respectively to 19.93 [atom/unit] $^{-1}$ and 0.56 (Fig.3).

The above equation has been proposed to represent the o-Ps yield versus the concentration of electron scavengers in solutions /22/. It is based on the assumption that the relative yield of Ps is proportional to the relative fraction of geminate electrons which remained unscavenged by the introduced electron scavenger. According to the spur model the Ps yield in polymers should be large due to the small size of the spur in solids at all, and the high values of dielectric constants in polymers. Relative high contributions of the spur mechanism in the Ps formation were estimated in /23/ for some polymers.

Fig.3. I_3/I_3^0 vs. Cl content.

The experimental data were fitted with the formula: $I_3 = I_3^0 [1 + (\alpha \cdot C)^\beta]^{-1}$ using the method of least squares. The fitting parameters α & β are given above.

The inhibition of positronium in the frame of the spur model of Ps formation is frequently explained by the possibility of the $[Cl^-, e^+]$ bound state formation. The existence of such state has been proposed many times in case of samples containing Cl and studied with use of PAS, e. g. in aqueous solutions of Cl^- ions /24/, in chlorine substituted hydrocarbons in non-polar liquids /25/, in polyvinyl chloride on thermal degradation /26/, in fluorinated elastomers with Cl in side groups /27/ and for alkali chlorides /28/.

In /28/ the stability of the $[Cl^-, e^+]$ bound state was established and its main characteristics were given, e. g. the full width at half maximum of the ACAR curve (11.2 mrad) as well as the positron lifetime (328 ps). Thus if the complex $[Cl^-, e^+]$ is formed it doesn't contribute to the long lifetime in the PAL spectra and to the narrow component in the ACAR curves. The changes in positron annihilation characteristics observed by us versus chlorine content don't contradict the supposition that the formation of the $[Cl^-, e^+]$ bound state is the reason of the Ps inhibition in the chloropolystyrenes. There is however a problem in what process the Cl^- ions could be produced. The increase in electron charge in vicinity of chlorine atoms is possible as a result of the inductive effect following the introduction of chlorine both into aromatic and aliphatic parts of the chloropolystyrene structure. It is known that introduction of chlorine enlarges the dipole moment of molecules (cf the values of the electric dipole moment in case of benzene and chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, toluene and 2-chlorotoluene, 3-chlorotoluene, 4-chlorotoluene, benzyl chloride and 2-chlorobenzyl chloride, 3-chlorobenzyl chloride, 4-chlorobenzyl chloride). Polar molecules with electric dipole moment greater than 1.625 D are guaranteed to possess positron complexes which, within the Bohr-Oppenheimer approximation, are stable with respect to positron detachment /29/. It seems to us that in chloropolystyrenes one may take into account the possibility of existence of the positron-unit complex $[RCl^-, e^+]$, possible to view as $[Cl^-, e^+]$ complex in the field of an R^+ ion. The influence of the electric dipole moment of fluorinated benzenes in cyclohexane-dichloromethane and in cyclohexane-carbon tetrachloride mixtures on positronium formation was reported in /30/. From the fig. 1 a tendency towards decrease in mean radius of free volume is seen when chlorine content increases in studies samples. The only exception is the sample A06 in which the highest amount of Cl atoms was substituted at α -carbons in the backbone /13/. That might result in effective stretching and stiffening of the chain.

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References

- /1/ Gregory,R.B, Procyk,A, in: Positron Annihilation Studies of Fluids, Ed. Sharma,S.C, World Scientific, Singapore 1988, p.254.
- /2/ De Benedetti,S, Richings,H.J, Phys. Rev. 85 (1952) 377
- /3/ Bell,R.E, Graham,R.L, Phys. Rev. 87 (1952) 236
- /4/ Bell,R.E, Graham,R.L, Phys.Rev. B 90 (1953) 644
- /5/ Page L.A, Heinberg,M, Phys. Rev. 102 (1956) 1545
- /6/ Kluin,J.E, Faupel,F, Materials Science Forum, 105-110 (1992) 1613
- /7/ Welander,M, Mauer,F.H.J, *ibid.*, p. 1811.
- /8/ Bertolaccini,M, Bisi,A, Gambarini,G, Zappa,L, J. Phys.C: Solid State Phys.7 (1974) 3827
- /9/ Bertolaccini,M, Bussolati,C, Zappa,L, Phys. Rev. 139A (1965) 696
- /10/ Thosar,B.V, Kulkarni,V.G, Lagu,R.G, Chandra,G, Phys. Lett. 21 (1966) 647
- /11/ Sikorski,R.T, Mirkiewicz,G, Varga,J, Biro,O, J. Thermal Anal., 36 (1990) 1795
- /12/ Loslew,I, Fedotowa,O, Praktikum Po Chirii Wysokomolekularnych Sojedinienii, Gozhimizdat, Moskwa (1962).
- /13/ Mirkiewicz,G, Ph.D. Thesis, to be published.
- /14/ Sikorski,R.T, Mirkiewicz,G, Eur. Polym. J. 24 (1988) 157
- /15/ Pielichowski,J, Puszyński,A, Preparatyka Związków Wielkocząsteczkowych, Politechnika Krakowska, Kraków 1978 p. 142.
- /16/ Rozenfeld,B, Baranowski,A, Jerie,K, Nukleonika 19 (1974) 817
- /17/ Baranowski,A, Dębowska,E, Appl. Phys. A51 (1990) 23
- /18/ Baranowski,A, Program FER, in a software of the Computer Library of the Department of Applied Nuclear Physics at Wrocław University.
- /19/ Kirkegaard,P, Pedersen,N.J, Eldrup,M, PATFIT-88: A Data Processing System for Positron Annihilation Spectra on Mainframe and Personal Computers,National Laboratory, 1989.
- /20/ Gregory,R.B, Zhu,Y, Nucl. Instr. & Methods in Physics Res. A290 (1990) 172
- /21/ Baranowski,A, Dębowska,M, Jerie,K, Mirkiewicz,G, Rudzińska-Girulska,J, Sikorski,R.T, Acta Phys. Polon., 83 (1993) 239.
- /22/ references /32/ & /33/ in Wikander,G, Mogensen,O.E, Pedersen,N.J, Chem. Phys. 77 (1983) 159
- /23/ Bisi,A, Gambarini,G, Zappa,L, N.Cim. 2D (1983) 1465
- /24/ Mogensen,O.E, Chem. Phys. 37 (1979) 139
- /25/ Wikander,G, Mogensen,O.E, Pedersen,J, Chem. Phys. 87 (1984) 149
- /26/ Khan,M.N.G.A, J. Phys. D3 (1970) 663
- /27/ Arifov,P.U, Vasserman,S.N, Tishin,S.A, in: Positron Annihilation, Eds. P.C. Jain, R.M. Singru and K.P. Gopinathan, World Scientific, p. 787.
- /28/ Nurmagambetov,S.B, *ibid.*, p. 770.
- /29/ Kurtz,H.A, Jordan,K.D, J. Chem. Phys. 75 (1981) 1876
- /30/ Zhang,Z, Ito,Y, Tabata,Y, Radiat. Phys. Chem. 36 (1990) 285