Free Volume and Tacticity in Polystyrenes

Ritva M. Dammert,[†] Sirkka L. Maunu,[†] Frans H. J. Maurer,[‡] Igor M. Neelov,[†,§] Satu Niemelä,[†] Franciska Sundholm,[*,†] and Camilla Wästlund[‡]

Laboratory of Polymer Chemistry, PB 55, University of Helsinki, FIN-00014 Helsinki, Finland, and Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Received November 14, 1997; Revised Manuscript Received September 9, 1998

ABSTRACT: Measurements of the free volume hole size distributions obtained from positron annihilation lifetime spectroscopy (PALS) in relation to the chain tacticity in polystyrene and poly(*p*-methylstyrene), and in relation to the static free volume distribution in modeled amorphous cells of these polymers are reported. The free volume distribution was estimated using the Voronoi tessellation of space and direct calculations of unoccupied space in modeled amorphous cells of the polystyrenes. The results indicate that the syndiotactic polystyrene and the syndiotactic poly(*p*-methylstyrene) have broader hole distributions than the more atactic samples. The polystyrenes have a maximum in the free volume hole size distribution at volumes smaller than for the poly(*p*-methylstyrenes). The calculations indicate the presence of a large portion of holes too small to be detected with positron annihilation. The small holes are related to structural features of the polymer chain itself. The calculated distribution of large holes in the polymers agree satisfactorily with the results from the PALS measurements. The difference is due to the irregular shapes of the holes in the calculated models as compared to the spherical potential wells assumed in the interpretation of results from PALS measurements.

Introduction

The concept of free volume in polymers has proved useful in discussing physical properties such as viscosity,[1] viscoelasticity,[2] the glass transition, and plastic yielding.[3] No unambiguous definition of polymer free volume is available. We will use the term free volume for the total unoccupied volume in the polymer material which is the difference between the specific volume and the total volume occupied by the atoms including their van der Waals radii. Despite a great deal of interest in the theoretical and experimental investigations of free volume, only limited information about the hole dimensions and distribution in polymers is available. The dependence of free volume on chemical structure has been reported in a few theoretical studies[4,5] in which the results have been correlated to gas permeability.

During the past years positron annihilation lifetime spectroscopy (PALS) has emerged as a technique suitable for detection of free volume hole sizes in polymers. Positrons from a ^{22}Na source are allowed to penetrate the polymer sample and the lifetime of single positrons in the sample is registered. The positron can annihilate as a free positron with an electron in the material (in approximately 0.4 ns) or form a metastable state called positronium (Ps) together with an electron. If the spins of the positron and the electron are antiparallel, the species is called *para*-positronium (*p*-Ps) and has an intrinsic lifetime of 0.125 ns. In *ortho*-positronium (*o*-Ps), which has a mean lifetime of 142 ns in a vacuum, the spins of the two species are parallel. The lifetime of *o*-Ps in polymers is shortened to 1−5 ns because the positron can pick off an electron with opposite spin from the surrounding medium and annihilate with it. A PALS spectrum of a polymer is usually found to consist of three different mean lifetimes, τ_1, τ_2, and τ_3, corresponding to the annihilation processes described. The relative probability of positrons annihilating with these lifetimes is given as I_1, I_2, and I_3, respectively. Since thermalized *o*-Ps is localized in cavities or regions of low electron density, the probability of the pickoff process is related to the free volume hole size. The *o*-Ps lifetime can be related to the free volume hole radius by a semiempirical equation[6,7] in which the free volume holes are assumed to be infinite spherical potential wells of radius R_0

$$\tau_3 = {}^1\!/_2[1 - (R/(R + \Delta R) + 1/(2\pi)(\sin(2\pi R)/(R + \Delta R))]^{-1} \quad (1)$$

It is also assumed that there is an electron layer in the region $R < r < R_0$, where $R = R_0 - \Delta R$. Nakanishi et al.[8] showed that $\Delta R = 1.66$ Å for materials containing simple covalent bonds. Both mean lifetimes and lifetime distributions can be extracted from the positron lifetime spectra, which means that also free volume hole size distributions in polymers can be obtained with this technique. There is, however, both an upper and a lower limit of the hole size that can be measured with PALS. The smallest detectable hole size is determined by the size of the positronium itself, which has a diameter of 1.06 Å. A theoretical analysis suggests that the minimum hole radius that can be sampled by *o*-Ps is approximately 1.85 Å.[9] The upper limit is often approximated to a diameter of 20 Å. The total free volume cannot be estimated with this method. In addition, it is important to realize that PALS is a dynamic method of measurement with a time scale of 10^{-9} s. Molecular vibrations with a frequency higher than 10^9 Hz will therefore contribute to the occupied volume.

The amorphous state of disorder in polymers and its relation to free volume distribution can be theoretically analyzed by different methods. Relaxed amorphous cells of the polymers can be constructed by molecular model-

---

[*] To whom correspondence should be addressed.

[†] University of Helsinki.

[‡] Chalmers University of Technology.

[§] On leave from the Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy pr. 31, 199004 St. Petersburg, Russia.

10.1021/ma971682m CCC: $18.00

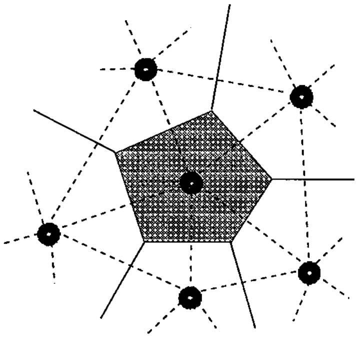

Figure 1. Two-dimensional Voronoi polyhedron around a central atom.

ing. In the Voronoi method of tesselation of space[10-13] the vectors connecting all pairs of atoms in the amorphous cells are perpendicularly bisected and a large number of intersecting planes is generated. The polyhedron associated with a given center is obtained by selecting the smallest of the polyhedra that is thus formed around it. To illustrate this, an example of a two-dimensional Voronoi polyhedron is shown in Figure 1. It has to be pointed out that the Voronoi polyhedron is always constructed around a center atom. Disordered systems such as the amorphous polymers generate a distribution of polyhedra with various shapes and sizes. As a Voronoi polyhedron around an atom identifies the available space, this information has been related to the free volume distribution in the polymer,[4] although it does not directly describe the hole sizes and the hole size distribution. We have previously discussed the distribution of Voronoi polyhedra in polystyrenes.[14] Other methods for calculating the free volume in polymers have been presented. Misra and Mattice[15] for instance, used a cluster analysis of a cubic grid in a similar analysis.

In the present paper we report measurements of the free volume hole size distributions obtained from positron annihilation lifetimes in relation to the chain tacticity in polystyrene and poly (*p*-methylstyrene). The experimental results are discussed in relation to the free volume distribution defined in terms of Voronoi polyhedra. In addition, to overcome the ambiguity with the central atom in the description of free volume with Voronoi polyhedra, we used the constructed amorphous cells in a further calculation to describe the holes in the polymer structure which had no coincidence with an atom. The calculation of the hole size distribution is described. The Voronoi tesselation method as well as the calculation of the holes in the amorphous cells gives statistical distributions of volumes as a static parameter independent of time.

Experimental Section

Materials. Styrene (Merck-Schuchardt >99%), *p*-methylstyrene (Aldrich >97%) were dried over calcium hydride and purified by fractional distillation in a vacuum. The monomers were stored in ampules sealed with Young's PTFE stopcocks at −25 °C. Tetrahydrofuran (THF, Prolabo, analytical grade) was dried and purified as described by Urwin and Stearne[16] and finally distilled into dry ampules sealed with Young's PTFE stopcocks. Methylcyclohexane (Merck-Schuchardt, analytical grade) and toluene (Merck, analytical grade) were purified as described by Perrin and Armarego.[17] *n*-Butyllithium (1.6 M in hexane, Aldrich), the titanocene catalyst $CpTiCl_3$ (Fluka >97%, and the cocatalyst poly(methyl alumoxane), MAO, 30% in toluene (Witco GmbH) were used as received.

Polymerizations. Anionic polymerizations were carried out under high vacuum at −78 °C in THF, or at ambient temperature in methylcyclohexane, in the usual way. *n*-Butyllithium was used as the initiator, and methanol as the terminator, respectively. The living nature of the polymerizations was observed as a typical orange-red color in the reaction mixture. In a typical experiment 100−150 mL of solvent was distilled into the reactor. The solvent was degassed in freeze−thaw cycles before the monomer (5−10 mL) and the initiator were added. When THF was used as the solvent, the initiator was added at −78 °C, before the monomer. With methylcyclohexane as the solvent, the monomer was added first, followed by the initiator at ambient temperature.

The syndiotactic polymers were prepared by purging a solution of monomer in toluene with argon, adding the catalyst under argon and degassing the mixture on a vacuum line, and filling the line with argon. The cocatalyst was then added with a syringe, and the mixture kept at ambient temperature with magnetic stirring. The polymers were precipitated into cold methanol, filtered off and dissolved in THF. This procedure was repeated 2−3 times, and the resulting white polymers were dried in a vacuum. Typical synthesis of polystyrene: 19.5 g of styrene in 150 mL of toluene was reacted with 0.055 mmol of $CpTiCl_3$ and 33 mmol of MAO (Al/Ti = 590) for 1.5 h. Typical synthesis of poly(*p*-methylstyrene): 16.1 g of *p*-methylstyrene in 150 mL of toluene was reacted with 0.08 mmol of $CpTiCl_3$ and 40 mmol of MAO (Al/Ti = 590) for 3 h. Polymer yields and characteristics are collected in Table 1.

Size exclusion chromatography, SEC, was used to determine the molar masses of the polymers. THF (LabScan HPLC grade) was used as the solvent in series of three 10 μm i.d. columns containing PL gels 500, 10000, and 100000 Å, respectively (Polymer Labs) at ambient temperature. The flow rate was 1.0 mL/min and the detector a UV-2 (Pharmacia) detector. The solvent was delivered with a Waters 510 pump. The injection volume was 20:l, and the concentration of the sample was 3 mg/mL. Calibration was done with polystyrene standards (Polymer Labs).

Thermal field flow fractionation, ThFFF, was done with an instrument consisting of a model SFC 500 syringe pump (Instrument Specialists), a C6W injection valve (Valco Instrument Co), an in house made ThFFF channel and an SP8450 UV detector (Spectra-Physics). A computer was used to control the instrument as well as to acquire the data and for data handling. The solvent was THF (Merck HPLC grade), the injection volume was 10:l, and the concentration of sample was 0.05−0.1% (w/w). Polystyrenes (Polyscience) were used as standards.

Light scattering was measured on a Brookhaven instrument with a BI-9000AT correlator, and a He−Ne 60 W laser at 632.8 nm. Atactic polystyrenes were measured at 25 °C in toluene (Rathburn glass distilled grade). Syndiotactic polystyrenes and poly(*p*-methylstyrenes) were measured in chloroform (LabScan HPLC grade) at 25 and at 30 °C, respectively. The refractive index increments were measured with an Optilab 903 refractometer (Wyatt Technology Corp.).

^{13}C NMR spectra were measured at ambient temperature in $CDCl_3$ on a Varian Gemini 2000 spectrometer. The tacticity of the polymers was analyzed on the base of the deconvolution results obtained with the PERCH software constructed by Reino Laatikainen and Matthias Niemitz at the University of Kuopio.

FT IR spectra were measured on a Nicolet 205 spectrometer from potassium bromide pellets, precision 2 cm^{-1}.

PALS measurements were performed at room temperature using a fast−fast coincidence system with CsF crystals. The ^{22}Na source, which had an activity of approximately 1.7 MBq, was sandwiched between two 8 μm thick Kapton foils. Then 2 mm thick samples, suitable for PALS measurements, were compression molded at 150 °C for 6 min. The samples were cooled under pressure with a cooling rate of 40 °C/min through the glass transition. The crystalline syndiotactic polystyrene had to be heat treated at 270 °C. Positron measurements were done 1−4 weeks after pressing. Identical pieces of the polymer sample were placed on both sides of the

Table 1. Properties of the Polymers Studied[a]

		$\langle M_n \rangle$		$\langle M_w \rangle$			PDI		
polymer	yield (%)	SEC	ThFFF	SEC	LS	ThFFF	SEC	ThFFF	P_r
PS1	88	14400	12000	17500	16900	14700	1.21	1.22	0.70
PS2	84	281200	274100	479300	493000	414700	1.25	1.22	0.55
sPS	11	29600	*b*	60100	65200	*b*	2.0		1.0
PMS1	92	26700	16300	30400	43500	16300	1.14	1.15	0.50
PMS2	72	15000	7700	16400	22200	8500	1.10	1.10	0.79
sPMS	23	15000	*b*	33800	43300	*b*	2.26		1.0

[a] PS = atactic polystyrene, sPS = syndiotactic polystyrene, PMS = atactic poly(*p*-methylstyrene), sPMS = syndiotactic poly(*p*-methylstyrene), PDI = $\langle M_w \rangle / \langle M_n \rangle$, and P_r = degree of syndiotacticity. [b] The syndiotactic samples were not soluble enough for the analysis.

source. The count rate was 670 cps, and the time resolution as measured with a ^{60}Co source was determined to 280 ps. Five spectra containing 3 million counts each were collected for all the different polymers. The measurements were performed in air at ambient temperature.

Two evaluation methods, POSITRONFIT[18] and MELT,[19,20] were used to extract positron and positronium lifetime information from the measured spectra. The POSITRONFIT program gives mean lifetimes and intensities and was used to evaluate each single spectrum into three lifetimes with corresponding intensities. The MELT program gives the distribution of lifetimes but also average lifetimes and intensities. For the MELT evaluations five spectra of the same polymer (corrected for t_0 drift) were added together and evaluated. No source corrections or constraints were applied for any of the evaluations. The best MELT fit was chosen by using the same criteria as used in ref 21. In this study, version 3.0 of the MELT program was used, and the entropy weight was kept constant (10^{-6}) in all evaluations.

Atomistic molecular modeling involved the construction of amorphous cells of polystyrene and poly(*p*-methylstyrene) of different tacticity. Further details of this procedure have been described.[5,14] The molecular mechanics and molecular dynamics calculations were done by using the INSIGHTII and DISCOVER software packages, which include the POLYMER and AMORPHOUS CELL modules.[22] The PCFF force field was used.[23] The molecular mechanics, the molecular dynamics calculations, and the construction of the amorphous cells, as well as the graphics, were all done on a Silicon Graphics Indigo 2 work station.

Models of 100 different conformations of each of the atactic, syndiotactic and isotactic, polymers were built as previously described.[14] Weighted averages for the rotational isomeric states (RIS) for the main chain C−C bonds of poly(*p*-methylstyrene) were not available; hence, values for the torsional angle were chosen close to the local potential energy minimum. To get comparable results, the same method was used for the polystyrenes. The amorphous cells were constructed by packing one chain consisting of 80 monomers into a cubic box under periodic boundary conditions. The density of the polystyrenes was taken to be 1.05 g cm^{-3}; the experimentally measured densities for atactic, syndiotactic, and isotactic polystyrene have been reported to be 1.0471, 1.0448, and 1.0575 g cm^{-3}, respectively.[24] For poly(*p*-methylstyrene), the value 1.01 g cm^{-3} was used, calculated with the method of van Krevelen,[25] which is included in the software used in this work. Refinement of the structures was started by minimization of all the 100 conformations of each tacticity using steepest descent minimization until the derivative of the energy was <5 kcal mol^{-1}. Afer this, 10 conformations with the lowest potential energies of each tacticity were chosen. The refinement of these structures was continued with an *NVT* (constant particle number, constant volume, constant temperature) molecular dynamics run of 100 ps duration at 1000 K. This was followed by conjugate gradient minimization until the energy derivatives were less than 0.01 kcal mol^{-1}.

The distributions of Voronoi polyhedra presented in this work have been calculated by minimization of the refined amorphous cells without *NPT* (constant particle number, constant pressure, constant temperature) molecular dynamics simulation, since the effect of the latter was negligible.

The static volumes of the holes of the unoccupied space in the polymers were calculated by a procedure similar to particle insertion. A probe particle with radius 1.0 Å was chosen (the radius of *o*-Ps is 1.06 Å). The particle was inserted randomly in the amorphous cells (10 of each conformation of both polymers) modeled by the method described above. The insertion was regarded as successful if the particle did not have any intersections with the atoms in the system. The atoms were taken to be hard spheres with diameters for carbon, d_C, = 4. 001 Å, and for hydrogen, d_H, = 2.995 Å, respectively.[22] For each cell, insertion was attempted 10^6 times of which 2000−4000 were successful.

In each insertion attempt the coordinates of the centers of the particles and of the carbon and hydrogen atoms were used. Three perpendicular rays were plotted from each probe center in directions *x*, *y*, and *z*. The first moment of intersection with the carbon or the hydrogen atoms was calculated. Thus the radii in positive directions of each hole is found. The radii in the negative directions were calculated along *x*, *y*, and *z* in a similar manner. The sum of these radii give the diameters d_{min}, $d_{average}$, and d_{max} of the holes in three perpendicular directions. The distributions of hole diameters were determined from these data, and used for calculating the distribution of free volumes V_{min}, $V_{average}$, and V_{max} as well as the total average free volume.

Results

Characterization of the Polystyrenes. Results of the anionic polymerizations and the titanocene-catalyzed polymerizations of styrene and of *p*-methylstyrene are collected in Table 1. The molar masses determined with SEC, ThFFF, and light scattering, respectively, are in good agreement. Details of the ThFFF method are discussed in a recent paper.[26] The yields of polymerization in the anionic polymerizations are quite good; the yields of syndiotactic polymers with the titanocene catalyst are reasonable, taking into account the complexity of the reaction. Details of the syntheses and the molar mass determinations of the polymers are discussed elsewhere.[27]

The tacticity of the polymers was determined from ^{13}C NMR solution spectra by deconvolution of the spectra with PERCH[28] software, and the degree of syndiotacticity (racemic dyad fraction) was calculated. The spectral region chosen for the deconvolution is the region of resonances by the quaternary aromatic carbon atoms C_1, with several overlapping chemical shifts in the region 142−147 ppm. The high field value is associated with syndiotactic structures, the low field resonance is associated with isotactic structures, and intermediate values are resonances from fragments with varying degree of atacticity.[29−31] The range of the C_1 chemical shifts in ^{13}C NMR spectra of anionically prepared polystyrene and the poly(*p*-methylstyrene) together with the deconvoluted curves are collected in Figure 2. Values of the degree of syndiotacticity expressed as the probability of occurrence of racemic

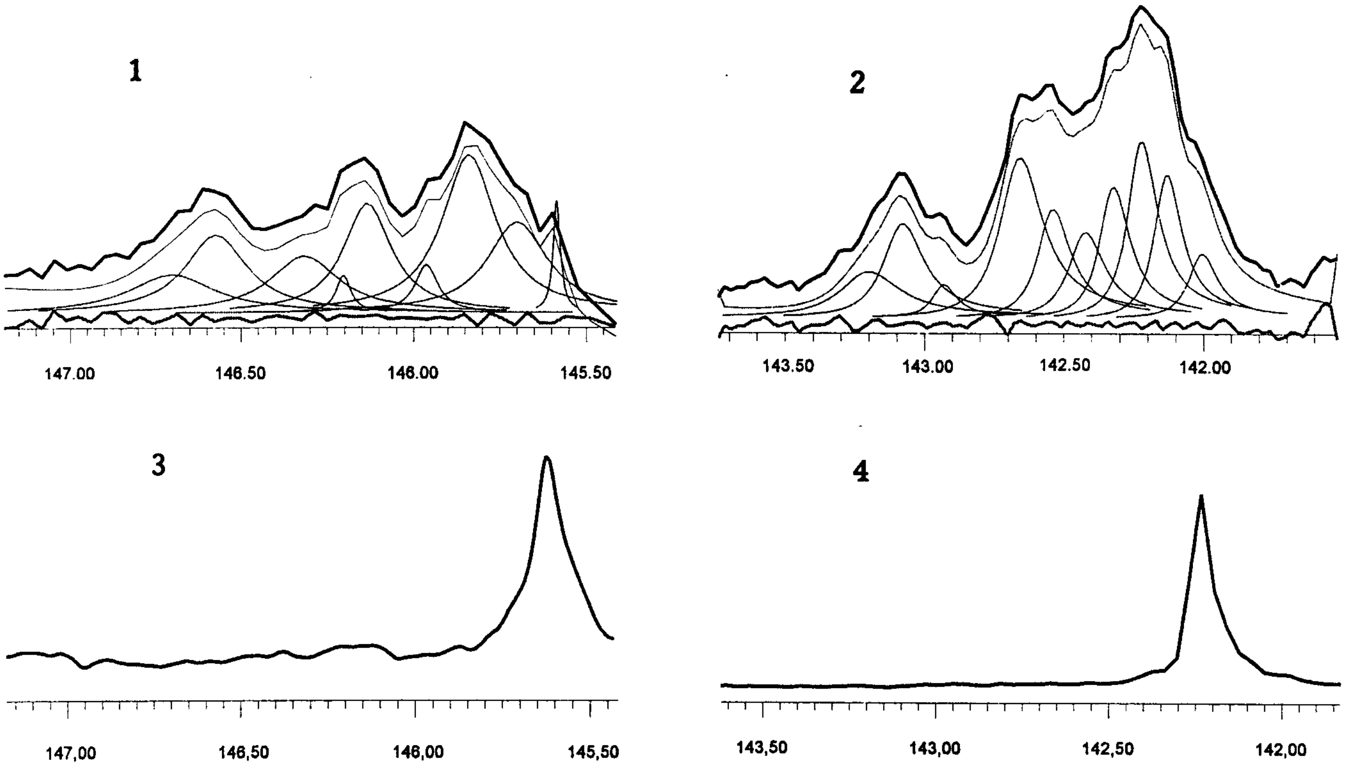

Figure 2. Deconvolution of ^{13}C NMR spectra of (1) polystyrene and (2) poly(*p*-methylstyrene), in the region of the C_1 resonance. (3) Corresponding resonance of syndiotactic polystyrene. (4) Corresponding resonance of syndiotactic poly(*p*-methylstyrene). Experimental spectrum thick line, deconvolution thin line, difference gray line.

dyads, P_r, calculated as described by Suparno et al.[32] are seen in Table 1. By varying the reaction conditions in the anionic polymerization, it is thus possible to vary the degree of syndiotacticity in polystyrene and its derivatives. The samples chosen for closer scrutiny in this study had $P_r = 0.50-0.55$ and $0.70-0.79$, respectively. The syndiotacticity of the catalytically prepared polymers was evaluated; the fraction of *rrrr* pentads was higher than 95%.

The tacticity and, in the case of the syndiotactic polymers, also the polymorphic forms of the polymers can be deducted from IR spectra. Guerra et al.[33] have shown that there are significant differences between spectra of polystyrene samples of different tacticity in the 500−1400 cm^{-1} region where a number of vibrations sensitive to the conformation of the polymer chain are found. The IR spectrum of syndiotactic polystyrene synthesized in this work is shown in Figure 3. The conclusion is drawn that the sample is amorphous from the broad and featureless appearance of the bands in the 900−1000 cm^{-1} and in the 1300−1400 cm^{-1} regions.[33] The IR spectrum of the syndiotactic poly(*p*-methylstyrene) sample is shown in Figure 4. This spectrum shows a broad featureless band around 550 cm^{-1} which is typical for the amorphous form.[34] Furthermore, bands typical of crystalline poly(*p*-methylstyrene) around 1165 cm^{-1} [34] are missing. The anionically prepared polymer samples showed no crystallinity.

The sample of syndiotactic polystyrene had to be melted at very high temperature (270 °C), however, to obtain a suitable sample for the PALS measurement. The sample crystallizes partly during the heat treatment. The IR spectrum of a sample of the heat-treated syndiotactic polystyrene shows that the polymer is in the α′-form[35] as clearly shown by the form of the absorptions in the 1300 cm^{-1} region, a sharp peak at 1220 cm^{-1}, the form of the peaks at 1150−1200 cm^{-1} and around 950 cm^{-1}, and finally a single peak at 538 cm^{-1}.[33] It is evident that the syndiotactic polystyrene has crystallized during the preparation of the sample for the PALS measurement.

Positron Lifetime Measurements. All positron lifetime spectra were successfully evaluated into three mean lifetimes and intensities with the POSITRONFIT program. The *o*-Ps lifetime (τ_3) and intensity (I_3) for each polymer are shown in Table 2, together with the mean free volume hole radius calculated using eq 1. A general observation is that the polystyrenes have smaller free volume holes than the poly(*p*-methylstyrenes). Moreover, the relative *o*-Ps intensity in the different samples is between 31% and 36%, with an exception for syndiotactic polystyrene which has a much lower intensity value of approximately 23%.

Syndiotactic poly(*p*-methylstyrene) does not crystallize by cooling from the melt or by annealing the amorphous state.[35] Thus the heat treatment during preparation of the samples for PALS measurements does not induce crystallinity in the poly(*p*-methylstyrene) sample. However, annealing does induce crystallinity in syndiotactic polystyrene.[33] We believe the low *o*-Ps intensity in syndiotactic polystyrene is caused by crystallinity. Several observations have been published concerning crystallinity and *o*-Ps intensity, showing an intensity decrease with increasing crystallinity. [36] This led to the conclusion that *o*-Ps is only annihilating in the amorphous phase. This seems to be true for many polymer systems, with some exceptions though. Poly(ethylene oxide)/ poly(methyl methacrylate) blends show no decrease in I_3 during isothermal crystallization even though the sample changes from amorphous to 19% crystallinity.[37]

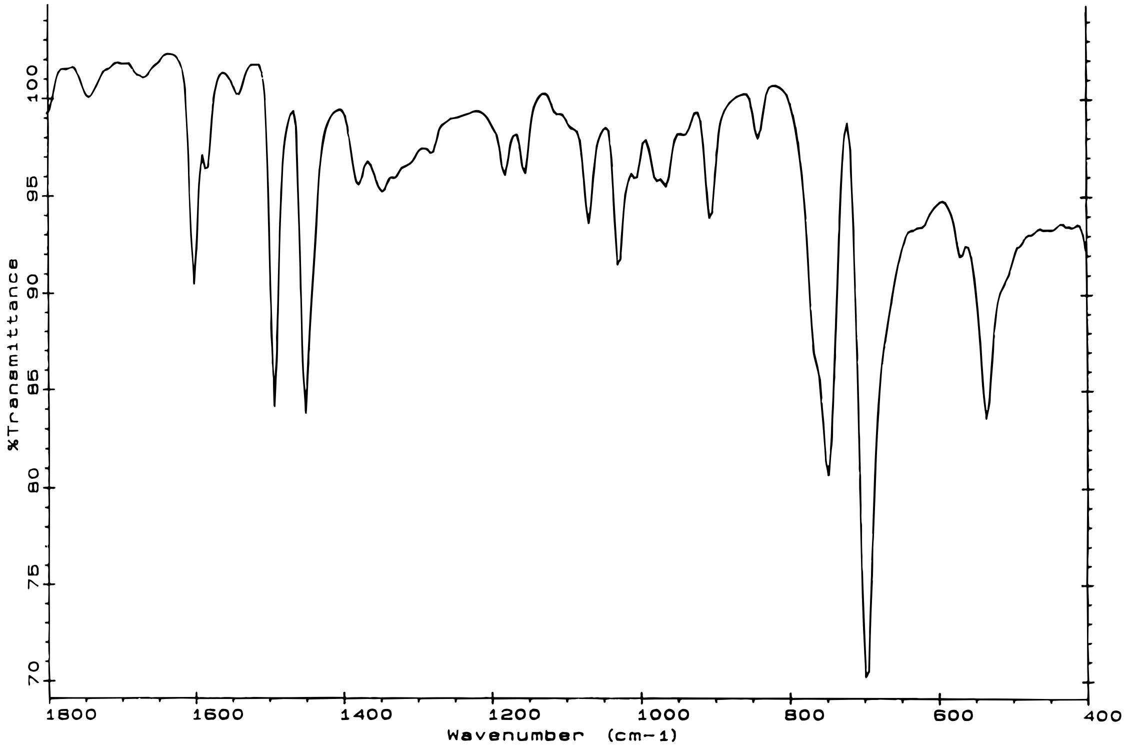

Figure 3. IR spectrum of amorphous syndiotactic polystyrene.

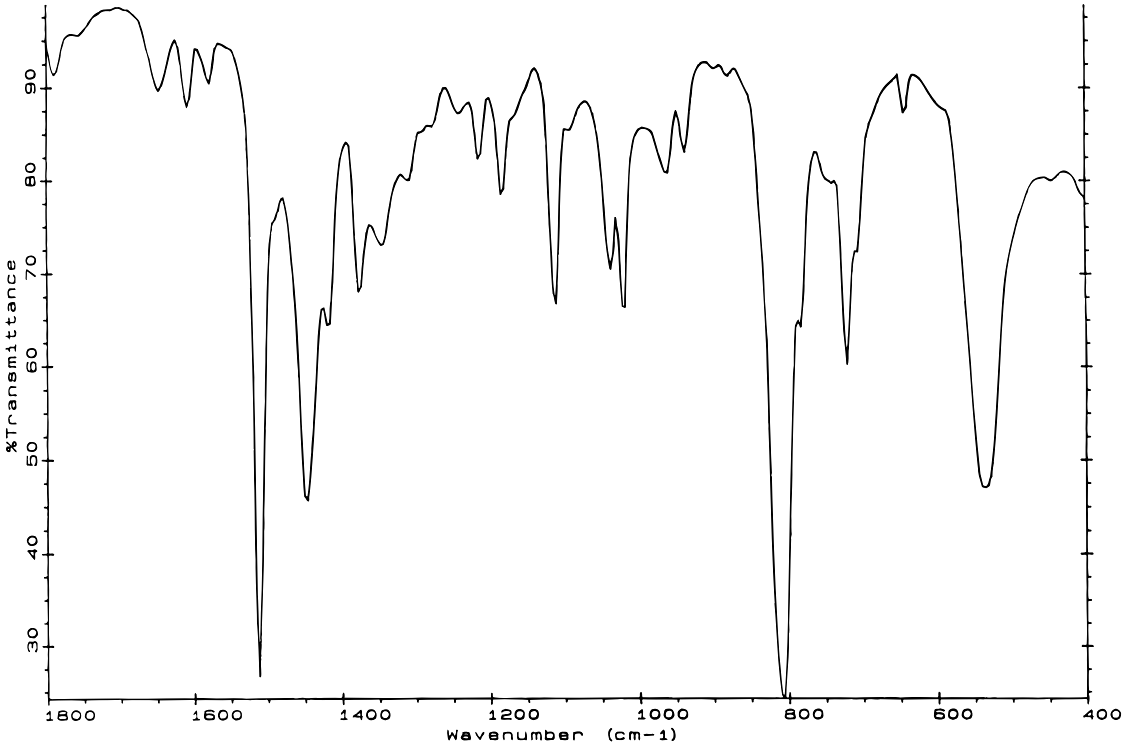

Figure 4. IR spectrum of amorphous syndiotactic poly(*p*-methylstyrene).

The MELT program gave average positron lifetimes, intensities and lifetime distributions. The average *o*-Ps lifetimes and intensities are given in Table 2. The POSITRONFIT and the MELT results are found to be rather consistent. *o*-Ps lifetime distributions for the polystyrenes are depicted in Figure 5. Equation 1 gives the corresponding radii of the free volume holes. In Figure 6 the free volume hole size distribution as determined with the positron lifetime method is shown. The results from the positron annihilation experiments indicate that the syndiotactic polystyrene and the syndiotactic poly(*p*-methylstyrene) have broader hole distributions than the more atactic samples. More significant is the difference between the two polymers. The polystyrenes have a maximum in the free volume hole size distribution around 110 Å^3, whereas the maximum for the poly(*p*-methylstyrenes) is around 130 Å^3. Yu et al.[38] used positron lifetime measurements to study free volume hole sizes in monodisperse atactic polystyrene over a wide temperature range. They found

Table 2. Average *o*-Positronium Lifetimes and Intensities for Polystyrenes Evaluated with POSITRONFIT and MELT Programs from Positron Lifetime Spectra[a]

	POSITRONFIT			MELT		
polymer	τ_3 (ns)	R (Å)	I_3	τ_3 (ns)	R (Å)	I_3
sPS	2.10 ± 0.02	2.95	22.9 ± 0.3	2.04	2.90	24.1 ± 1.7
PS1	2.07 ± 0.02	2.92	33.4 ± 1.2	2.06	2.91	33.0 ± 1.5
PS2	2.11 ± 0.01	2.95	31.3 ± 0.5	2.09	2.94	31.6 ± 1.6
sPMS	2.20 ± 0.03	3.03	35.6 ± 1.2	2.22	3.05	34.3 ± 2.0
PMS1	2.27 ± 0.02	3.09	31.1 ± 0.7	2.26	3.08	30.9 ± 1.6
PMS2	2.26 ± 0.01	3.09	31.1 ± 0.4	2.22	3.05	32.0 ± 0.9

[a] The average hole radii corresponding to the average lifetimes are calculated using eq 1. Abbreviations are as in Table 1.

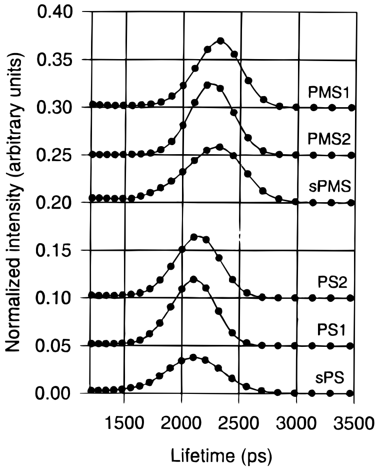

Figure 5. *o*-Positronium lifetime distributions in polystyrenes and in poly(*p*-methylstyrenes). For abbreviations and degrees of tacticity, see Table 1.

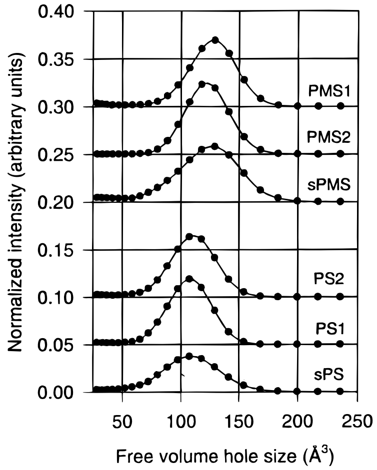

Figure 6. Free volume hole size distributions in polystyrenes and in poly(*p*-methylstyrenes) calculated from lifetime distributions in Figure 5. For abbreviations and degrees of tacticity, see Table 1.

an average free volume hole size of 100−110 Å^3 at 20 °C, which is in good agreement with our results. Also Liu et al. [39] found similar hole size distributions in atactic polystyrene at 25 °C.

Molecular Modeling and Calculation of Free Volume. The torsional angle distribution of the main chain was calculated as an average of 10 minimized conformations for the polymer chain models. The *trans*/*gauche* ratio was found to be 54/46 for atactic polystyrene and 55/45 for isotactic and syndiotactic polystyrene. The corresponding values for poly(*p*-methylstyrene) are 53/47 for the atactic form and 54/46 for the stereoregular forms. Similar values have been reported for atactic polystyrene.[40] Thus there are no significant differences between the atactic and the stereoregular polymers in the amorphous state in this respect. The same conclusion can be drawn from the calculated values of the solubility parameters, for all the polymer models the solubility parameter is 14−16 (J cm^{-3})$^{0.5}$.

The amorphous state disorder in polystyrene and poly(*p*-methylstyrene) of different tacticities were studied with molecular mechanics and molecular dynamics simulations. The construction of representative models for the amorphous polymers is based on the use of a force field, PCFF, the parameters of which are critical for the accuracy of the model. The models we have built are totally amorphous, nonoriented and non-cross-linked. In addition, the behavior of the material was assumed to be isotropic. The resulting edge lengths of the cells were 23.62 and 24.96 Å for polystyrenes and poly(*p*-methylstyrenes), respectively.

The use of the values of the experimental densities in this kind of calculation, as was done in this work, leads to relatively high values of the pressure in the system at room temperature. Since the shape and the size of the cell are kept constant during the refinement of the structure some strain remains. The remaining strain in the amorphous cells of the modeled polymers is of the same order of magnitude in all cases independent of the tacticity of the chain. Partly this is because the large phenyl side groups complicate the relaxation of the polystyrene chain, and partly this is because the cell is packed with one long chain only.

In the Voronoi tesselation the distribution of polyhedra was calculated for the amorphous cells of the polymers taking all atoms into account. The results are shown in Figure 7. It is seen that there is no clear dependence of the distribution of Voronoi polyhedra on chain tacticity, but there is a difference between the polystyrenes and the poly(*p*-methylstyrenes). A considerable fraction of polyhedra appear at sizes <5.5 Å^3: in polystyrenes 12.6% and in poly(*p*-methylstyrenes) 16.0%, respectively, of the total volume. This size corresponds to the space required by the carbon atoms in the main chain methylene groups and the methyl substituents, respectively. The largest fraction of polyhedra have sizes 6.5−9.5 Å^3, 42.2% in polystyrenes and 36.1% in poly(*p*-methylstyrenes), respectively. For both types of polymers there is a broadly distributed fraction of polyhedra >10.5 Å^3. This size corresponds to the space required by the hydrogen atoms. Since this fraction is larger in the poly(*p*-methylstyrenes) (48.0%) than in the polystyrenes (45.4%), the conclusion is drawn that the methyl groups require space and cause this effect. A similar effect of a methyl substituent was found for polysulfones and their substituted counterparts.[5]

To reduce the disturbance of the center atom in the Voronoi tesselation, the holes in the constructed amorphous cells were also estimated by calculating the mean diameters of holes distributed within the amorphous cells of the polystyrenes constructed by a procedure resembling particle insertion. Images of the holes inside the periodic cells were plotted for atactic, isotactic, and syndiotactic polystyrenes and poly(*p*-methylstyrenes), respectively. These images resemble each other in all the amorphous cells because the fluctuations of the hole structures for the different initial conformations are usually greater than the differences between the polymers. The same holds for the different stereoisomers of

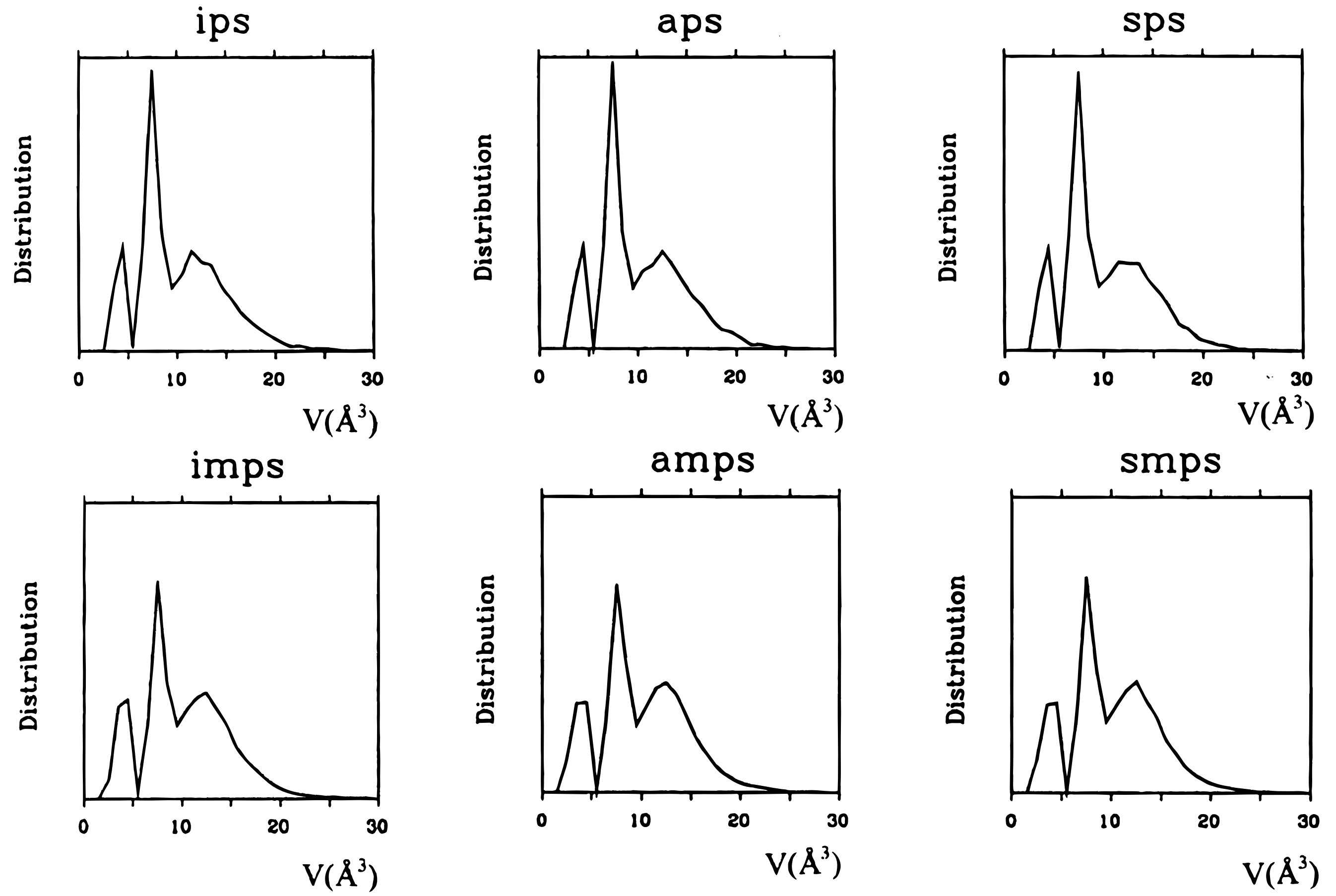

Figure 7. Distribution of Voronoi polyhedra constructed taking all atoms into account in amorphous models of isotactic polystyrene (ips), atactic polystyrene (aps), syndiotactic polystyrene (sps), isotactic poly(*p*-methylstyrene) (imps), atactic poly(*p*-methylstyrene) (amps), and syndiotactic poly(*p*-methylstyrene) (smps).

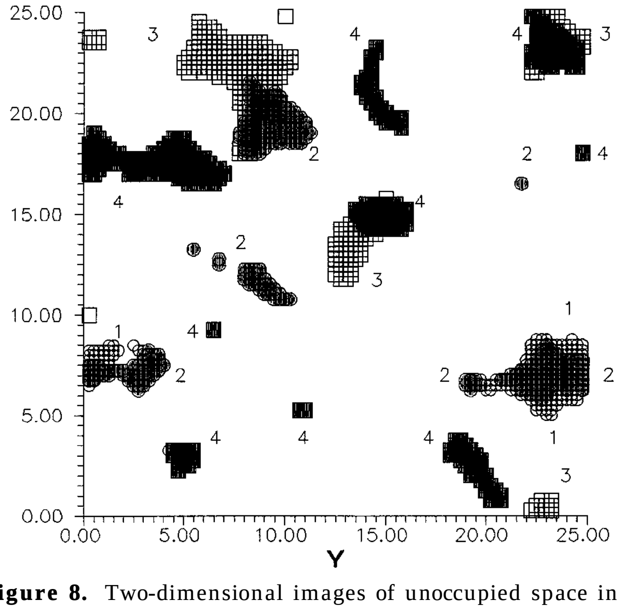

Figure 8. Two-dimensional images of unoccupied space in an amorphous cell of atactic poly(*p*-methylstyrene) in the *x* direction in planes 5 Å apart.

the polymers. The distribution of hole images in one amorphous cell of atactic poly(*p*-methylstyrene) is shown in Figure 8 as an example. The figure shows images in planes along the *x* axis at 5 Å distance from each other. The nonspherical shape of the unoccupied space is obvious.

Following the construction of the holes of unoccupied volume with radii > 1 Å in the amorphous cells, the distributions of free volume were calculated. Different methods can be used for the calculation of these distributions. In this work the procedure involves the construction of three perpendicular diameters called $d_{\min}$, d_{average}, and $d_{\max}$, respectively, through the same point for each inserted particle. From the values of the diameters the corresponding volumes are calculated, which in turn are used to estimate the distributions of unoccupied volume in each case. An example of such distributions of $V_{\min}$, V_{average} (from $d_{\min}d_{\text{average}}d_{\max}$), and $V_{\max}$ in atactic polystyrene and poly(*p*-methylstyrene), respectively, are seen in Figure 9, in which the results are shown on a linear scale. The curves have been normalized with respect to the total area. With this method of estimating the distribution of free volume in the two polymers under consideration, the difference between the stereoforms was too small to be significant.

For both polymers distributions of $V_{\min}$ have a maximum at 10–20 Å^3, of V_{average} at 30–40 Å^3, and of $V_{\max}$ at 70–80 Å^3, respectively; see Figure 9. However, when the average volume from the total distribution is calculated, it is found that for polystyrene the average volume is 60.0 Å^3; for poly(*p*-methylstyrene), it is 62.6 Å^3. The distributions of the free volumes for the two polymers thus differ from each other, the average volumes in polystyrene are smaller with a larger portion of holes with small volumes than in poly(*p*-methylstyrene). This is clearly seen on the insert in Figure 9 in which the distribution curves of V_{average} of the two polymers are shown plotted on a logarithmic scale, the normalization is with respect to total area. In addition,

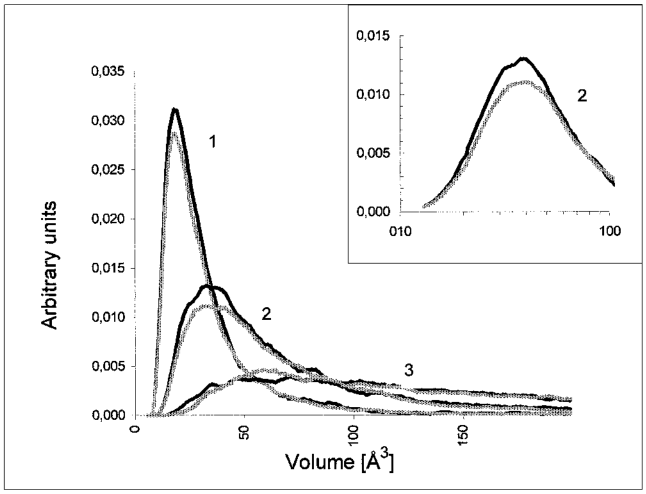

Figure 9. The relative distribution of holes in amorphous cells of atactic polystyrene (full line) and atactic poly(*p*-methylstyrene) (grey line). Curves 1 correspond to $V_{\min}$, curves 2 to V_{average}, and curves 3 to $V_{\max}$, respectively. Insert: curves 2 on a logarithmic scale.

the curves for $V_{\max}$ have a long tail of considerable intensity toward larger volumes; the average free volumes obtained for $V_{\max}$ are 99.4 and 100.6 Å^3, respectively. The anisotropy of the free volume holes in the two polymers is expressed as 1:1.95:3.22 ($V_{\min}$:V_{average}:$V_{\max}$) for polystyrene and 1:1.94:3.12 for poly(*p*-methylstyrene), respectively.

Discussion

The modeling of the molecular structure of the stereoisomers of polystyrene and poly(*p*-methylstyrene) in the glassy state enables the evaluation of properties which are not easily available by conventional techniques. The construction of the relevant models has been done with very great care and the validity of the models has been checked by comparison with experimental data. Thus, e.g. X-ray diffraction curves were calculated for the amorphous polymer models, and an exact match was found between our simulated and the reported experimental curves.[33,42,43] In the X-ray diffraction pattern the smallest spacings must be due to periodicities in the chain itself, i.e., distances between neighboring phenyl rings and between next neighboring phenyl rings. Small holes of free volume are enclosed in the structure between the aromatic rings. The conclusion is drawn that these holes are seen also in the calculated models, most clearly in the distribution of free volume estimated by the Voronoi tesselation method; see Figure 7. Only the largest spacing corresponds to structures large enough to participate in the transport of particles or to participate in the process of positron annihilation. Therefore holes with radii <1 Å were neglected in the calculations of the unoccupied space in the structures.

The accuracy of the molecular models calculated by the method described is critically dependent on the choice of the force field. Parametrization of the force field has been carefully considered in this case, and it was found that the PCFF force field gave the best results. Despite this, some of the results indicate a slight inaccuracy in the parameters. Thus, the strain in the amorphous cells remaining after introducing experimental densities for the polymers may originate in inaccurate parameters for the intermolecular interaction in the force field used. The experimental value of the solubility parameter for atactic polystyrene is 16–20 (J cm^{-3})$^{0.5}$.[41] The low calculated values, 14–16 (J cm^{-3})$^{0.5}$, also point in this direction. Since the error is fairly small and of the same magnitude for all the polymers studied, the results of the calculations of free volume are comparable to each other, and the models are considered to be relevant.

Comparing the results of the calculations with the Voronoi tessellation method and of calculations of the volumes of unoccupied space with the particle insertion method in the amorphous cells under consideration, see Figures 7 and 9, we find that they indicate a large portion of the free volume to be due to very small holes, the size of which is considerably smaller than holes detected by the positron annihilation method. In the calculations the role of these small cavities related to the molecular structure of the chain may be emphasized in the Voronoi tesselation method, possibly exaggerated due to the normalization procedure. The distribution of the free volume modeled by the particle insertion method also shows a large fraction of small holes, smaller than detectable with PALS. This is obviously due to the fact that the cut off in the modeling was made at holes with radii >1 Å, whereas the PALS as used senses holes where the radius is >1.85 Å.[9] Thus we find the results from the modeling experiments in good agreement with the experimental results.

The distribution of the holes with larger volumes in the two models are similar, but they do not indicate dependendence of the stereoregularity of the chain, possibly due to the fact that the calculations show negligible differences in the potential energy of the stereoforms. The distribution curves for poly(*p*-methylstyrene) are broader and show larger average hole volumes than in polystyrene in both models. This is in accordance with the experimental results.

Attention is drawn to the shape of the holes in the calculation of the unoccupied space—it is very highly irregular. This is also the most probable real situation. Both the shape and in part the volume of the cavities fluctuate with time, which could not be included in the models presented here, however. Due to the irregularity of the shape of the holes the direct comparison of the results from the calculations and from the interpretation of the PALS results may not be adequate since the POSITRONFIT and the MELT programs use a model in which the positron resides in a spherical potential well, the volume of which is calculated. Despite this we find that the agreement between the theoretical models and the PALS results is very good.

Conclusions

The present results from positron annihilation experiments and molecular modeling show that the tacticity of the chains in polystyrene and poly(*p*-methylstyrene) have only a very minor influence on the distribution of the free volume in these polymers. There are indications from the positron annihilation experiments that the syndiotactic polymers have a broader distribution of free volumes than the more atactic polymers. On the other hand, the methyl substituent broadens the distribution of free volumes considerably according to the modeling experiments, which is documented in the positron annihilation results as longer lifetimes and larger volumes of the holes. The calculations of the distribution of free volume holes indicate a large fraction of very small holes due to spacings between the functional groups in the polymers. These holes are smaller than those detected by positron annihilation experiments, and they are not supposed to contribute essentially to the transport of small molecules in the polystyrenes.

Acknowledgment. C.W. and F.H.J.M. are grateful to Ann Rempling for technical assistance upon compression molding, and to Henrik Ramebäck for preparing the radioactive source. The Chalmers part of the work was supported by the Swedish Research Council for Engineering Sciences. Grants from The Academy of Finland and from Societas Scientiarum Fennica have enabled the stay of I.M.N. as visiting senior scientist at the University of Helsinki.

References and Notes

(1) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471. Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 2701.
(2) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York 1980.
(3) Chow, T. S. *Adv. Polym. Sci.* **1992**, *103*, 149.
(4) Rigby, D.; Roe, R. J. *Macromolecules* **1990**, *23*, 5312.
(5) Niemelä, S.; Leppänen, J.; Sundholm, F. *Polymer* **1996**, *37*, 4155.
(6) Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499.
(7) Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51.
(8) Nakanishi, H.; Wang, S. J.; Jean, Y. C. In *Positron Annihilation Studies of Fluids;* Sharma, S. C., Ed.; World Science Publ.: Singapore, 1988; p 292.
(9) McCullagh, C. M.; Yu, Z.; Jamieson, A. M.; Blackwell, J.; McGervey, J. D. *Macromolecules* **1995**, *28*, 6100.
(10) Finney, J. L. *Proc. R. Soc. London A* **1970**, *319*, 459 and 479.
(11) Ludovice, P. J.; Suter, U. W. In *Computational Modelling of Polymers*; Bicerano, J., Ed.; Marcel Dekker: New York 1992; p 401.
(12) Tanemura, M.; Ogawa, T.; Ogita, N. *J. Comput. Phys.* **1983**, *51*, 191.
(13) Medvedev, N. N. *J. Comput. Phys.* **1986**, *67*, 223.
(14) Raaska, T.; Niemelä, S.; Sundholm. F. *Macromolecules* **1994**, *27*, 5751.
(15) Misra, S.; Mattice, W. *Macromolecules* **1993**, *26*, 7274
(16) Urwin, J.; Stearne, J. M. *Makromol. Chem.* **1964**, *60*, 194.
(17) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, England, 1988; pp 222 and 217.
(18) PATFIT-88, Risø National Lboratory, Denmark.
(19) Shukla, A.; Peter, M.; Hoffman, L. *Nucl. Instr. Methods A* **1995**, *335*, 310.
(20) Shukla, A. Ph.D. Thesis No. 2744, Geneva University, 1995.
(21) Wästlund, C.; Maurer, F. *Nucl. Instr. Methods B* **1996**, *117*, 467.
(22) INSIGHTII, Version 4.0.0, DISCOVER, Version 2.9.8/96.0/4.0.0, POLYMER, Version 4.0.0, and AMORPHOUS CELL, Version 8.0., MSI Inc., San Diego, CA, 1996.
(23) *DISCOVER User Guide*, parts 1 and 3, *Force field Simulation*; September MSI Inc.,: San Diego, ca, 1996.
(24) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78.
(25) Van Krevelen, D. W. *Properties of Polymers*, 2nd ed.;, Elsevier: Amsterdam, 1990.
(26) Dammert, R.; Jussila, M.; Vastamäki, P.; Riekkola, M.-L.; Sundholm, F. *Polymer* **1997,** *38*, 6273.
(27) Dammert, R. Ph.D. Thesis, University of Helsinki, Finland, 1997.
(28) PERCH software by R. Laatikainen and H. Niemitz, University of Kuopio, Kuopio, Finland, 1996.
(29) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465. Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. Pellechia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Macromol. Chem. Rapid Comm.* **1987**, *8*, 277.
(30) Soga, K. *Macromol. Chem. Rapid. Commun.* **1988**, *9*, 23.
(31) Matsuzaki, K. *Macromol. Chem. Rapid. Commun.* **1994**, *15*, 479.
(32) Suparno, S.; Lacoste, J.; Raynal, S.; Regnier, J. F.; Schué, F.; Sempere, R.; Sledz, J. *Polym. J.* **1980**, *12*, 861.
(33) Guerra, G.; Musto, P.; Karasz, F. E.; MacKnight, W. J. *Makromol. Chem.* **1990**, *191***,** 2111.
(34) Guerra, G.; Dal Poggetto, F.; Iuliano, M.; Manfredi, C. *Makromol. Chem.* **1992**, *193***,** 2413.
(35) Iuliano, M.; Guerra, G.; Petraccone, V.; Corradini, P.; Pellecchia, C. *New Polym. Mater.* **1992**, *3***,** 133.
(36) Nakanishi, H.; Jean, Y. C.; Smith, E. G.; Sandreczki, T. C. *J. Polym. Sci., B: Polym. Phys.* **1989**, *27*, 1419.
(37) Wästlund, C.; Schmidt. M.; Schantz, S.; Maurer, F. H. J. *Polym. Eng. Sci.*, in press.
(38) Yu, Z.; Yashi, U.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2637.
(39) Liu, J.; Deng, Q.; Jean, Y. C. *Macromolecules* **1993**, *26*, 6**,** 7149.
(40) Han, J.; Boyd, R. H. *Polymer* **1996**, *37*, 1797.
(41) Brandrup, J., Immergut, E. H., Eds. *Handbook of Polymer Chemistry*; Wiley: New York, 1974.
(42) Schubach, H. R.; Nagy, E.; Heise, B. *Colloid Polym. Sci.* **1981**, *259*, 789.
(43) Mitchell, G. R.; Windle, A. H. *Polymer* **1984**, *25*, 906.

MA971682M