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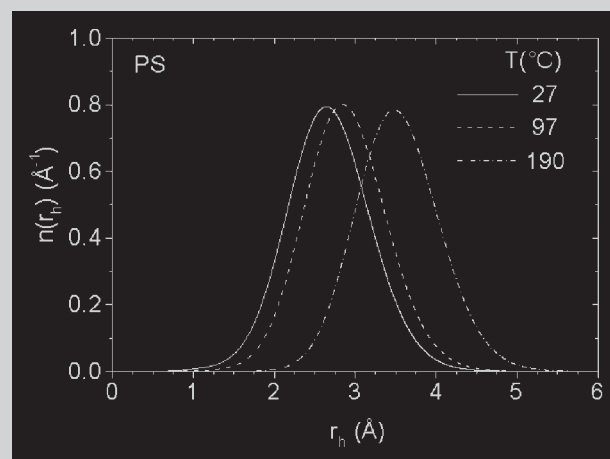
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Summary: The structure of the free volume and its temperature dependence between 25 and 190 °C of copolymers of styrene with acrylonitrile, SAN (0 to 50 mol-% AN), is studied by pressure volume temperature (PVT) experiments and positron annihilation lifetime spectroscopy (PALS). In this second part of the work, PALS data are reported from which the temperature dependence of the mean size and size distribution of local free volumes (subnanometer size holes) is analysed. The mean hole volume, v_h , varies in PS between 105 Å³ (27 °C) and 220 Å³ (190 °C), and shows a systematic decrease with increasing AN content, at T_g from 121 Å³ for PS to 102 (±2) Å³ for SAN50. The specific number of holes, N'_h , estimated from a comparison of PVT and PALS results, is independent on the temperature and the composition of SAN, $N'_h = (0.56 \pm 0.02) \times 10^{21} \text{ g}^{-1}$ which corresponds to $N_h(T_g) = N'_h/V(T_g) = 0.59 \text{ nm}^{-3}$ and $1/N_h(T_g) = 1.7 \text{ nm}^3$ for the volume which contains one hole. The analysed size distributions of the holes above T_g follow the compressibility of the free volume as it is predicted by the theory of thermal volume fluctuation. Moreover, we showed that the bulk elasticity modulus follows mastercurves as a function of v_h above and below T_g .



Free volume hole radius distribution $n(r_h)$ in PS for three different temperatures.

The Structure of the Free Volume in Poly(styrene-co-acrylonitrile) from Positron Lifetime and Pressure Volume Temperature (PVT) Experiments

II. Local Free Volume from Positron Annihilation Lifetime Spectroscopy (PALS)

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Introduction

The aim of our research is to characterise the microstructure of the free volume in a series of copolymers of styrene with

acrylonitrile, SAN (0–50 mol-% AN). For doing this we employed positron annihilation lifetime spectroscopy (PALS),^[2–4] a method which allows the measurement of the mean size and size distribution of sub-nanometer size

local free volumes,^[3–7] and pressure volume temperature (PVT) experiments.^[8] This paper is the second part of our work which consists of two papers (for Part I see ref. ^[1]). In the first part^[1] we reported on PVT experiments which were analysed using the Simha-Somcynsky equation of state (S-S eos),^[9,10] a lattice-hole theory which describes the structural disorder in an amorphous material by a lattice with a fraction h of unoccupied cells. From this analysis the temperature and pressure dependence of the specific occupied, V_{occ} , and free volume, V_f , their isobar thermal expansivities and their isothermal compressibilities have been determined.

In this part of the work we report the PALS experiments and compare the results from this method with the PVT data. Despite a great deal of interest in investigations of free volume in polymers, only limited information about its real structures, the hole dimensions and the size and shape distribution, is available. Various thermodynamic theories describe the fluctuations of the free volume per molecule as normal (Gaussian) distributed (Bueche^[11]), or as an exponential decreasing function (Cohen and Turnbull^[12]). Monte Carlo simulations delivered more insight into the structure of amorphous polymers and showed that the unoccupied, free volume is a single, multi-interconnected open space. When a probe molecule with a size larger than typically 0.5 Å is inserted, the free volume decays into discrete local empty volumes (holes). The fraction of free volume available for occupation by probe molecules decreases in an exponential-like manner with the size of these molecules.^[13–19]

The mentioned limited information about the hole dimensions and distributions are mainly due to a lack of suitable probes for open volumes of atomic and molecular dimensions. Some groups studied the polymer dilatation in gas sorption experiments^[20,21] and concluded on the mean size of holes and width of size distribution. Photochromic and fluorescent probe studies^[22] deliver more directly hole sizes, but are sensitive mainly to larger holes due to the size of the characterising molecules (3–10 Å). Density fluctuations have been studied by small-angle X-ray scattering (SAXS) and correlated to macroscopic thermodynamic parameters.^[23–26]

During the past decade, positron annihilation lifetime spectroscopy (PALS)^[2–4] has developed to be the most important method for studying sub-nanometre size holes in polymers.^[3–7] In molecular solids and liquids, a fraction of the positrons injected from a radioactive source form positronium^[3,4] and these can annihilate from the para (p -Ps, singlet spin state) or the ortho state (o -Ps, triplet spin state) with a relative formation probability of 1:3. Three components appear in the lifetime spectrum of amorphous polymers and these are attributed to the annihilation of p -Ps, free (not Ps) positron, and o -Ps.

Ps is formed in small local free volumes (holes) that form the (excess) free volume in amorphous polymers, or, if

formed elsewhere (in the interstitial free volume), trapped by these holes (Anderson localisation^[27]) after a diffusion over a mean path of ~ 1 nm.^[28] Due to annihilation of o -Ps with an electron other than its bound partner, and with opposite spin, during a collision with a molecule in the hole wall the o -Ps lifetime reduces from its value in a vacuum, 142 ns (self annihilation), to the low ns-range (pick-off annihilation, po).^[3,4] The smaller the hole, the higher the frequency of collisions and the shorter the o -Ps life. Based on a semi-empirical model^[29–31] the o -Ps pick-off annihilation rate λ_{po} , the inverse of the o -Ps lifetime τ_{po} , is related to the hole (assumed spherical) radius (r_h) via

$$\lambda_{\text{po}} = 1/\tau_{\text{po}} = 2ns^{-1} \left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi} \sin \left(\frac{2\pi r_h}{r_h + \delta r} \right) \right] \quad (1)$$

where δr ($= 1.66$ Å^[30,31]) describes the penetration of the Ps wave function into the hole walls. Assuming that spin conversion and chemical quenching of Ps are negligible,^[3,4] then the experimental o -Ps lifetime τ_3 is described by Equation (1), $\tau_3 = \tau_{\text{po}} = 1/\lambda_{\text{po}}$.

PALS itself is able to measure the mean volume of the holes and, with larger limitations, their size distribution,^[15,32–37] but not directly the hole density and the hole fraction. However, a correlation of PALS results with the (excess) free volume estimated from the macroscopic volume by the help of the S-S eos theory allows to estimate the hole density.^[38–43] In one of our previous works some of us have shown that in thermal expansion experiments the direct comparison of the hole volume from PALS with the specific volume allows the number density of holes and their entire volume fraction to be estimated.^[44] In this way, all parameters of hole free volume can be determined. This method has been successfully applied by several groups.^[42–47] In the analysis of the experiments it is, however, usually assumed that the occupied volume does not expand.^[42–47] As the thermal expansion of crystals show^[48] this may be too strong a simplification. We will therefore discuss the estimation of the hole density from the comparison of the hole volume $v_h = (4/3)\pi r_h^3$ with both the specific total volume, V , and the specific free volume, $V_f = hV$, estimated with the S-S eos theory, and compare both results.

For the analysis of the positron lifetime spectra we used the new routine LT in its latest version 9.0^[49,50] which allows both discrete and log normal distributed annihilation rates $\lambda = 1/\tau$. From the distribution of the o -Ps annihilation rate, $\lambda_3 = 1/\tau_3$, the mean size and the size distribution of free volume holes can be calculated. The results will be compared with those obtained from the well-known routines CONTIN^[51] and MELT.^[52] We will correlate the analysed hole size distribution with theoretical models describing the thermal volume fluctuation. We discuss also relations between the bulk elasticity modulus of amorphous polymers and the free volume. We will show that there are distinct changes in the free volume parameters with the composition of the SAN copolymers although T_g changes only slightly.

Experimental Part

The characterisation of the samples is given in Part I of our work,^[1] the relevant material parameters for this part are recapitulated in Table 1. The PALS measurements were carried out using a fast-fast coincidence system^[2–4] with a time resolution of 230 ps (²²Na source) and a channel width of 50.2 ps. Two identical samples of 1.5 mm thickness and $8 \times 8 \text{ mm}^2$ area were sandwiched around a $1 \times 10^6 \text{ Bq}$ positron source: ²²NaCl, deposited between two 2 μm thick Aluminium foils. To prevent sticking of the source to the samples at higher temperatures, each sample was covered with an additional foil of 8 μm thick Kapton. Source corrections and time resolution (a sum of two Gaussians) were determined by measuring a defect-free p-type silicon reference ($\tau = 219 \text{ ps}$). The temperature of the samples, placed in a vacuum chamber, was varied, at maximum between room temperature and 190 °C, in steps of 10 K, respectively, with an uncertainty of $\pm 1 \text{ K}$. Each lifetime spectrum contained ca. 5×10^6 coincidence counts, which is sufficiently high to be analysed with LT9.0 in its distribution mode.

Conventionally the lifetime spectra of amorphous polymers are decomposed into three discrete exponentials,^[3,4] $s(t) = \sum (I_i/\tau_i) \exp(-t/\tau_i)$, $\sum I_i = 1$, $i = 1, 2, 3$, where the components are attributed to annihilation of the para state of positronium (*p*-Ps, $\tau_1 \sim 160 \text{ ps}$), free (not Ps) positrons ($\tau_2 \sim 410\text{--}460 \text{ ps}$), and the ortho state of positronium (*o*-Ps, $\tau_3 = 1.9\text{--}3.2 \text{ ns}$). Since *o*-Ps annihilates from holes of free volume which have a size and shape distribution the *o*-Ps lifetime will also show a distribution.^[32–36] As mentioned, LT in its distribution mode assumes that for some, or all of the annihilation channels, the annihilation rates λ , $\lambda = 1/\tau$, follow a log-normal function.^[49,50] The non-linear least-squares fit of these functions, convoluted with the resolution function, to the spectra provides the annihilation parameters τ_i and I_i , as well as the width of the corresponding distribution (standard deviation σ_i of the lifetime τ_i). To reduce the statistical scatter in the fitted parameters, we assumed in the final fits that only the *o*-Ps lifetimes τ_3 are distributed.

The assumption in LT9.0 of log-normal distributed annihilation rates λ for each annihilation channel comes from the many

years experience with the routine CONTIN,^[51] a Laplace inversion technique, which delivers usually (three) Gaussian-like peaks in the $\log \lambda$ space. Similar distributions are analysed with MELT,^[52] a maximum-entropy technique. The advantage of LT9.0 is that the fixing of the functional shape of the distribution allows to reduce distinctly the degree of freedom in the fits to the spectra, avoids artefacts^[35–37] and reduces remarkably the scatter in the analysed distribution width.

The analysis of our lifetime spectra with CONTIN and MELT delivered similar annihilation parameters to the LT9.0 analysis. From the analysis of simulated spectra we found, in agreement with our previous works,^[35–37] that both routines analyse somewhat too small widths of the *o*-Ps lifetime distributions connected with slightly too large lifetimes τ_3 and too small intensities I_3 . Therefore, we will discuss in this paper mainly the results obtained from LT9.0.

Results and Discussion

Mean Hole Volume from PALS

The positron lifetime analysis delivered almost constant τ_1 (*p*-Ps annihilation) values while τ_2 (*e*⁺ annihilation) increases slightly with increasing *T*. The *o*-Ps lifetime τ_3 which responds to free volume properties exhibited an almost linear variation with a strong increase in the slope around T_g . For PS τ_3 changes from 2.14 ns at room temperature to 2.35 ns at T_g , and further to 3.20 ns at 190 °C. Our experiments for PS agree well with those from the literature.^[31,39,41,45,47,53] With increasing content of AN comonomer τ_3 shows a systematic decrease over the whole range of temperatures. For SAN50, τ_3 varies between 1.95 and 2.85 ns. The width of the *o*-Ps lifetime distribution for PS changes from $\sigma_3 = 0.35 \text{ ns}$ at 25 °C to 0.60 ns at 190 °C. The values for the SAN copolymers are slightly larger. From σ_3 the width of the hole size distribution may be calculated. These values will be discussed in detail in the last paragraph of this paper.

Table 1. Sample characterization and volume parameters estimated from PALS data (see text).

Quantity	Uncertainty	PS	SAN22	SAN38	SAN50
AN content (mol-%)	$\pm 0.2\%$	0	22.1	38.4	50.6
AN content (wt-%)	$\pm 0.1\%$	0	12.6	24.1	34.3
M_n ($\text{kg} \cdot \text{mol}^{-1}$)		175	108	74	67
M_w ($\text{kg} \cdot \text{mol}^{-1}$)		394	203	153	131
T_g (DSC, °C)	± 2	104	104	110	108
T_g (PALS, °C)	± 3	97	99	99	99
T_0' (PALS, °C)	± 5	−7	−7	−6	−4
v_{hg} (\AA^3)	± 2	121.0	112.7	107.7	102.1
e_{hg} ($\text{\AA}^3 \cdot \text{K}^{-1}$)	± 0.03	0.24	0.21	0.19	0.19
e_{hr} ($\text{\AA}^3 \cdot \text{K}^{-1}$)	± 0.03	1.12	1.07	1.03	0.99
α_{hg} (10^{-3} K^{-1})	± 0.3	1.95	1.85	1.81	1.81
α_{hr} (10^{-3} K^{-1})	± 0.3	9.26	9.45	9.57	9.68
N'_h (from V_f) (10^{21} g^{-1})	± 0.02	0.53	0.58	0.56	0.56
N'_h (from V) (10^{21} g^{-1})	± 0.02	0.55	0.59	0.57	0.57
$N_{hg} = N'_h/V(T_g)$ (nm^{-3})	± 0.02	0.55	0.61	0.59	0.60
$1/N_{hg}$ (nm^3)	± 0.07	1.9	1.7	1.8	1.8

The relative intensity of the *o*-Ps annihilation, I_3 , showed a slight increase with T , in case of PS from 32 to 36%. The level of I_3 decreases with increasing content of AN comonomer, for SAN50 I_3 varies from 17–18%. As discussed previously, this decrease is due to the inhibition of Ps formation by the polar nitrile groups.^[54] The *o*-Ps intensity I_3 does not have a clear relation to the free volume,^[34,55] but mirrors the Ps formation probability P , $I_3 = 3P/4$.^[3,4] This value is affected by many different parameters, therefore we will not discuss this parameter in our paper.

In the following we focus our discussion on the hole volume v_h calculated from τ_3 via Equation (1) and $v_h = 4\pi r_h^3/3$. As can be observed in Figure 1, v_h varies in PS from $v_h = 105 \text{ \AA}^3$ ($r_h = 2.93 \text{ \AA}$) at 27°C to $v_h = 220 (\pm 2) \text{ \AA}^3$ ($r_h = 3.74 (\pm 0.02) \text{ \AA}$) at 190°C with a distinct increase in the slope around T_g . The same behaviour is observed for the copolymers with hole volumes decreasing with increasing content of AN comonomer in the whole range of temperatures.

At low temperatures, *o*-Ps is trapped in local free volumes within the glassy matrix and τ_3 , and hence v_h , show the mean size of static holes. The averaging occurs over the hole sizes and shapes. The slight increase of v_h with temperature mirrors the thermal expansion of free volume in the glass due to the anharmonicity of molecular vibrations and local motions in the vicinity the holes. In the rubbery state, $T > T_g$, the molecular and segmental motions increase rapidly resulting in a steep rise in the hole size with temperature. Now v_h represents an average value of the local free volumes whose size and shape fluctuate in space and time.

Above 180°C the experiments deviate somewhat from the fitted line to lower values. It is known^[36,43] that at a critical temperature T_k ("knee" temperature), a tendency of

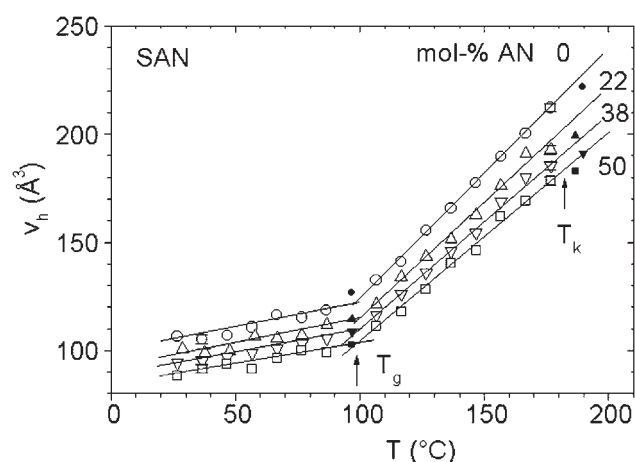


Figure 1. The mean hole volume v_h of SAN copolymers as function of temperature T . The AN comonomer content varies from 0 to 50 mol-%. The lines are linear fits to the data represented by empty symbols. Above the "knee" temperature T_k the *o*-Ps lifetime and thus v_h does not anymore represent correctly the true hole volume (see text).

levelling-off of the *o*-Ps lifetime expansion can be observed while the macroscopic volume shows a continuous increase (see Part I^[1]). The *o*-Ps lifetime and the hole size calculated from τ_3 do not mirror the true mean hole size anymore. In the literature, different possible reasons for this behaviour are discussed. One of these could be that the structural relaxation time reaches the order of the *o*-Ps lifetime of $\sim 2 \text{ ns}$ leading to a smearing of holes during the life of *o*-Ps (see ref.^[36,43] and references given therein).

From linear least-squares fits in the temperature ranges between room temperature and $T_g - 10 \text{ K}$, and $T_g + 10 \text{ K}$ and $T_k = 180^\circ\text{C}$, the values of T_g , the mean hole volume at T_g , v_{hg} , and the slopes are estimated (Figure 1). The T_g s agree with those obtained from the PVT data (Part I^[1]) within the uncertainties of both experiments and are lower by 5 to 11 K than those from DSC (Table 1). As shown in Figure 1, v_{hg} decreases with increasing content of AN comonomer from 121 \AA^3 for PS to $102 (\pm 2) \text{ \AA}^3$ for SAN50. These results differ from the work of Wästlund and Maurer^[54] who observed constant hole sizes at room temperature but agree well with the behaviour of the specific total and free volume at T_g detected in Part I.^[1] The thermal expansivity of the hole volume, e_h , decreases slightly with increasing content of AN comonomer, $e_{hg} = dv_h/dT$ ($T < T_g$) = $0.24 - 0.19 \text{ \AA}^3 \cdot \text{K}^{-1}$ and $e_{hr} = dv_h/dT$ ($T > T_g$) = $1.12 - 0.99 \text{ \AA}^3 \cdot \text{K}^{-1}$. The coefficient of thermal hole expansion in the glassy state decreases slightly, $\alpha_{hg} = e_{hg}/v_{hg} = 1.95 - 1.81 \times 10^{-3} \text{ K}^{-1}$, while this value is constant for the rubbery state, $\alpha_{hr} = e_{hr}/v_{hg} = (9.5 \pm 0.2) \times 10^{-3} \text{ K}^{-1}$. The α_{hr} values are larger by a factor of ~ 15 than those of the macroscopic coefficient of thermal expansion, α_r .^[1] From this a fractional hole free volume of $f = V_f/V \approx \alpha_r/\alpha_{hr} \approx 0.07$ follows from which the number density of holes may be estimated.

Hole Density from the Comparison of PALS and PVT Results

A more accurate estimate of hole density may be obtained by comparing PALS and PVT experiments in the following way. As we have shown in a previous paper,^[44] the mean number of holes per mass unit, N'_h , may be estimated from one of the relations,

$$V_f = V_{f0} + N'_h v_h \quad (2)$$

$$V = V_{occ} + V_{f0} + N'_h v_h. \quad (3)$$

Here, the free volume V_f estimated from the S-S eos analysis of PVT data, $V_f = hV$, (Part I^[1]) is expressed by $N'_h v_h$, the term V_{f0} may count for a possible deviation of the mean hole volume v_h estimated from the *o*-Ps lifetime τ_3 from the true mean hole volume,^[42,43] v_h^{true} ,

$$v_h = v_h^{\text{PALS}} = v_h^{\text{true}} - v_{h0}. \quad (4)$$

$v_h = v_h^{\text{PALS}}$ may be smaller than v_h^{true} ($v_{h0} > 0$) since the volume of stretched holes is underestimated by

Equation (1).^[15,56–58] It might be, however, also larger than the true average of the hole size distribution ($v_{h0} < 0$) as the result of a lower detection threshold (about $20 \text{ \AA}^{3[57]}$) and a possible preference to larger holes.^[59,60] Both effects act in opposite directions but it is not clear which sign and size the resulting effect may have. For simplicity we assume that v_{h0} is constant and not affected by the value of v_h , then also N'_h is not affected ($V_{f0} = N'_h v_{h0}$). In principle, all values in Equation (2) and (3) apart from V_{f0} (as assumed) may vary with the temperature.^[43,44]

Figure 2 shows the specific free volume, $V_f = hV$, and Figure 3 the specific volume, V , which were determined in Part I^[1] of this work, each plotted vs. the hole volume v_h . The straight lines are due to linear fits of Equation (2) and (3) to the data in the temperature range between $T_g + 10 \text{ K}$ and T_k . One observes that both V_f and V follow linear functions for the data from above T_g with slopes which do not differ for SAN copolymers of different composition.

The V_f data follow almost the same linear functions below T_g as above. From this behaviour we may conclude that the hole number per mass unit, N'_h , is constant in the whole range of temperatures, it is independent of the temperature in the rubbery state and freezes in below T_g . From the data above T_g we estimated N'_h from

$$N'_h = dV_f/dv_h = E_f/e_h \quad (5)$$

where $E_f = dV_f/dT$ is the expansivity of the specific free volume V_f . The estimated hole densities N'_h are shown in Table 1. They do not depend on the composition of the SAN copolymer and amount to $N'_h = (0.53\text{--}0.58 (\pm 0.02)) \times 10^{21} \text{ g}^{-1}$. The intersection of the V_f vs. v_h lines with the abscissa does not show systematic deviations from zero. V_{f0} , varies between -0.005 and 0.008 , the fluctuations

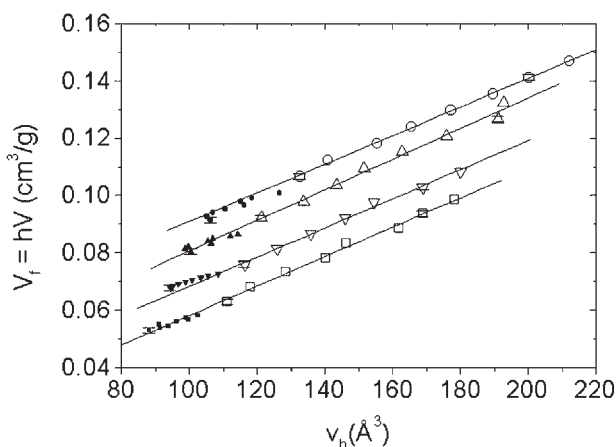


Figure 2. Plots of the specific (excess) free volume, $V_f = hV$, vs. the mean hole volume v_h for the SAN copolymers. The lines are linear fits to the data above T_g and below T_k (empty symbols). The filled symbols are data from below T_g . For clarity, the curves were upwards shifted on the vertical scale, each by 0.01 units to the former one, except SAN50 (Symbols as in Figure 1).

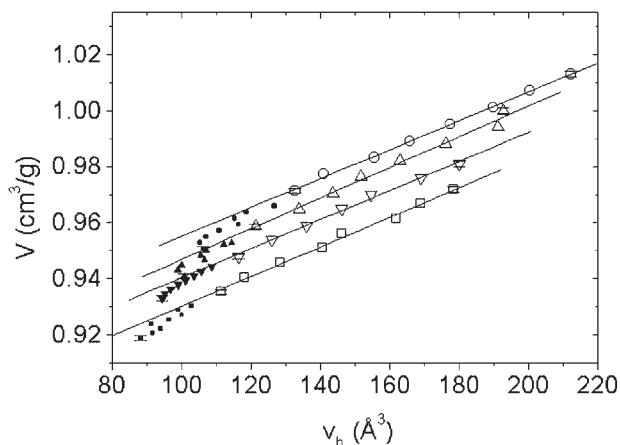


Figure 3. As Figure 2, but the specific volume, V . (Unlike in Figure 2, here the data are not shifted.)

are smaller when including into the fits the data below T_g , $V_{f0} = 0$ to -0.004 . From these results we may conclude that the *o*-Ps lifetime mirrors the true mean hole size well.

We note that in the case of the specific volume curves (Figure 3) the values below T_g are increasingly lower with decreasing temperatures than predicted by the extrapolation of the lines obtained from the linear fits above T_g . This deviation is due to the abrupt increase in the coefficient of thermal expansion of the occupied volume, V_{occ} , from $\alpha_{occ,r} = 0.22 \times 10^{-4} \text{ K}^{-1}$ above T_g to $\alpha_{occ,g} = 0.98 \times 10^{-4} \text{ K}^{-1}$ below. We have observed this surprising effect in the analysis of PVT data with the S-S eos and discussed it in Part I^[1] in detail. It is now confirmed by the PALS results shown in Figure 3.

From the V vs. v_h plots the hole density can be estimated using

$$N'_h = dV/dv_h - dV_{occ}/dv_h = (E - E_{occ})/e_h \quad (6)$$

where $E = dV/dT$ and $E_{occ} = dV_{occ}/dT$ are the expansivities of the specific total and occupied volume. Here, the slope dV/dv_h must be corrected by the term dV_{occ}/dv_h to take into account the possible variation of the occupied volume with the temperature. From $dV_{occ}/dv_h = E_{occ}/e_h$ we estimate this correction to be small, $\sim 0.018 \times 10^{21} \text{ g}^{-1}$, above T_g , but not negligible below, $0.37 \times 10^{21} \text{ g}^{-1}$ to $0.49 \times 10^{21} \text{ g}^{-1}$. The results shown in Table 1 were estimated from the data from above T_g . Both estimates for N'_h , from Equation (5) and (6), agree almost completely. It is rather satisfactory that the simple phenomenological formula Equation (3) gives the same results for N'_h as Equation (2) where here the advanced S-S eos theory must be used to calculate V_f .

We remark that Equation (6) can be rewritten as $f = V_f/V = N'_h v_h/V = (\alpha - \alpha_{occ}^*)/\alpha_{hr}$ or $f = (\alpha - \alpha_{occ})/(\alpha_h - \alpha_{occ})$. The latter relation is frequently used in the literature.^[45,47,61–65] Since α_{occ} is usually not known, several authors use the approximation $\alpha_{occ} = \alpha_g$.^[47,61–65] Other groups have assumed $\alpha_{occ} = 0$.^[45] As our results from

Part I^[11] show, $\alpha_{\text{occ},r} \approx 0$ above T_g and $\alpha_{\text{occ},g} \approx \alpha_g/2$ below are realistic approximations.

Our results for the mean specific hole number can be compared with $N'_h = 0.6 \times 10^{21} \text{ g}^{-1}$ estimated by Yu et al.^[39] and $N'_h = 0.8 \times 10^{21} \text{ g}^{-1}$ by Bohlen and Kirchheim,^[45] both for PS from a comparison of macroscopic with the hole volume using Equation (3). From our hole numbers per mass unit, $N'_h = (0.54\text{--}0.57) \times 10^{21} \text{ g}^{-1}$, the corresponding volume related hole number density, $N_h(T)$, can be calculated for a give temperature T using $N_h(T) = N'_h/V(T)$. These values calculated for T_g vary for our SAN system between $N_{hg} = N_h(T_g) = 0.55$ to 0.61 nm^{-3} (Table 1, Figure 4).

The constancy of the hole density, N'_h , is a surprising and interesting result confirmed by all other works in the literature related to this question.^[42,43,45,46] It means that the entire segmental motion above T_g , which is allowed by the holes but also creates new holes, is mirrored in the mean size (and size distribution) of the local free volumes but not in their mean number density. Due to this, the polymer dynamics as seen, for example, via the polymer viscosity,^[66] is observed to be clearly related to the hole size detected by PALS. The same was found to be true for the diffusion of small guest molecules (gases^[67,68] and ions^[69,70]) in polymers.

Important results of our work from part I^[11] and this part are summarised in Figure 4. The excess or hole free volume fraction, $f_g = (V_g - V_{\text{occ},g})/V_g = V_{fg}/V_g$, and the mean local free (hole) volume, v_{hg} , all at T_g , decrease with increasing mole content X_{AN} of the AN comonomer as

$$f_g = 0.0736(\pm 0.001) - 2.0(\pm 0.3) \times 10^{-4} X_{AN} \quad (7)$$

$$v_{hg} = 121.0(\pm 1) - 0.37(\pm 0.03) X_{AN} \quad (8)$$

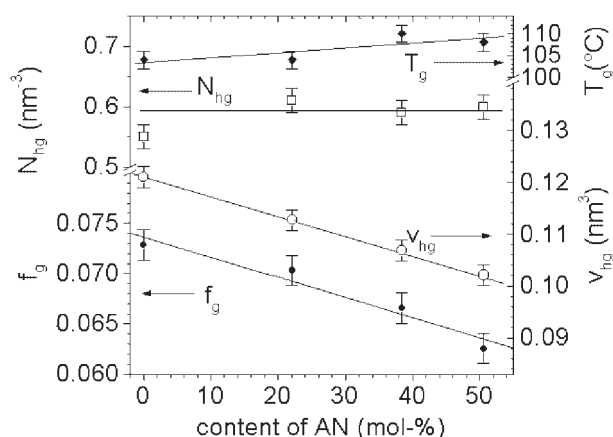


Figure 4. Free volume parameters of SAN copolymers. Shown are the glass transition temperature T_g (DSC), the hole (excess) free volume fraction, $f_g = h_g = (V_g - V_{\text{occ},g})/V_g = V_{fg}/V_g$, the mean hole volume, v_{hg} , and the mean number density of holes, $N_h = N'_h/V_g$, all at T_g .

Here X_{AN} is given in mol-% and v_{hg} in \AA^3 . The hole density $N_h = N'_h/V_g$ does not vary with the content of AN. f_g and v_{hg} decrease clearly with the content of SAN comonomer although the T_g is almost constant or shows a slight increase. For a larger series of polymers with T_g s varying between 220 and 420 K, Srithawatpong et al.^[46] have observed that v_{hg} and N'_h increase linearly and, due to this, f_g quadratically with T_g . The data show, however, a very large scatter. This rule is obviously not valid within a series of polymers showing small variations in T_g but having a different structural and/or chemical nature.

Our results show, as already found in past,^[46,71] that the glass transition is not an iso-free volume transition, but occurs probably at iso-relaxation times. The distribution of local free volumes, $g(v)$, in rubbery polymers is frequently described by $g(v) = (\gamma/v_f) \exp(-\gamma v/v_f)$ derived by Cohen and Turnbull^[12] with the help of statistical mechanics. Here v is volume of an individual hole and v_f the mean hole volume, usually these values are considered with respect to one molecule or mer. From this the relation $\ln(\tau/\tau_0) = -\gamma v^*/v_f$ where τ is the relaxation time of the motion, v^* the minimum free volume to permit motion, and τ_0 and $\gamma = 0.5$ to 1 are constants, is derived. This relation works well when substituting v_f by v_h as determined by PALS.^[67–70] With the linear thermal expansion of v_h in the rubbery state (Figure 1), $v_h = e_{hr}(T - T'_0)$, this relation leads directly to the well known Vogel-Tammann-Fulcher law,^[72] $\ln(\tau/\tau_0) = -B/R(T - T_0)$ with $B/R = \gamma v^*/e_{hr} T_0$, the Vogel temperature, is the temperature where the extrapolated relaxation time τ becomes infinite. $T'_0 = T_g - (v_{hg}/e_{hr})$ which is where the extrapolated free volume disappears corresponds to the Vogel temperature. Both relations, $T_0 = T'_0$ and $B/R = \gamma v^*/e_{hr}$, were confirmed recently by some of us for the ion conduction in rubbery poly(ethylene oxide).^[69,70] γv^* will differ for different diffusing probe molecules, but also for different polymers and different relaxation processes. This explains, due $\ln(\tau/\tau_0) = -\gamma v^*/v_f$, that for a glass transition occurring at a structural iso-relaxation time of $\tau \sim 100$ s, the mean free volume v_f , or $V_f = N'_h v_h$, may differ.

From dielectric relaxation experiments on PS the Vogel temperature of the segmental motion (α -relaxation) was determined to be $T_0 = 266 \text{ K}$.^[73] The T'_0 values obtained from the v_h vs. T plots are shown in Table 1. For the SAN copolymers $T'_0 = 266\text{--}269 \text{ K}$ (from v_h) and $T'_0 = 248\text{--}258 \text{ K}$ (from V_f ^[11]) were found. These values agree well with the Vogel temperature T_0 for PS. For SAN, the T'_0 values are related to the glass transition via $T'_0(\text{PALS}) = T_g(\text{PALS}) - (103\text{--}106) \text{ K}$.

Compressibility and Hole Volume

The isothermal compressibility $\kappa = -(1/V)[dV/dP]_T$ ($P \rightarrow 0$) of the SAN copolymers were determined from the PVT experiments in Part I.^[11] It was found that κ

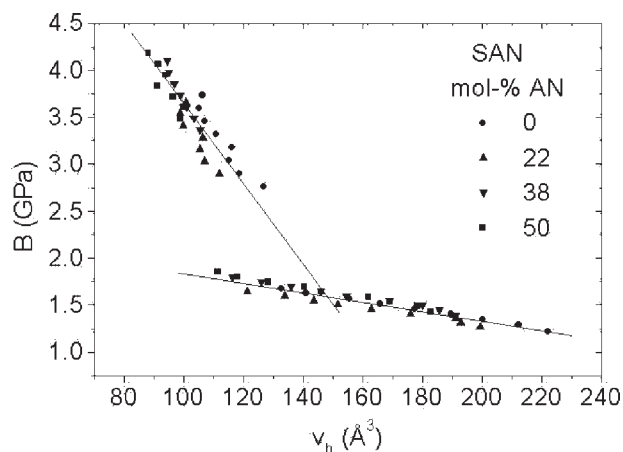


Figure 5. Plot of the isothermal compression modulus, $B = 1/\kappa$ for $P \rightarrow 0$, vs. the hole size v_h for the SAN copolymers. The data below and above T_g , each were fitted to a straight line.

decreases with increasing content of AN comonomer. This led to the conclusion that the decrease in κ is mainly due to the decreasing free volume. In order to proof the correlation in more detail we have plotted, following Schmidt et al.,^[41] the bulk elasticity modulus, $B = 1/\kappa$ for $P \rightarrow 0$, versus different quantities. We found that plots of B vs. T , V , and f do not give uniform mastercurves. However, when plotting B vs. either V_f or v_h , all data follow mastercurves. Figure 5 shows the B vs. v_h plots for all of our SAN copolymers. The data above and below T_g were fitted each by straight lines which delivered the relations

$$B_{T < T_g} = (7.7 \pm 0.4) - (41 \pm 4) \times 10^{-3} v_h \quad (9a)$$

$$B_{T > T_g} = (2.4 \pm 0.5) - (5.3 \pm 0.3) \times 10^{-3} v_h \quad (9b)$$

Here, B is given in GPa and v_h in \AA^3 . While for the rubbery state the fits are sufficiently good, a larger scatter of experimental data around the mastercurve is observed for the glassy state. The parameters of both equations are close to those found by Schmidt et al.^[41] for a larger series of polymers. These interesting relations show that the compressibility of an amorphous polymer at a temperature T and ambient pressure can be determined from the values of the mean local free volume as determined by PALS.

Hole Size Distribution and Thermal Volume Fluctuation

In this section we will discuss the holes size distribution that is calculated from the o -Ps annihilation rate distribution denoted by $\alpha(\lambda)$. The routine LT9.0 calculates from the fits to the spectra the mean annihilation rate, λ_3 , $\tau_3 = 1/\lambda_3$, and the standard deviation of the $\alpha(\lambda)$ distribution, $\sigma(\lambda_3)$, $\sigma_3 = \sigma(\tau_3) = \tau_3[\exp(\sigma(\lambda_3)^2) - 1]^{0.5}$. With Equation (1) and the known distribution $\alpha(\lambda)$ the hole radius probability

distribution, $n(r_h) = -\alpha(\lambda)d\lambda_3/dr_h$, can be calculated,^[32,33]

$$n(r_h) = -3.32\{\cos[2\pi r_h/(r_h + \delta r)] - 1\}\alpha(\lambda)/(r_h + \delta r)^2 \quad (10)$$

The fraction of the free-volume holes with radii between r_h and $r_h + dr_h$ is $n(r_h)dr_h$. Figure 6a shows $n(r_h)$, selected for three different temperatures, 27 °C, 97 °C – a temperature near the glass transition temperature, and 190 °C. The distributions can be approximated by a Gaussian with centres of 2.66, 2.86, and 3.50 \AA , and standard deviations of ca. 0.50 \AA . The shape of the distributions analysed with CONTIN^[51] or MELT^[52] are very similar, except with slightly smaller widths, and are therefore not shown. From Equation (10) the volume weighted hole volume distribution, $g(v_h) = n(r_h)/4\pi r_h^2$, and the number weighted hole volume distribution, $g_n(v_h) = g(v_h)/v_h$, can be calculated. $g(v_h)$ gives the volume fraction of free-volume holes with volume between v_h and $v_h + dv_h$, while $g_n(v_h)$ shows the number fraction of holes with volume between v_h and $v_h + dv_h$. These distributions are shown in Figure 6b and 6c. From $g(v_h)$ the fractional free volume distribution, $g(f)$, can be calculated where $g(f) = g(v_h)/\langle N_h \rangle$ and $f = \langle N_h \rangle v_h$ (upper and right y-scale in Figure 6b). In this paragraph r_h , v_h , N_h , and f denote individual values while the symbol $\langle \dots \rangle$ indicates the number average of a value fluctuating in the space or time. The distribution $g(v_h)$ shows a shape which can be approximated by a Γ -function. The distributions have centres of mass at 63, 82, and 162 \AA^3 , and widths which increases with increasing temperature. The normalisation of the distributions is $\int g(v_h)dv_h = \int v_h g_n(v_h)dv_h = \langle v_h \rangle \langle N_h \rangle = \langle f \rangle$ (integration from 0 to ∞) where $\langle f \rangle$ is the mean fractional hole free volume, $\langle v_h \rangle$ and $\langle N_h \rangle$ are the mean volume and the mean number density of holes. The curves shown in Figure 6a to 6c are normalised to $\langle f \rangle = 1$. The distribution $g_n(v_h)$ may be even approximated by a Γ -function or more roughly by a Gaussian in agreement with the theoretical considerations of Robertson^[74] and Bueche.^[11]

The distributions $g_n(v_h)$ differ, however, from the decreasing exponential derived by Cohen and Turnbull for the free volume distribution, as mentioned above. To the best of our knowledge this distribution has not been detected directly in any experiments. From it however, as discussed above, the VTF law may be derived, which has been confirmed by experiment. This correlation has also been confirmed by PALS experiments.^[66–70] The discrepancy is usually explained by the lower detection threshold of PALS,^[57] estimated to be $\sim 20 \text{\AA}^3$. In addition to this, we point out that when applying the Cohen-Turnbull theory to real polymers, a lower boundary hole size appears which is given by the interstitial free volume, that is the free volume in the most dense packing, per mer (typically in the order of 30% of the volume of a mer). Moreover, the values of $\gamma v^*/v_f$ in the Cohen-Turnbull relation, $\ln(\tau/\tau_0) = -\gamma v^*/v_f$, estimated from small molecule diffusion in polymers have

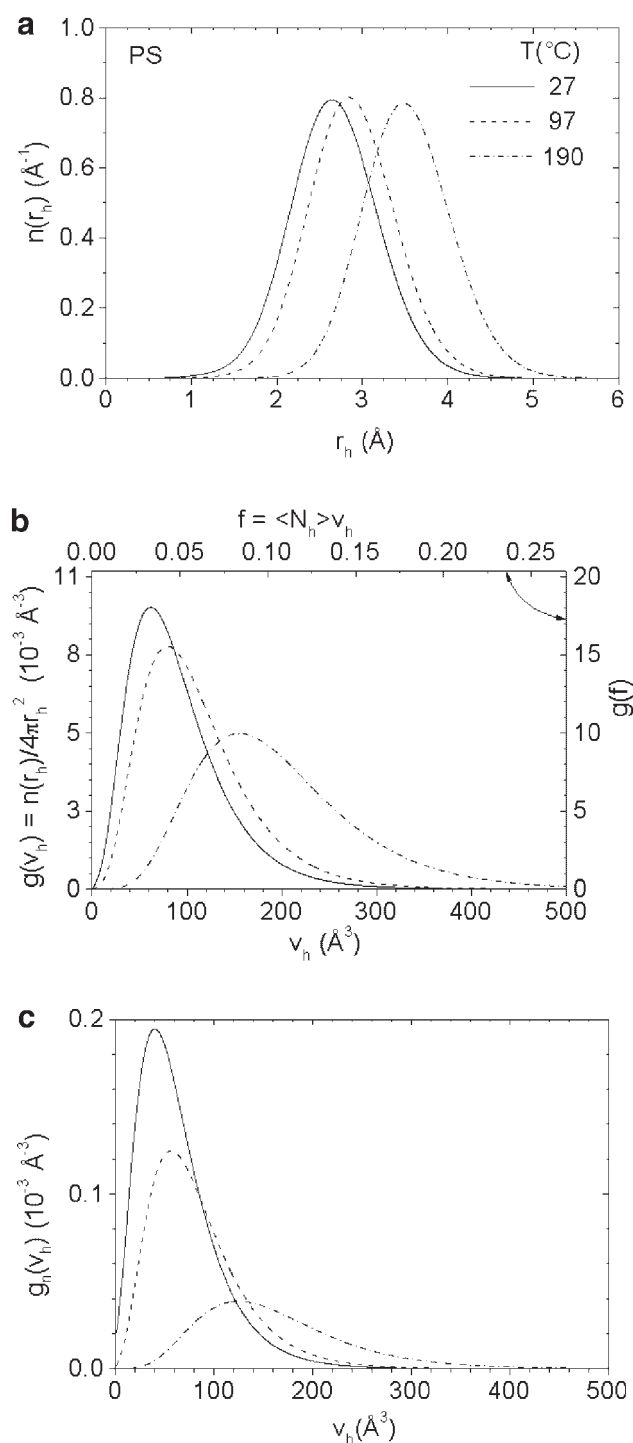


Figure 6. (a) Free volume hole radius distribution $n(r_h)$ in PS for three different temperatures. (b) As for Figure 6a, but the volume weighted hole volume distribution $g(v_h) = n(r_h)/4\pi r_h^2 \cdot v_h g_n(v_h)$. The functions show also the distribution of the fractional free volume $f = \langle N_h \rangle v_h$ (upper scale). (c) As for Figure 6a, but the number density hole volume distribution $g_n(v_h)$.

values of $\gamma v^*/v_f \approx 10$ which corresponds to $\gamma v^* = 0.4\text{--}0.8 \text{ nm}^3$ (gas molecules^[67,68]) and $0.8\text{--}1.2 \text{ nm}^3$ (ions^[69,70]). These volumes are far in the right wing of the volume distributions shown in Figure 6c. The wing can be fitted by

an exponentially decreasing function with sufficient accuracy. That means that the Gaussian or Γ -function shape of the hole size distributions analyzed by PALS is not in contradiction with the VTF law derived from the Cohen-Turnbull relation. These considerations show that only the largest holes of the excess free volume contribute to the mobility of chain segments or diffusion of guest molecules in amorphous polymers.

Next we compare the hole volume distribution calculated from the distribution of the *o*-Ps lifetime with the theory of thermal fluctuation.^[74,75] For comparison of the PALS data with the theory we have plotted in Figure 7 the root-mean-square fluctuation in the fractional free volume which we define by

$$\delta f_{\text{rms}} = (\langle \delta V_f^2 \rangle / \langle V \rangle^2)^{1/2}, \quad (11)$$

where $\langle \delta V_f^2 \rangle = \langle (V_f - \langle V_f \rangle)^2 \rangle$ is the variance of the specific free volume fluctuation. Assuming that the thermal fluctuations in N'_h can be neglected in comparison with v_h , then δf_{rms} can be expressed by

$$\delta f_{\text{rms}} = (\langle N'_h \rangle / \langle V \rangle) \langle \delta v_h^2 \rangle^{1/2} \quad (12)$$

where $\langle \delta v_h^2 \rangle = \langle (v_h - \langle v_h \rangle)^2 \rangle$. We have calculated the variance of the hole volume distribution, $\langle \delta v_h^2 \rangle$, as the second moment of the number weighted hole volume distribution, $g_n(v_h)$. The more simple estimate $\delta v_{h,\text{rms}} \approx [v_h(\tau_3 + \sigma_3) - v_h(\tau_3 - \sigma_3)]/2$ behaves like $\delta v_{h,\text{rms}} = (\langle \delta v_h^2 \rangle)^{0.5}$ but is about 25% larger than this value. The value of $\delta v_{h,\text{rms}} = (\langle \delta v_h^2 \rangle)^{0.5}$ increases almost linearly in PS from 45 \AA^3 at 25 °C to 52 \AA^3 at T_g and further to 80 \AA^3 at 190 °C. Similar values are observed for the SAN copolymers. We found no systematic variation of $\delta v_{h,\text{rms}}$ as a function of the copolymer composition.

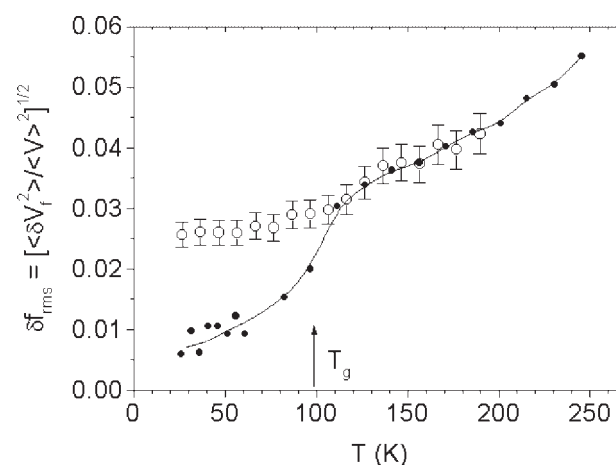


Figure 7. Root-mean-square fluctuation of the fractional free volume, $\delta f_{\text{rms}} = [\langle \delta V_f^2 \rangle / \langle V \rangle^2]^{0.5}$ derived from the PALS data (empty symbols) and the thermodynamic fluctuation theory (filled symbols). The fit of this theory to the PALS data delivered a fluctuation volume (Equation (13)) of $\langle V \rangle = 2.15 \pm 0.2 \text{ nm}^3$.

Figure 7 displays δf_{rms} for PS, as an example. δf_{rms} shows a typical glass transition behaviour. Although the scatter is large, one observes a flat increase below T_g , and a stronger one above. In thermal equilibrium the spatial fluctuations of free volume are identical with the time fluctuations. PALS detects these fluctuations as long as the relaxation times for segmental motion are smaller than the *o*-Ps lifetime of 2–3 ns. Below T_g most of the fluctuations are “frozen-in” and quasi-static.

Following conventional thermodynamics^[74,75] the mean square fluctuation of the volume V about its mean value $\langle V \rangle$ at equilibrium is related to the second derivative of the Helmholtz free energy F via $\langle \delta V^2 \rangle = -k_B T / (d^2 F / dV^2)_{\langle V \rangle}$. With $(d^2 F / dV^2)_{\langle V \rangle} = -(dP / dV)_{\langle V \rangle}$ and assuming that the fluctuations in the free and occupied volume are independent, $\langle \delta V^2 \rangle = \langle \delta V_f^2 \rangle + \langle \delta V_{\text{occ}}^2 \rangle$, one obtains for the root-mean-square fluctuation in the fractional free volume^[11,20,23–26,41,74–76]

$$\delta f_{\text{rms}} = (k_B T \kappa_f \langle V_f \rangle / \langle V \rangle^2)^{1/2} = (k_B T \kappa_f^* / \langle V \rangle)^{1/2} \quad (13)$$

where $\kappa_f = -[1/V_f][dV_f/dP]_T$ is the (isothermal) compressibility of the free volume and $\kappa_f^*(T) = -[1/V][dV_f/dP]_T$ is the fractional compressibility of the free volume. These values have been discussed in Part I.^[1]

Thermal fluctuations are considered in a sub-volume $\langle V \rangle$ embedded in, and being in thermodynamic contact with, a much larger one. While $\langle \delta V_f^2 \rangle / \langle V \rangle$ of Equation (13) is independent of the chosen subvolume, $\langle \delta V_f^2 \rangle$ depends on it and $\langle V \rangle$ must be chosen as the volume in which the fluctuations are desired. Robertson^[74] considered this question as follows. For vinyl-type polymers, a chain segment of roughly four backbone carbon atoms, or two monomer units, plus 12 nearest neighbours of like size is expected to constitute a segmental rearrangement cell. This would yield 26 monomer units which occupy at T_g a volume of 4.3 nm^3 .

We point out that the sub-volume $\langle V \rangle$ in Equation (13) has a similar meaning than the co-operative rearranging region (CRR) in the theories of dynamic heterogeneity of glass forming liquids.^[77,78] In the framework of the fluctuation approach to the glass transition by Donth,^[73,78] it has been calculated from heat capacity spectroscopy data that the size of the CRR at T_g is typically $1\text{--}10 \text{ nm}^3$. Domains of similar size were detected in nuclear magnetic resonance experiments by Spiess and collaborators.^[79] Possibly, the hole detected by *o*-Ps may be considered as the inner part of the CRR (the Glarum-Levey defect^[78]), and the volume which contains one hole, $1/N_h$, can be identified with a CRR.

From this discussion we expect a size of few nm^3 to be typical for the sub-volume $\langle V \rangle$, and we will use this volume as fitting parameter in the right hand side of Equation (13). Figure 7 shows the δf_{rms} data calculated from Equation (13) and fitted to the PALS data in the temperature range between 120°C and 200°C . The fit delivered $\langle V \rangle = 2.15$

$(\pm 0.1) \text{ nm}^3$ for PS which corresponds to 13 monomer units. We found similar values for the SAN copolymers. The estimated $\langle V \rangle$ volumes are reasonably close to the values of $1/N_h$ which vary between 1.9 nm^3 for PS and 1.8 nm^3 for SAN50 (at T_g), and close to the value 2.6 nm^3 assumed by Robertson.^[74] Unlike the PALS data, the calculations from Equation (13) show a clear step at T_g to distinctly lower values and a further decrease with decreasing temperature. This step is due to the step in the compressibility κ_f^* (see Part I^[1]). A similar discrepancy was observed when comparing electron density fluctuations studied by SAXS with this theory.^[23,24] The reason for the step is, that although Equation (13) can be used as an approximation of the volume fluctuation below T_g , it describes only the dynamic contribution of the disorder. Below T_g however, the sample is out of thermal equilibrium and contains, as well as a dynamic contribution of thermal motion, a quasi-static component due to the “frozen-in” disorder. Both components are detected by PALS.

Conclusion

The structure of the free volume in SAN derived from PALS and PVT experiments shows a systematic variation with the content of AN comonomer (0 to 50 mol-%) although T_g is only slightly increasing, $T_g(\text{DSC}) = 104\text{--}110^\circ\text{C}$. The specific volume, V_g ($V_g/V_w = 1.60$), the occupied volume, $V_{\text{occ},g}$ ($V_{\text{occ},g}/V_w = 1.47$), and the (excess) free volume, V_{fg} , all at T_g , decrease with increasing content of AN comonomer. The variation in V_{fg} is from 0.070 to $0.058 \text{ cm}^3 \cdot \text{g}^{-1}$, that of the fractional free volume, f_g , from 0.073 to 0.063 (± 0.003). The occupied volume shows an unexpected decrease in its coefficient of thermal expansion at T_g which is confirmed by the PALS results.

The mean local free (hole) volume at T_g , v_{hg} , decreases from 121 \AA^3 for PS to $102 (\pm 2) \text{ \AA}^3$ for SAN50. In PS v_h varies from 105 \AA^3 at 27°C to 220 \AA^3 at 190°C with a distinct increase in the slope at T_g . A similar variation is observed for the SAN copolymers. The expansivities of the hole volume, e_{hg} and e_{hr} , decrease with increasing AN content, while the corresponding coefficients of thermal expansion, α_{hg} and α_{hr} , are almost constant.

Surprisingly, but in complete agreement with works of other groups, the density of holes per mass unit, N'_h is independent of the temperature and, as we found, also of the composition, $N'_h = (0.56 \pm 0.02) \times 10^{21} \text{ g}^{-1}$. This value corresponds to a volume related hole density at T_g of $N_h = N'_h/V_g = 0.59 \text{ nm}^{-3}$. The size of the volume which contains one hole is $1/N_h = 1.7 \text{ nm}^3$. This volume may possibly be identified with the co-operating rearranging region (CRR) in the theory of dynamic heterogeneity of glass forming liquids. The temperature independence of N'_h shows that the segmental motion above T_g is mirrored in the mean size (and size distribution) of the holes, but not in their mean

number density. Therefore, direct relations between the polymer dynamics and the hole volume v_h can be observed. The analysed size distributions of the holes above T_g follow the values of the free volume compressibility as it is predicted by the theory of thermal volume fluctuation. Below T_g , the free volume structure freezes in, but shows a small decrease in the specific and hole volume, V_f and v_h , while, as before, N'_h is constant. Moreover, we showed that the bulk elasticity modulus, $B = 1/\kappa$, of the SAN copolymers follows a mastercurve as a function of v_h above and below T_g .

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- [1] G. Dlubek, J. Pionteck, D. Kilburn, *Macromol. Chem. Phys.*, accepted for publication.
- [2] R. Krause-Rehberg, H. Leipner, "Positron Annihilation in Semiconductors", Springer Verlag, Heidelberg 1999.
- [3] O. E. Mogensén, "Positron Annihilation in Chemistry", Springer-Verlag, Berlin, Heidelberg, New York 1995.
- [4] Y. C. Jean, P. E. Mallon, D. M. Schrader, "Principles and Application of Positron and Positronium Chemistry", World Scientific, Singapore 2003.
- [5] [5a] Y. C. Jean, *Microchem. J.* **1990**, 42, 72; [5b] Y. C. Jean, in: *Positron Annihilation, Proc. of the 10th Int. Conf.*, Y. J. He, B.-S. Cao, Y. C. Jean, Eds., *Mater. Sci. Forum* **1995**, 175–178, 59.
- [6] R. A. Pethrick, *Progr. Polym. Sci.* **1997**, 22, 1.
- [7] Y. Ito, T. Suzuki, Y. Kobayashi, *Radiat. Phys. Chem.* **2000**, 58, no. 5–6, p. 401 ff.
- [8] P. Zoller, C. J. Walsh, "Standard Pressure-Volume-Temperature Data for Polymers", Technomic Publ. Co., inc., Lancaster, Basel 1995.
- [9] R. Simha, T. Somcynsky, *Macromolecules* **1969**, 2, 342.
- [10] L. A. Utracki, R. Simha, *Macromol. Theory Simul.* **2001**, 10, 17.
- [11] F. Bueche, *J. Appl. Phys.* **1955**, 26, 738.
- [12] [12a] M. H. Cohen, D. Turnbull, *J. Chem. Phys.* **1959**, 31, 1164; [12b] D. Turnbull, M. H. Cohen, *J. Chem. Phys.* **1970**, 52, 3038.
- [13] S. Vleeshouwers, J.-E. Kluin, J. D. McGervey, A. M. Jamieson, R. Simha, *J. Polym. Sci., Part B: Polym. Phys.* **1992**, 30, 1429.
- [14] R. M. Dammert, S. L. Maunu, F. H.-J. Maurer, I. M. Neelov, S. Niemelä, F. Sundholm, C. Wästlund, *Macromolecules* **1999**, 32, 1930.
- [15] H. Schmitz, F. Müller-Plathe, *J. Chem. Phys.* **2000**, 112, 1040.
- [16] C. Nagel, E. Schmidtke, K. Günther-Schade, D. Hofmann, D. Fritsch, T. Strunsky, F. Faupel, *Macromolecules* **2000**, 33, 2242.
- [17] S. Misra, W. L. Mattice, *Macromolecules* **1993**, 26, 7274.
- [18] S. S. Rane, P. D. Gujrati, *J. Chem. Phys.* **2002**, 116, 3947.
- [19] S. Arizzi, P. H. Mott, U. W. Suter, *J. Polym. Sci., Part B: Polym. Phys.* **1992**, 30, 415.
- [20] [20a] R. Kirchheim, *Macromolecules* **1992**, 25, 6952; [20b] R. Kirchheim, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, 31, 1373.
- [21] S. S. Jordan, W. J. Koros, *Macromolecules* **1995**, 28, 2228.
- [22] J. G. Victor, J. M. R. Torkelson, *Macromolecules* **1987**, 20, 2241.
- [23] J. H. Wendorff, E. W. Fischer, *Kolloid Z. Z. Polym.* **1973**, 251, 876.
- [24] W. Wiegand, W. Ruland, *Prog. Colloid Polym. Sci.* **1979**, 66, 355.
- [25] R. Simha, S. C. Jain, A. M. Jamieson, *Macromolecules* **1982**, 15, 1517.
- [26] R. E. Robertson, R. Simha, J. G. Curro, *Macromolecules* **1984**, 17, 911.
- [27] A. H. Baugher, W. J. Kossler, K. G. Petzinger, R. H. Pater, *Mater. Sci. Forum* **1997**, 255–257, 57.
- [28] K. Hirata, Y. Kobayashi, Y. Ujihira, *J. Chem. Soc., Faraday Trans.* **1997**, 93, 139.
- [29] S. J. Tao, *J. Chem. Phys.* **1972**, 56, 5499.
- [30] M. Eldrup, D. Lightbody, J. N. Sherwood, *Chem. Phys.* **1981**, 63, 51.
- [31] N. Nakahishi, Y. C. Jean, in: *Positron and Positronium Chemistry, Studies in Physical and Theoretical Chemistry*, Vol. 57, D. M. Schrader, Y. C. Jean, Eds., Elsevier, Amsterdam 1988, p. 159.
- [32] J. Liu, Q. Deng, Y. C. Jean, *Macromolecules* **1993**, 26, 7149.
- [33] R. B. Gregory, *J. Appl. Phys.* **1991**, 70, 4665.
- [34] D. L. Wang, T. Hirade, F. H.-J. Maurer, M. Eldrup, N. J. Petersen, *J. Chem. Phys.* **1998**, 108, 4656.
- [35] [35a] G. Dlubek, C. Hübner, S. Eichler, *Nucl. Instrum. Methods Phys. Res., Sec. B* **1998**, 142, 191; [35b] G. Dlubek, C. Hübner, S. Eichler, *Phys. Status Solidi A* **1998**, 157, 351.
- [36] G. Dlubek, M. Supej, V. Bondarenko, J. Pionteck, G. Pompe, R. Krause-Rehberg, I. Emri, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, 41, 3077.
- [37] [37a] G. Dlubek, St. Eichler, C. Hübner, C. Nagel, *Nucl. Instrum. Methods Phys. Res., Sec. B* **1999**, 149, 501; [37b] G. Dlubek, St. Eichler, C. Hübner, C. Nagel, *Phys. Status Solidi A* **1999**, 174, 313.
- [38] Y. Kobayashi, W. Zehng, E. F. Meyer, J. D. McGervey, S. Jamison, R. Simha, *Macromolecules* **1989**, 22, 2302.
- [39] Z. Yu, U. Yashi, J. D. McGervey, A. M. Jamieson, R. Simha, *J. Polym. Sci., Part B: Polym. Phys.* **1994**, 32, 2637.
- [40] M. Schmidt, F. H.-J. Maurer, *Macromolecules* **2000**, 33, 3879.
- [41] M. Schmidt, M. Olsson, F. H.-J. Maurer, *J. Chem. Phys.* **2000**, 112, 11095.
- [42] M. Schmidt, F. H.-J. Maurer, *Polymer* **2000**, 41, 8419.
- [43] G. Dlubek, V. Bondarenko, J. Pionteck, M. Supej, A. Wutzler, T. Krause-Rehberg, *Polymer* **2003**, 44, 1921.
- [44] G. Dlubek, J. Stejny, M. A. Alam, *Macromolecules* **1998**, 31, 4574.
- [45] J. Bohlen, R. Kirchheim, *Macromolecules* **2001**, 34, 4210.
- [46] R. Srithawatpong, Z. L. Peng, B. G. Olson, A. M. Jamieson, R. Simha, J. D. McGervey, T. R. Maier, A. F. Halasa, H. Ishida, *J. Polym. Sci., Part B: Polym. Phys.* **1999**, 37, 2754.
- [47] K. Hagiwara, T. Ougizawa, T. Inoue, K. Horata, Y. Kobayashi, *Radiat. Phys. Chem.* **2000**, 58.
- [48] R. P. Quirk, M. A. A. Alsamarie, "Physical Constants of Polyethylene", in: *Polymer Handbook*, J. Brandrup, E. H. Immergut, Eds., 3rd Edition, John Wiley & Sons, New York 1985, p. V/15.

- [49] J. Kansy, *Nucl. Instrum. Methods Phys. Res., Sec. A* **1996**, 374, 235.
- [50] J. Kansy, *LT for Windows, Version 9.0*, March 2002, PL-40-007 Katowice, Inst. of Phys. Chem. of Metals, Silesian University, Bankowa 12, Poland, private communication.
- [51] [51a] R. B. Gregory, Y. Zhu, *Nucl. Instrum. Methods Phys. Res., Sec. A* **1990**, 290, 172; [51b] R. B. Gregory, *Nucl. Instrum. Methods Phys. Res., Sec. A* **1991**, 302, 496.
- [52] [52a] A. Shukla, M. Peter, L. Hoffmann, *Nucl. Instrum. Methods Phys. Res., Sec. A* **1993**, 335, 310; [52b] L. Hoffmann, A. Shukla, M. Peter, B. Barbiellini, A. A. Manuel, *Nucl. Instrum. Methods Phys. Res., Sec. A* **1993**, 335, 276.
- [53] J.-E. Kluin, F. Faupel, *Mater. Sci. Forum* **1992**, 105–110, 1613.
- [54] C. Wästlund, F. H.-J. Maurer, *Polymer* **1998**, 39, 2897.
- [55] T. Hirade, F. H.-J. Maurer, M. Eldrup, *Radiat. Phys. Chem.* **2000**, 58, 465.
- [56] Y. C. Jean, H. Shi, G. H. Dai, C. M. Huang, L. Liu, *Mater. Sci. Forum* **1995**, 175–178, 691.
- [57] B. Jasinska, A. E. Koziol, T. Goworek, *Acta Phys. Pol., A* **1999**, 95, 557.
- [58] B. Jasinska, A. E. Koziol, T. Goworek, *J. Radioanal. Nucl. Chem.* **1996**, 210, 617.
- [59] Y. Ito, *Mater. Sci. Forum* **1995**, 175–178, 627.
- [60] K. Süvegh, M. Klapper, A. Domján, S. Mullins, A. Vértes, *Radiat. Phys. Chem.* **2000**, 58, 539.
- [61] G. Dlubek, K. Saarinen, H. M. Fretwell, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1513.
- [62] H. A. Hristov, B. Bolan, A. F. Ye, L. Xie, D. W. Gidley, *Macromolecules* **1996**, 29, 8507.
- [63] J. Krištiak, J. Bartoš, K. Krištiakova, O. Šauša, P. Bandžuch, *Phys. Rev. [Sect.] B* **2001**, 49, 6601.
- [64] M. L. Williams, R. F. Landel, J. D. Ferry, *J. Am. Chem. Soc.* **1955**, 77, 3701.
- [65] R. Simha, R. F. Boyer, *J. Chem. Phys.* **1962**, 37, 1003.
- [66] J. Bartoš, J. Krištiak, O. Šauša, P. Bandžuch, J. Zrubcová, *Macromol. Symp.* **2000**, 158, 111.
- [67] K. Okamoto, K. Tanaka, M. Katsube, H. Kita, O. Sueoka, Y. Ito, *Polymer J.* **1993**, 223, 275.
- [68] C. Nagel, K. Günther-Schade, D. Fritsch, T. Strunskus, F. Faupel, *Macromolecules* **2002**, 35, 2071.
- [69] D. Bamford, G. Dlubek, A. Reiche, M. A. Alam, W. Meyer, P. Galvosas, F. Rittig, *J. Chem. Phys.* **2001**, 115, 7269.
- [70] D. Bamford, A. Reiche, G. Dlubek, F. Alloin, J.-Y. Sanchez, M. A. Alam, *J. Chem. Phys.* **2003**, 118, 9420.
- [71] R. Simha, P. S. Wilson, *Macromolecules* **1973**, 6, 908.
- [72] [72a] H. Vogel, *Phys. Z.* **1921**, 22, 645; [72b] G. Tammann, W. Hesse, *Z. Anorg. Allg. Chem.* **1926**, 156, 245; [72c] G. S. Fulcher, *J. Am. Ceram. Soc.* **1925**, 8, 339.
- [73] S. Kahle, J. Korus, E. Hempel, R. Unger, S. Höring, K. Schröter, E. Donth, *Macromolecules* **1997**, 30, 7214.
- [74] R. E. Robertson, “Free-Volume Theory and its Application to Polymer Relaxation in the Glassy State”, in: *Computational Modelling of Polymers*, J. Bicerano, Ed., Marcel Dekker, Midland, MI 1992, p. 297.
- [75] A. D. Kompanejev, “*Theoretische Physik*”, Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig 1969, p. 530.
- [76] R. E. Robertson, *J. Polym. Sci., Polym. Phys. Ed.* **1979**, 17, 597.
- [77] W. Götze, L. Sjörgen, *Rep. Progr. Phys.* **1992**, 55, 241.
- [78] E.-J. Donth, “*The glass transition: Relaxation dynamics in liquids and disordered materials*”, Springer, Berlin 2001.
- [79] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Tohr, H. W. Spiess, *Phys. Rev. Lett.* **1998**, 81, 272.