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Constraints and Thermal Expansion of the Free Volume in a Micro-phase Separated Poly(ester-adipate)urethane

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ABSTRACT: The free volume behavior of a thermoplastic poly(ester)urethane (TPU) versus temperature is investigated by positron annihilation lifetime spectroscopy and dilatometry. A discrepancy with the free volume predicted by the lattice-hole theory is found. The agreement is restored by assuming anisotropic expansion of the free volume holes, which in fact results in expansion mainly in two dimensions. This finding is perfectly compatible with a polymer structure based on rheological,

thermal, and TEM data which envisage TPU as formed by short soft segments limited in their movements by chain connectivity and confined by physical crosslinks due to the hard segments. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2016**, *00*, 000–000

KEYWORDS: free volume; lattice-hole model; positron annihilation lifetime spectroscopy

INTRODUCTION Thermoplastic polyesterurethanes (TPUs) are a class of polymers of increasing interest^{1,2} and their properties strictly depend on chemical details of the polymeric chain and the resulting microstructure. TPUs are randomly coupled multi-block copolymers of alternating soft (polyester macro-diol) and hard (isocyanate-based) segments. Hard segment domains strengthen the material by physical crosslinks, whereas the soft phase is responsible for material flexibility,³ thus determining a rubber-like behavior at room temperature. Microstructural changes taking place during the solidification process have been extensively investigated^{3–5} by using rheological and calorimetric techniques. Furthermore, hard segment-rich irregular spherulites, consisting of thin fibrils that are able to extend between and connect the spherulite boundaries, have been observed by transmission electron microscopy measurements on thermoplastic polyurethanes of varying hard phase content.⁶ Consequently, soft domains formed by short polyester chains can be envisaged to be confined between crosslinks due to hard blocks. This should influence the free volume holes configuration and their thermal behavior. Indeed, the presence of chain connectedness strongly reduces the number of possible movements of macromolecular strands; this is expected to hinder the expansion of soft segments in some specific directions, with a consequent anisotropic growth of the holes. In the present paper we aimed to explore this subject and to this purpose we investigated an amorphous TPU by means

of positron annihilation lifetime spectroscopy (PALS) and dilatometry.

PALS is an experimental technique suitable to investigate free volume in polymers.⁷ It is based on the fact that a fraction of positrons injected in the material generate positronium (Ps), an unstable bound electron–positron system which gets trapped in the sub-nanometric holes forming the free volume.⁸ Lifetime of ortho-Ps (*o*-Ps)—the ground state sublevel with parallel spins—is mainly determined by annihilation of the positron with one of the electrons belonging to the cavity in a relative singlet state. This involves a correlation between *o*-Ps lifetime and typical average sizes of the host cavity. To obtain information on the average volume of such a cavity the hole has to be framed within a suitable geometry. Previous papers reported PALS studies in polyurethanes with the aim of correlating the free volume to the mechanical properties⁹ or to the composition of the membranes;¹⁰ investigating the effects of neutron irradiation;¹¹ studying the interchain interactions in polyurethane/PMMA blends;¹² getting information on membranes permeability.¹³ Nevertheless, combined use of PALS and dilatometry was never published, at the best of our knowledge. In fact, dilatometric data are essential to calculate the theoretical free volume fraction *h* within the framework of the lattice-hole theory¹⁴ as well as to build an experimental free volume fraction by complementing PALS results. Therefore, PALS and dilatometric measurements were carried out in a range of

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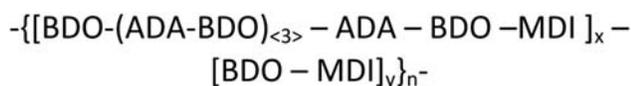


FIGURE 1 The chemical structure of the TPU investigated in this work. Brackets (< >) indicate an average value of the macrodiol molecular weight. $\langle x/y \rangle = 3/2$.

temperatures to obtain the free volume fraction in the investigated TPU. Comparison with the theoretical free volume fraction¹⁴ allowed us to conclude that the temperature expansion of the free volume holes is partially constrained, producing anisotropic dilation.

EXPERIMENTAL

Material

The polyesterurethane under investigation is based on 4,4'-methylendiphenyl 1,1'-diisocyanate (MDI), 1,4-butanediol (BDO), and a polyester macro-glycol such as polybutylenadipate ester (PBA). PBA is a condensation macrodiol between adipic acid (ADA) and 1,4-butanediol. The chemical structure of the TPU used for this work is shown in Figure 1 and its most important properties are listed in Table 1.⁵ The relative amount of soft and hard segments is given by the average ratio of $\langle x/y \rangle$ that in this polymer is equal to 3/2.

Characterization Techniques

Specific volume data were obtained by a GNOMIX dilatometer; they were collected in the range from 308 to 440 K. Specific volumes at atmospheric pressure were estimated by extrapolating the values at 10 MPa according to the GNOMIX PVT software, based on the Tait equation.

Concerning the positron annihilation lifetime spectroscopy, the positron source consisted of a droplet of ²²Na from a carrier-free neutral solution (activity: 0.3 MBq), dried between two identical Kapton foils (DuPontTM, thickness 7.6 μm), which were afterward glued together. The source was placed in the center of a small copper cup, containing the sample to be analyzed and in direct contact with the heat exchanger of a liquid nitrogen cryostat (DN 1714 Oxford Instruments). Stability of the temperature was ensured within 1 K. All the measurements were carried out in a vacuum. Positron annihilation lifetime spectra were collected through a conventional fast-fast coincidence set-up having a resolution of about 300 ps. Each spectrum contained about 3 × 10⁶ counts; deconvolutions were carried out through the computer code *LT*,¹⁵ with a suitable correction for the positrons annihilated in Kapton.

RESULTS AND DISCUSSION

The phase transition behavior and the microstructure modification of the final solid state of the investigated thermoplastic polyurethane have been explored by measuring thermal and rheological properties^{3–5} during the phase transition at different annealing times and temperatures. For the sake of completeness we briefly report the main findings.

DSC measurements show a structural organization of the hard segments during the early stage of the phase transition.³ In the course of isothermal annealing of the TPU, the system undergoes a transition from a liquid-like to a solid-like behavior on passing through a critical gel state. At later stages, rheological measurements indicate the presence of a second step of structural evolution, related to the micro-phase separation between hard and soft segments. This second step proceeds at a much lower rate compared to the first one, and is responsible for a gradual “maturation” of the solidified TPUs, a feature that is technologically particularly relevant for this class of elastomeric materials.¹⁶

Therefore, the polyurethane used in this work presents an order–disorder phase transition during annealing from the highest temperature. Such a transition, strictly related to the building up of interactions between hard segments (formation of hydrogen bonds), is responsible for a large increase in the mechanical properties of the system.

Glass transition temperature, $T_g = 244$ K as given in Table 1, has been found to be independent of the thermal history, which is expected for amorphous polymers quenched at any temperature higher than T_g . In fact, wide angle X-ray diffraction measurements, performed on the sample subjected to an annealing procedure,⁴ clearly show that the polymer can be classified as amorphous.

On the basis of the previous results a schematic illustration of the microstructures for fully developed phase-separated TPUs is proposed in Figure 2, which takes also into account the results from transmission electron microscopy measurements on thermoplastic polyurethanes of varying hard phase content⁶ already recalled in the introduction.

Figure 2 is a speculative hypothesis of the microstructure, nevertheless it gives the chance to schematize the soft blocks as polymer chains confined between the hard blocks, which act as physical crosslinks. Furthermore, looping of chains, always present in a system of interpenetrating macromolecules, causes mutual obstruction to their motion. Finally, entanglements arising from the chain connectivity act as a further hindrance to the chain movements. The free volumes arising from adjacent soft segments should be influenced by the presence of all these constraints which are expected to hinder the expansion of the free volume with temperature.

TABLE 1 Properties of the Investigated TPU

M_n^a (kDa)	M_w^a (kDa)	R_g (nm) ^a	η (dL g ⁻¹) ^a	ΔH_C (J g ⁻¹) ^b	T_c^b (K)	T_g^b (K)	λ (s) ^c
34.2	73.5	11.4	1.52	10.5	358	244	1.2

^a From coupled DRI/DV/MALS-GPC measurements. R_g is the radius of gyration. Intrinsic viscosity is given by η .

^b From DSC cooling ramps at 5 K min⁻¹. T_c is defined as the temperature where the max DSC signal is observed.

^c Longest relaxation time at 408 K.

F1
T1

F2

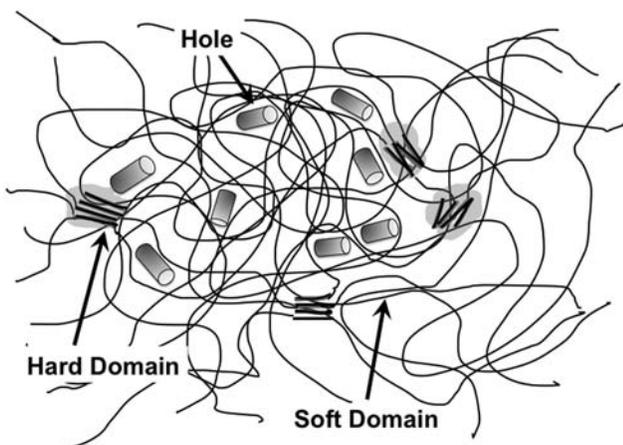


FIGURE 2 Schematic illustration of the microstructures for fully developed phase-separated TPUs.

In order to check this guess we carried out dilatometric and PALS measurements.

F3 Dilatometric results (Fig. 3) show a very good linear relationship between the TPU-specific volume V and temperature in the interval 315–430 K; correlation coefficient is 0.999.

Dilatometric data allow to compute the free volume fraction h within the framework of the lattice-hole theory.¹⁴ This last supplies an equation of state, which is valid for amorphous polymeric structures at equilibrium, that is, above the glass transition temperature. Consequently, our discussion will be limited to a temperature interval above T_g . At atmospheric pressure the equation of state is expressed in terms of reduced thermodynamic coordinates $\tilde{T} = T/T^*$ and $\tilde{V} = V/V^*$, where T^* and V^* are scaling parameters which depend on the specific material. Parameters T^* and V^* result from a fitting procedure by means of the following expression¹⁷ which is successfully used for a wide class of polymers:¹⁸

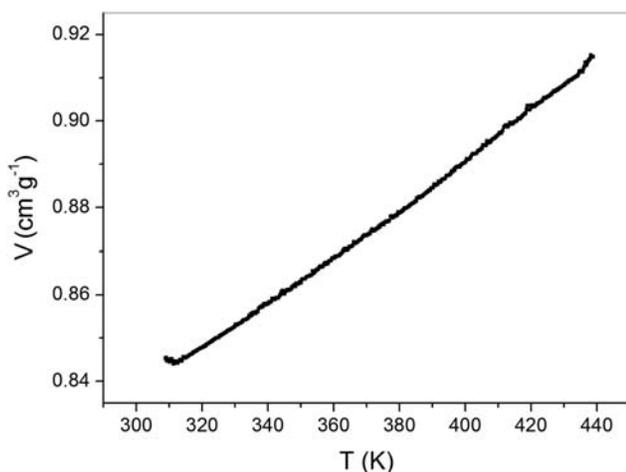


FIGURE 3 Specific volume in the investigated TPU as a function of temperature.

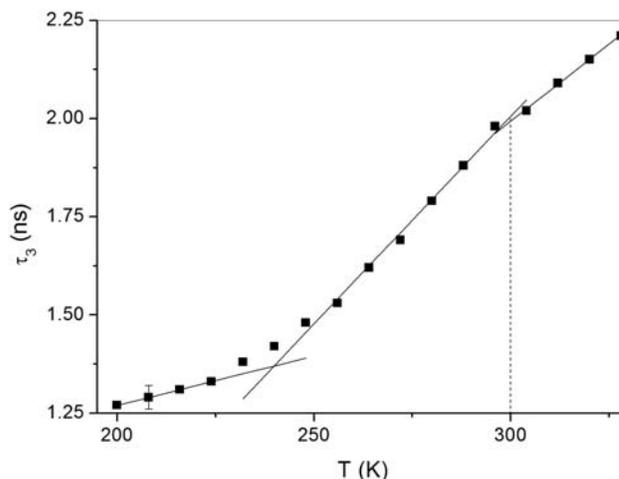


FIGURE 4 *o*-Ps lifetime versus temperature in the investigated TPU.

$$\ln \frac{V}{V^*} = A + B \left(\frac{T}{T^*} \right)^{3/2} \quad (1)$$

T being the absolute temperature; the values of the coefficients A and B are -0.1033 and 23.835 , respectively. In the case of TPU $V^* = 0.809 \text{ cm}^3 \text{ g}^{-1}$ and $T^* = 9341 \text{ K}$. h is derived from the equation of state once T^* is known; in the range of temperatures investigated in this work the behavior of the free volume fraction h versus T is perfectly linear. For our structure we calculated the Van der Waals volume V_w ¹⁹ and we found $V_w = 0.556 \text{ cm}^3 \text{ g}^{-1}$. The two values found for V^* and V_w are in very good agreement with the general relationship $V^* = 1.45V_w$ valid for macromolecules to which the Simha–Somcynsky equation of state applies.²⁰ This supports the use of the lattice-hole theory to investigate our TPU.

Positron annihilation lifetime spectra were analyzed in three components; statistical tests of the goodness of the fit (normalized χ^2) supplied values in the range 0.94–1.06. The shortest lifetime component is attributed to positrons annihilated in the bulk as well as to para-Ps annihilations. The intermediate component originates from positrons annihilated into defects and free volume holes; their lifetime is higher than the shortest one since the electron density surrounding the positron is lower with respect to the bulk. According to the common interpretation the longest component is due to *o*-Ps decays and the discussion will be limited to it. Figure 4 shows the *o*-Ps lifetime τ_3 versus the temperature T for the investigated TPU: a linear trend is visible below the glass transition temperature T_g , followed by a still linear but steeper regime. Such a behavior can be understood by considering that Ps is trapped into the free volume holes and therefore it probes their dependence on the temperature. Indeed, below T_g interchain motions are strongly hindered and the free volume shows only small variations with temperature; above T_g chain segments become mobile and the free volume increases with the temperature at a higher rate; accordingly, the expansion coefficient is higher than in the glassy state.

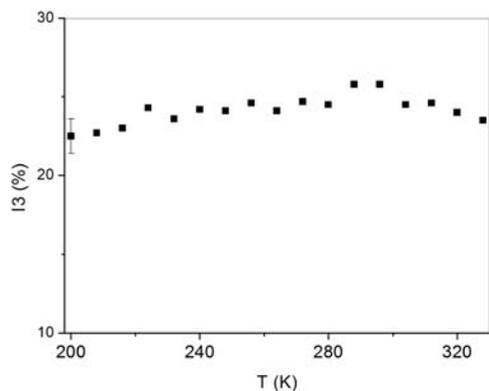


FIGURE 5 o-Ps intensity as a function of temperature in the investigated TPU.

Above 300 K a reduced increase of τ_3 with temperature is visible. This trend is commonly observed in many polymers and various explanations were proposed: formation of a Ps bubble,²¹ digging of holes by Ps itself,²² or a relaxation time of the molecular chains which is comparable to Ps lifetime.²³ In this last case Ps would not be any longer able to correctly probe the size of the host cavity. Whatever the adopted explanation, there is a general agreement on the contention that in this temperature region Ps cannot give reliable information on the free volume hole.²⁴ Therefore, we will limit our discussion to temperatures below 300 K.

F5 For the sake of completeness Figure 5 shows the behaviour of o-Ps intensity I_3 versus the temperature, although this parameter is not involved in the subsequent discussion.

Data shown in Figure 4 have been transformed into average sizes of the free volume holes by using the Tao–Eldrup model^{25,26} (eq 2): the cavity hosting positronium is assumed to be a spherical void with an effective radius R . Such a positronium trap has a potential well with finite depth. For calculations convenience the depth is considered to be infinite, and the radius is increased to $R + \Delta R$ by an empirical quantity²⁷ ΔR (0.166 nm), which describes the penetration of the Ps wave function into the bulk.

The electron density is supposed to be zero for $r < R$ and constant for $r > R$. The relationship between o-Ps lifetime τ_3 and radius R is the following:

$$\tau_3 = \tau_0 \left[\frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(2\pi \frac{R}{R + \Delta R} \right) \right]^{-1} \quad (2)$$

where $\tau_0 = 0.5$ ns. Other relationships were deduced between τ_3 and the typical size s of a nonspherical cavity (e.g., cubic,²⁸ prismatic,²⁸ or cylindrical²⁹).

Total free volume is the sum of an interstitial free volume (V_{if}) and of the hole free volume (V_f). The first consists of local empty spaces too minute to localize even a small probe such as Ps. It is associated to the occupied volume.⁸ The

second, the ‘excess’ free volume, is accessible to Ps and is calculated as the hole fraction in the lattice-hole theory.⁸

Specific hole free volume V_f can be expressed as the product of the number N of holes per unit mass times the average hole volume v_h :

$$V_f = Nv_h \quad (3)$$

If v_h represents the cavity volume of size s which expand isotropically, then $v_h \propto s^3$. The most usual assumption is $v_h = \frac{4}{3}\pi s^3$, with $s = R$ obtained from eq 2.

Specific volume is then given by:³⁰

$$V = Nv_h + V_{occ} \quad (4)$$

where V_{occ} is the occupied specific volume, sum of the Van der Waals volume, and the interstitial free volume previously defined:⁸ $V_{occ} = V_{vdW} + V_{if}$. For the TPU here discussed, N can be assumed constant, that is, independent of the temperature, at least at $T > T_g$. Indeed, Figure 6 shows the specific volume V versus the average hole volume v_h , calculated in spherical approximation: data are fitted by straight lines and correlation coefficients are in all cases higher than 0.99. Specific volume was evaluated at the same temperature of positron data using a linear interpolation from the data shown in Figure 3. This is justified by the fact that thermal analysis³ does not evidence any phase transition or change of the structure of TPU above the glass transition up to the minimum investigated temperatures by dilatometry (320 K). In the absence of structural changes a linear behaviour of the specific volume versus temperature is a very common feature for amorphous polymers.³¹

F6

According to eq 4, slope and intercept of V versus v_h in Figure 6 give N and V_{occ} , respectively. Cubic, cylindrical, or prismatic geometries produce a linear correlation, too, although with different values for N and V_{occ} .

Fractional free volume f can be evaluated according to the definition:³⁰

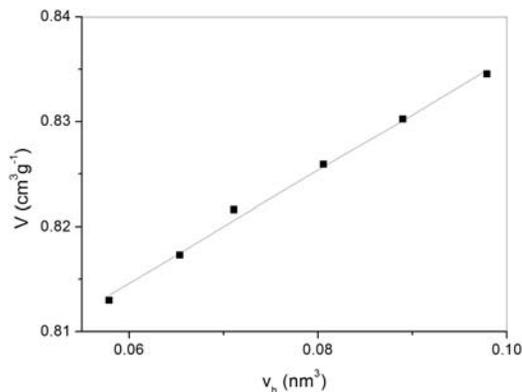


FIGURE 6 Specific volume V versus the hole average volume v_h in the investigated TPU above the glassy phase.

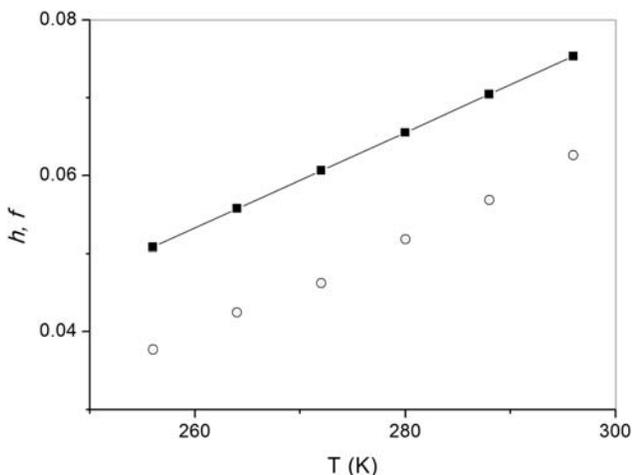


FIGURE 7 Comparison between free volume fractions: theoretical, h (continuous line) and evaluated from PALS and dilatometric data, f . Empty circles: spherical holes; squares: ‘anisotropic’ holes.

$$f = \frac{V_f}{V} = \frac{Nv_h}{Nv_h + V_{occ}} \quad (5)$$

F7 Its behavior versus the temperature is shown in Figure 7 together with the theoretical free volume fraction h . Values of f obtained using a spherical cavity geometry (empty circles in Fig. 7) are systematically lower than h ; furthermore, expansion coefficient of f is higher than the corresponding theoretical values.

The same type of discrepancy has been obtained using cubic, prismatic, or cylindrical hole geometry.

Therefore, the reason of the deviation from the theory has been addressed to the assumption of isotropic expansion of holes: $v_h \propto s^3$. Dropping the isotropic assumption, a cylindrical geometry has been considered to model the holes, but the expansion along the direction of the radius s is supposed to be free, while the height l grows slower than the radius such as:

$$\frac{l}{l_0} = \left(\frac{s}{s_0}\right)^k \quad (6)$$

where l_0 and s_0 are the values corresponding to the lowest investigated temperature and k is a parameter expected to be less than one ($k = 1$ corresponds to isotropic expansion).

In order to make a quantitative calculation the ratio $q = l_0/s_0$ was given a numerical value of 3. This is nevertheless irrelevant for the following discussion. Holes volume equation becomes the following:

$$v_h = \pi l s^2 = \pi l_0 \frac{s^{2+k}}{s_0^k} = \pi q s_0^{1-k} s^{2+k} = \pi q s_0^{3-p} s^p \quad (7)$$

where $p = 2 + k$. Cavity volume expansion can be written as a power law of the size s while the other geometrical dimension increases at lower rate or remains constant.

In order to determine parameter p , o -Ps lifetime τ_3 has been transformed into the radius s of the cylindrical cavity, using the pertinent equation²⁹ modified to take into account the growth of the height (eq 6). Afterward, hole volume v_h has been calculated according to eq 7, for a fixed p . Specific volume V versus v_h has been linearly fitted for each p (analogous to that used for spherical holes, see Fig. 6) and parameters N and V_{occ} have been obtained. These quantities have been used in eq 5 to calculate the fractional free volume f and finally compared with the theoretical h . The best agreement between f and h (Fig. 7, squares) is obtained for $p = 2$. Similar values of p were found using various q ratios, with differences of the order of 6%, that is, below the statistical uncertainty associated to p and evaluated about 10% by propagation of the errors. Therefore, the result obtained ($p = 2$) is almost independent of q .

Equation 7 has been already used to discuss similar results found in some perfluoropolyethers.³² The fact that the free volume holes in the investigated TPU grow only in two dimensions is in agreement with the polymer model proposed in Figure 2 and gives it a micro structural rationale. Indeed, according to Figure 2, the presence of hard blocks, which carry out physical crosslinks in the form of hydrogen bonding, combined with chain connectedness and looping, hinder the movements of the soft polymer strands.

N and V_{occ} corresponding to the best fit value of p are $7.4 \times 10^{20} \text{ g}^{-1}$ and $0.77 \text{ cm}^3 \text{ g}^{-1}$, respectively. We point out that only the order of magnitude of N has to be considered, since the proportionality factor between v_h and s^p depends on the choice of q and s_0 (eq 7).

Concerning the assumptions used to frame the free volume hole, we observe that extensions of Tao-Eldrup model to nonspherical holes^{33,34} imply, in principle, a different temperature dependence of the Ps lifetime along the axes of the cavity hosting Ps. In fact, the decomposition of the Ps wavefunction along the main axes of the hole entails a higher overlap with the walls corresponding to the shortest axis. However, this different temperature dependence is not important for Ps lifetimes lower than 2 ns, which is the highest value investigated in the present work, as it is shown in Figure 3 of ref. 35. In addition, the aspect ratio q decreases by increasing the temperature for the model here adopted. Therefore, a diverse temperature dependence of radius and height of our cylindrical holes is expected to be negligible.

We observe that very long cylindrical holes, which expand in isotropic way, could explain our results, since the Ps lifetime would mirror only the bi-dimensional increase with temperature of the section of the cylinder. However, the guess of cigar-like holes which are extended in length is not compatible with the physical structure of TPU, involving high connectivity and looping among neighboring soft segments.

CONCLUSIONS

In this work we showed PALS and specific volume results of an amorphous thermoplastic polyurethane. By combining the

data from the two techniques we were able to evaluate the free volume fraction that was compared to the analogous theoretical quantity. A disagreement with the theory is found if the free volume holes are framed as spheres; the discrepancy remains even if the geometry of the cavities is changed. Conversely, a good agreement with the theory is obtained if the assumption of isotropic expansion of the cavities with temperature is removed. Of course, the model of 'anisotropic' growth is rather crude since it neglects that various kinds of cavity geometries may be present at the same time in the microstructure. Our cylindrical assumption should not be taken literally because free volume holes can be generally envisaged to be irregularly shaped. Nevertheless, our results point out that free volume expansion does not occur isotropically, but that in some directions it is reduced with respect to others. The anisotropic model is compatible with the dynamics of macromolecular chains subjected to constraints. In particular, when applied to our TPU, PALS experiment points out an anisotropic bidimensional growth of the holes with the temperature. Indeed, the exponent p of the power law relating the volume to unconstrained average size of the holes shows values close to 2. This is in agreement with the polymer model proposed in Figure 2 on the basis of the results obtained with the classical techniques, which envisages strong obstacles to the movements of the soft chains, due to hard blocks exerting physical crosslinks through hydrogen bonding, as well as to physical constraints among polymer strands arising from the chain connectivity.

Anisotropic holes growth was found also in a homologous series of perfluorinated oligomers³² and in low molecular weight polypropylene glycols.³⁶ The present study extends the results to the case of a polymeric structure with higher molecular weight.

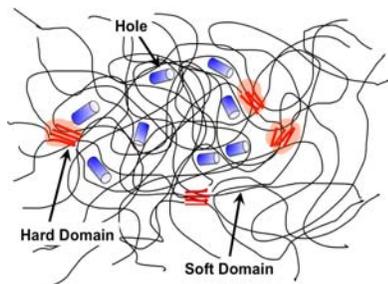
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Positron annihilation lifetime spectroscopy and dilatometry are used to evaluate the free volume increase with temperature in a thermoplastic polyesterurethane. Comparison with the predictions of the Simha-Somcynsky theory shows a discrepancy when the free volume holes are supposed to grow isotropically. Agreement is recovered for holes expanding only in two dimensions. The result supports the picture of a polymer composed of soft segments constrained by chain connectivity, looping and by hard blocks exerting physical crosslinks.