FREE VOLUME STUDY ON THREE TYPES OF SHAPE MEMORY POLYMERS BY POSITRON ANNIHILATION

Y. UJIHIRA, H.-L. LI AND K. ITO

Research Center for Advanced Science and Technology, The University of Tokyo
4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

Temperature dependence of nanoscopic environment of shape memory polymers such as polynorbornene ($T_g \approx$ 313 K), polyurethane ($T_g \approx$ 321 K = dynamic viscoelasticity, destruction of hydrogen bond $\approx$ 353 K) and styrene-butadiene copolymer (T_m = 333 K) is observed in terms of free volume parameters — average size, numerical concentration and size distribution — estimated from positronium lifetime measurement, and mechanisms of their shape recoveries are discussed at a molecular level.

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1. Introduction

Special type of polymers, such as polynorbornene (commercial name: Norsorex, CdF Chimie of Paris, linear polymer of 2,2,1-bicyclo hept-2-ene strained monomers, having one rigid, five-membered ring and one double bond as illustrated in Fig. 1a [1, 2]), trans-polyisoprene (Kurare Co. Ltd.), polyurethane (Mitsubishi Heavy Industry Co. Ltd.; Fig. 1b [3, 4]) and styrene-butadiene copolymer (commercial name: Asmer, Asahi Chemical Industry Co. Ltd., linear polymer of copolymated polystyrene and butadiene as illustrated in Fig. 1c [5]) were designed as shape memory polymers (SMP's) and had various practical applications such as oil spill recovery, autochalk valve, seal, gypsum, lining, sound insulation rolls, damping, and gaskets.

These polymers show a shape memory phenomenon by a thermal process, where the polymer is shaped at higher temperature than a shape recovery temperature (T_r). Then, the shaped polymer is cooled down to temperature lower than a glass transition temperature (T_g) where a significant change of elasticity occurs, keeping the shape of the polymer as designated in a mold. Once the polymer receives a mechanical deformation below T_g, a strain is generated in the polymer. An original shape of the deformed SMP is recovered by heating it to higher temperature than T_r, because the strain remained in the polymer is liberated by the motion of backbone chains to achieve thermal equilibrium.
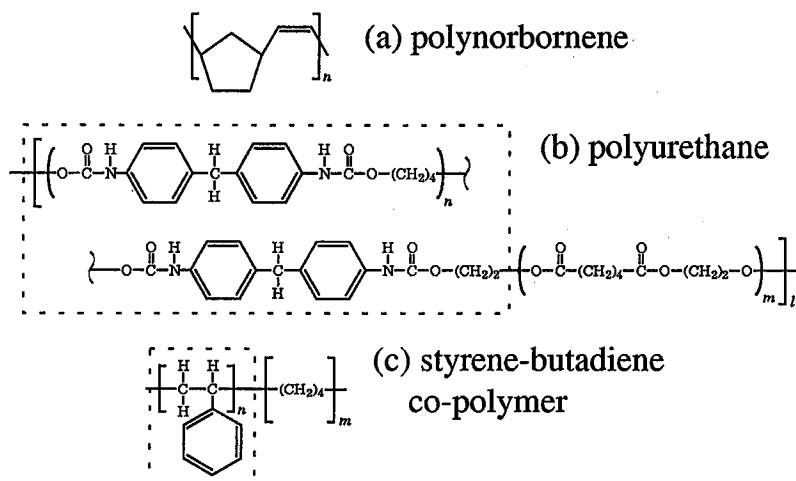
Fig. 1. Molecular structure of three shape memory polymers. Hard segments of these polymers are indicated in squares with the dashed line.

In the present paper, temperature dependence of a nanoscopic environment of three types of the SMP — polynorbornene, polyurethane and styrene-butadiene copolymer — is presented in terms of free volume parameters — average size, numerical concentration and size distribution of free volume. The free volume parameters were estimated by means of the positron annihilation lifetime measurement. The shape recovery effect of the SMP is attributed to the queer thermal behavior discovered in the present studies and mechanisms of the shape recovery are discussed at a molecular level.

2. Experimental section

A highly efficient fast-fast coincidence positron annihilation lifetime apparatus with a time resolution of $\approx$ 220 ps was used. The positron source of $\approx 3.7 \times 10^5$ Bq of ^{22}NaCl, sealed in Kapton foils with a thickness of 7.5 μm, was sandwiched in between two identical specimens and contained in a thermal chamber (temperature was controlled within ± 1 K). Decay curves of the positron annihilation, measured for 10 hours to collect approximately 4×10^6 counts, were decomposed into three or four lifetime components with a non-linear least squares fit (PATFIT-88 [6]) and with an inverse Laplace transformation (CONTIN [7, 8]) to obtain lifetime distributions of a positronium (Ps). Details are described in the previous papers already published [9, 10]. Lifetime of ortho-positronium (o-Ps) is converted to free volume size following to a Nakanishi–Jean equation [11],

$$\tau = 0.5 \left[1 - \frac{R}{R + 0.166} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + 0.166} \right) \right]^{-1} . \tag{1}$$

3. Results and discussion

3.1. Variation of free volume in polynorbornene with temperature

Variations of a free volume size calculated from τ_{3b} and its intensity of o-Ps as a function of temperature are shown in Figs. 2a and b, respectively. It reveals that the free volume size increases from 297 to 343 K on the whole. The increase below $\approx$ 308 K (T_g) can be interpreted as a dilation of both crystalline and amorphous regions in the glassy state and that of above $\approx$ 308 K is mainly based on the dilation of the free volume size by the initiation of backbone chain movements in the rubbery state. A small contraction of the free volume size is observed between
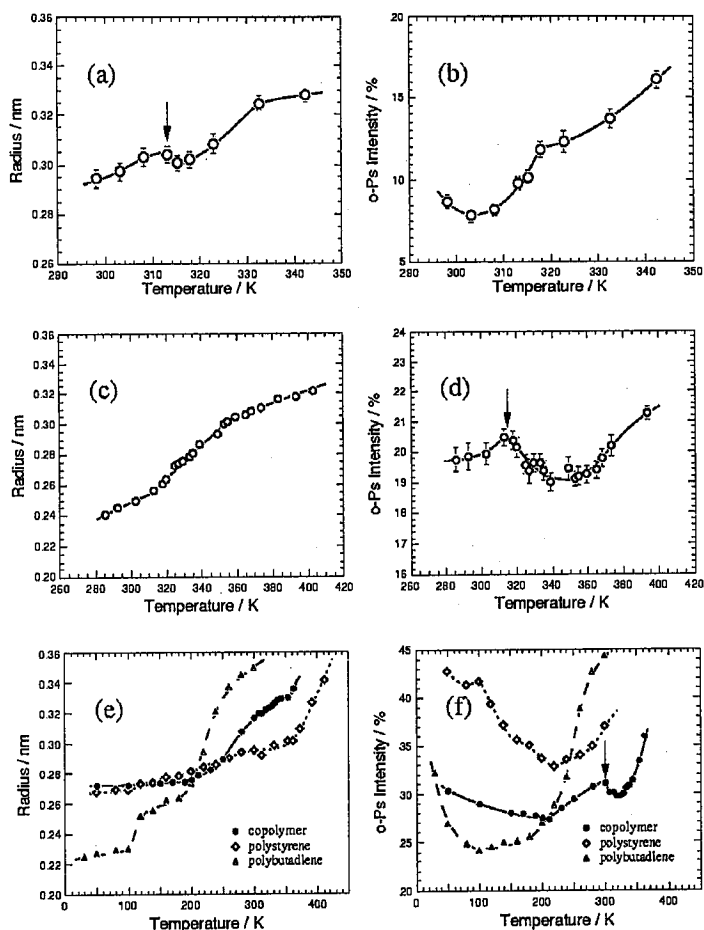

Fig. 2. Variations of lifetimes and intensities of *ortho*-positronium in three shape memory polymers: (a) and (b) for polynorbornene, (c) and (d) for polyurethane, (e) and (f) for styrene-butadiene copolymer.
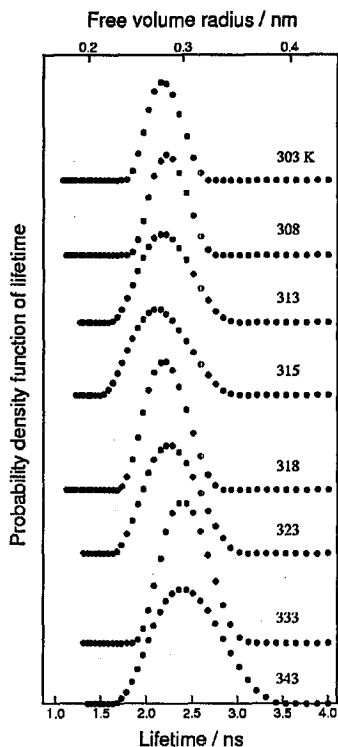
Fig. 3.   Annihilation lifetime distributions of o-Ps in polynorbornene near glass transition temperature.

308 and 313 K. An increase in the numerical concentration of the free volume, which is estimated from I_{3b}, represents a production of the new free volumes in the amorphous region with exception just above T_g. A generation of the new amorphous region is due to a transformation of the crystalline region into the amorphous one by the elevation of temperature above T_g since both the size and the numerical concentration of the free volume increase.

The macroscopic shape recovery phenomenon is speculated to result from relaxation of an internal stress of the hard segment units due to movements of backbone chains of the amorphous soft segment above T_g. The dilation of the free volume holes due to the micro-Brownian motion should be partially restricted by the ordered and arrayed crystalline stacks of five-membered ring in the polynorbornene. The free expansion of the free volumes is expected to be regulated even above T_g by the prevailing restrictive force. This force may disturb the free movement of the soft segments between the five-membered crystalline edges in the rearrangement of the soft segments of amorphous state to achieve a new equilibrium state. Thus, the soft segments are tightly drawn each other making junctions in the rotation of the hard segments, which results in the reduced free volume size and an increased free volume numbers around T_g, minimizing the volume change of nano-spaces and coming to the thermal equilibrium of the polymer chain of a

molded shape. It is concluded that an original shape is recovered by the rearrangement of the backbone chains of a distorted polymer chain in a non-equilibrium state into the equilibrium state.

Temperature dependence of a size distribution of the free volume, shown in Fig. 3, reveals that peak positions of the size distributions coincide with the average sizes of the free volume obtained by the PATFIT analyses as shown in Fig. 2a. The size becomes bigger with an increase in temperature up to T_g (308 K), then, smaller from T_g to T_r (318 K), and bigger above 323 K. A FWHM (full width at half maximum) of the size distribution does not vary much with respect to temperature except near T_g. It suggests that the amorphous region of the Norsorex are fairly controlled by the internal forces due to the stack of five-membered ring and that the transformation of the polymer chain of the soft segments is able under the reasonable restriction since the free volume size distribution becomes broad for the realization of the shape memory due to a thermal equilibrium.

3.2. Variation of free volume of polyurethane with temperature

A linear polyurethane, composed of hard segments well ordered by hydrogen bondings between amide and carbonyl groups and the soft segment in between, shows temperature dependence of size and numerical concentration of the free volume as shown in Figs. 2c and d. While the free volume hole size showed slight changes near T_g ($\approx$ 315 K and $\approx$ 353 K), the numerical concentration of the free volume shows significant queer decrease by the elevation of temperature from $\approx$ 315 K to $\approx$ 353 K. New free volumes seemed to be generated above 353 K by a partial collapse of the hard segment unit bundles due to the reconstruction of the hydrogen bonding to acquire the thermal equilibrium, which is supported also by FTIR observation of the same SMP. The insignificant variation of the free volume size suggests that a restriction of the thermal motion of the soft segment in an amorphous phase is not affected much due to the formation of a crystalline region of the linear hard segments. The queer thermal behavior of the numerical concentration of the free volume discovered around $\approx$ 353 K agrees well with the transformation temperature probed by the dynamic viscoelasticity measurement. This result suggests that the shape recovery of the polyurethane is realized due to the hydrogen bonding interacting between the hard segments. It revealed that the hydrogen bonding among the hard segments significantly affects ordering of the polymer chains in the SMP and results in the shape memory effect.

3.3. Variation of free volume of polystyrene-polybutadiene copolymer with temperature

Variations of a size and a numerical concentration of the free volume in an amorphous region against temperature are shown in Figs. 2e and f, together with those of neat polystyrene and polybutadiene for comparison. Critical variations of the free volume size are recognized at $\approx$ 200 K (T_g of amorphous polybutadiene) and $\approx$ 360 K (T_g of amorphous polystyrene), whereas a queer thermal behaviors of the numerical concentration of the free volume are observed

at $\approx$ 200 K and 320 $\approx$ 323 K (T_m of crystalline polybutadiene). The anomalous thermal behavior of the numerical concentration of the free volume of the polystyrene-polybutadiene copolymer at 320 $\approx$ 323 K may be related to the configurational recovery of the nanoscopic regulation of the crystalline polybutadiene bundles functioning as the hard segment unit. It is suggested that the shape recovery of polystyrene-polybutadiene copolymer is realized due to the interaction between a crystalline polybutadiene region and amorphous polystyrene region. Polymer chains in amorphous polybutadiene phase may work as strain absorber of the applied stresses which variates the lamination structure of crystalline region of polybutadiene. Variation of the elasticity of the amorphous polystyrene at T_r affects ordering of the crystalline lamination of the SMP recovering the original shape and a restoration of the soft segment to an equilibrium state in the recovering process.

4. Conclusion

Temperature dependence of a nanoscopic environment probed by free volume, estimated by the positron annihilation lifetime measurement, in three types of the SMP, are described. The shape recovery mechanism of the SMP is interpreted by the queer thermal behavior around glass transition temperature. The peculiar clicks are found just above T_g, which suggests that the macroscopic shape recovery process follows the decrease in size or numbers of free volumes due to the relaxation of the internal stress followed by the rearrangements of the hard and soft segments in the nanoscopic structure.

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