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Positron Annihilation Lifetime Spectroscopy and Large Molecule Diffusion into a Polyurethane Matrix

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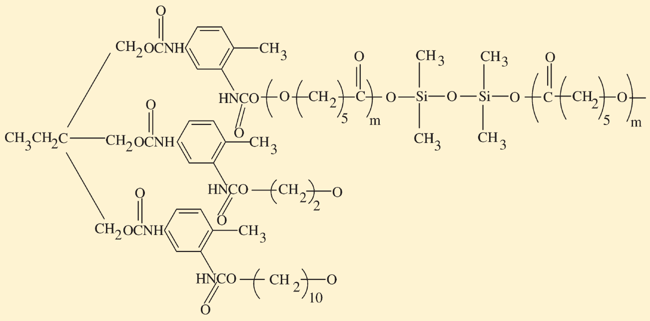

ABSTRACT: Positron annihilation lifetime spectroscopy (PALS) measurements are reported on a three polyurethane (PU) materials created by the reaction of polymeric toluene diisocyanate with either ethylene glycol, 1,10-decanediol, or a silicone containing diol. Dynamical mechanical analysis indicated that the glass transition temperature of the PU's were respectively 118, 95, and −40 °C. Whereas the ethylene glycol and 1,10-decanediol materials exhibited a glass−rubber transition, the silicone containing PU showed rubber characteristics over the temperature 0−180 °C. The PALS measurements on the silicone-based PU's showed significantly larger voids dimensions than the other PU's. Void collapse is observed to occur on the time scale of the oPs measurements. The permeation of dioctyl phthalate, 2-ethylhexylbenzyl phthalate, nonylphenol ethoxylate, isopropyl myristate, and oleic acid into a polyurethane matrix was measured gravimetrically. The silicone containing material at low temperatures exhibits relative simple permeation behavior however deviations from simple Fickian-type behavior are observed at higher temperature. Surprisingly, the ethylene glycol and 1,10-decanediol exhibited no significant absorption over a period of 5 months with the exception being nonylphenol ethoxylate. A comparison of the void sizes with the molecular dimensions for the lowest energy conformations of the permeants obtained using theoretical calculations indicate that for the silicone-based material the diffusion cross section for the permeants is larger than the available void size. The permeation process is considered to occur by a reptation type of motion of the permeants into channels created by the phase segregation of the flexible segments.

INTRODUCTION

Positron annihilation lifetime spectroscopy (PALS) is an important method for assessing void structure at a molecular scale.[1,2] A number of papers have demonstrated a correlation between the rate of diffusion in rigid polymer matrices and the void size as measured by PALS.[3−7] In most studies the molecules diffusing are typically nitrogen, helium, argon, oxygen, carbon dioxide, and water and have dimensions which are comparable to those of the available free volume. The diffusion behavior observed will often follow the classical descriptions of permeation into rigid media.[8,9] Correlations have been shown between the void size, as measured by PALS and small molecule diffusion characteristics into rigid polymer matrices. Deviations from simple behavior are observed when the diffusion molecules are able to undergo specific interactions with the polymer matrix. Polyurethanes (PU) at low temperatures may exhibit rigid characteristics matrices and at higher temperatures become elastomers.[10,11] PALS studies have been reported for a number of polyurethanes based on methylene diisocyanate (MDI) as the reactive monomer.[12−14] The free volume in the PU's changes with the isocyanate content and the characteristics of the species used to link the isocyanate molecules. PU's created using polyester polyols of poly(butylene adipate) (PBA), poly(ethylene adipate) (PEA), and poly(hexamethylene adipate) (PHA) showed that the free volume increased markedly as the materials were raised through their glass−rubber transition (T_g). Studies of water vapor permeation indicate that hydrophilicity as well as free volume controls the permeation process. Increasing the molecular weight of the polyol allows crystallite formation and significant reduction in free volume.[13] Similar conclusions were obtained from studies of PU's created from MDI and chain extended with poly(ethylene oxide)—suppression of chain crystallization being important in achieving the highest free volume.

In this paper, the permeation characteristics to large molecule permeants are observed for three polyurethanes created using polymeric toluene diisocyanate (TDI) with either ethylene glycol, 1,10-decanediol, or a silicone containing diol. Unlike MDI, TDI does not promote phase separation and creation of hard block structure and the matrix formed is usually assumed to be significantly more disordered than when MDI is used.[3,4] Toluene diisocyanate (TDI) is more toxic than 4,4-diphenylmethane diisocyanate (MDI), and hence a polymeric form of TDI was used which retains the reactivity but has significantly lower toxicity (Figure 1).

Three diols were investigated: ethylene glycol, 1,10-decanediol, and a hydroxyl-terminated polydimethylsiloxane copolyester

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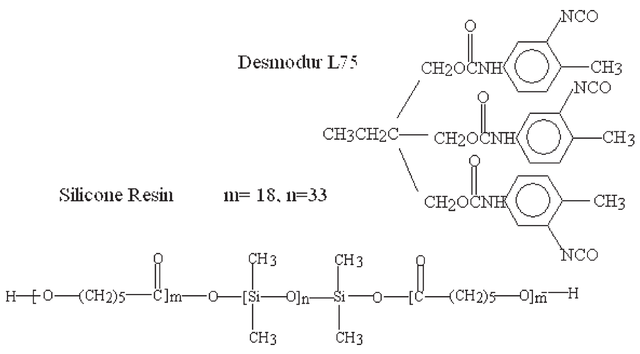

Figure 1. Chemical structure of polymeric toluene diisocyanate.

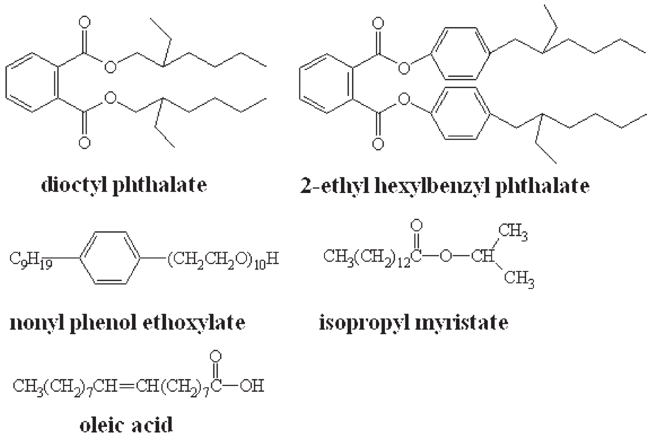

Figure 2. Chemical structures of permeants.

(Figure 1). The 1,10-decanediol will increase the hydrophobic nature of the matrix, whereas the ethylene glycol will create a very dense strong hydrogen-bonded matrix. The diol-terminated polydimethylsiloxanes will be very hydrophobic but also very flexible (Figure 1).

■ EXPERIMENTAL SECTION

Materials. The diols 1,10-decanediol (mp = 100 °C) and ethylene glycol (mp = −13 °C, bp = 196−198 °C) were obtained from Sigma-Aldrich Chemical Co., Dorset, UK. The diol-terminated silicone material was supplied by ICI UK and had the structures shown in Figure 1 and was a liquid at room temperature. The polymeric TDI (Desmodur L75) was supplied by Bayer Plc as a 75% solids solution in ethyl acetate. The isocyanate was degassed under vacuum for 30 min at 30 °C and then heated slowly to 70 °C over a period of 30 min and then held at 70 °C for a further 30 min. This reduces the ethyl acetate content to ~15%.

Sample Formation. Films 5 cm in diameter and ~2 mm thick were created by curing appropriate stiochiometric mixtures of the diol and isocyanate. The components were mixed and then degassed under vacuum for 1 min and 45 s at 110 °C and then cured for a further 15 min at ambient pressure and a temperature of 110 °C. The films were then postcured at 140 °C for 3 h and cooled in a desiccator to ambient temperature. The cure process was monitored using infrared spectroscopy, and in all cases the isocyanate peak (~2275 cm^{-1}) was absent in the final films.

Permeants. The permeants used were dioctyl phthalate (MW 390), 2-ethylhexylbenzyl phthalate (MW 542), nonylphenol ethoxylate (MW 644), isopropyl myristate (MW 270), and oleic acid (MW 282) (Figure 2), all obtained from Aldrich Chemical Co. All were used as received. The solubility parameters for the permeants are 18.15 $(\mathrm{MPa})^{1/2}$ (dioctyl phthalate), 19.58 $(\mathrm{MPa})^{1/2}$ (2-ethylhexylbenzyl phthalate), 18.38 $(\mathrm{MPa})^{1/2}$ (nonlphenol ethoxylate), 16.61 $(\mathrm{MPa})^{1/2}$ (isopropylmystate), and 19.03 $(\mathrm{MPa})^{1/2}$ (oleic acid).

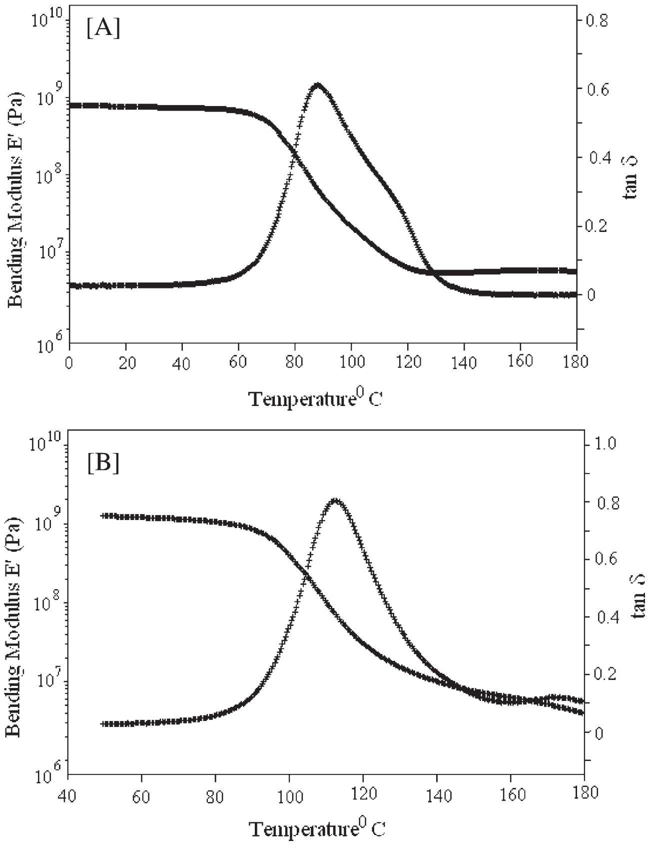

Figure 3. DMTA traces for (A) Desmodur L75 + 1,10-decanediol and (B) ethylene glycol.

Table 1. Glass Transition Temperatures of the Polyurethane Samples

sample	T_g (°C)	secondary peak temp (°C)
1,10-decanediol + Desmodur L75	95 ± 3	115 ± 4
ethylene glycol + Desmodur L75	118 ± 3	175 ± 4
Silicone B + Desmodur L75	−40 ± 3	/

Gravimetric Measurements. Square-shaped samples were cut (~15 mm × ~15 mm × 3 mm) and stored in a desiccator for at least 1 day before use. The sample thicknesses was measured at several locations using a digital micrometer (precision = ±0.005 mm), and the mean value was recorded. The initial weight of the samples was measured using a Mettler balance PM100 to an accuracy of ±0.001 g. These samples were soaked in screw-tight test bottles containing 15−20 mL in a thermostatically controlled oven at the required temperature. Samples were removed periodically, wiped to remove excess solvent, and weighed. The time which the sample was out of the solvent was kept to less than 1 min. The mass changes in the samples were plotted up against time and an equilibrium values estimated M_∞. Plots were created of the normalized masses against the square root of time divided by the thickness. The diffusion coefficient D was calculated from the initial linear slope using the relation

$$\frac{M_t - M_0}{M_\infty - M_0} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{l^2}\right) \tag{1}$$

where l is the thickness of the sample, M_0 is the initial mass of the sample, and M_t and M_∞ are the masses at time t and at equilibrium.[8,9]

Positron Annihilation Lifetime Spectroscopy. The method used has been described previously and uses a fast−slow configuration.[15] A ^{22}NaCl source sealed between two layers of Kapton using epoxy adhesive was placed between two samples of the PU polymer. Calibration of the system was carried out using benzophenone single crystals which have a lifetime time of 331 ps. The lifetime data were least-squares analyzed using POSITRONFIT.[16] Analysis was carried out fixing the two short lifetime components t_1 and t_2 at 0.4 ns and 0.125 ns, respectively. The long-lived o-Ps component is well separated from the two shorter lifetime components and readily deconvoluted. The average hole size was calculated using the relationships derived by Tao[17]

$$\tau_{\text{o-Ps}} = \frac{1}{\lambda} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{2}$$

where $\tau_{\text{o-Ps}}$ is the o-Ps lifetime (ns) and R (nm) the hole radius. R_0 equals R + DR and DR = 0.1656 nm.[18] The cavity volume is then calculated using the relationship

$$V_c = \left(\frac{4\pi}{3}\right)R^3 \tag{3}$$

A 1 cm^2 samples of molded alkyd resin were cut out and formed a sandwiched around the ^{22}Na source. A temperature scan from 30 to 70 °C in 10 °C intervals was carried out, and the data are an average of three separate runs.

Dynamic Mechanical Thermal Analysis. The Rheometrics dynamic mechanical thermal analyzer (DMTA)[19] was used in three point bending mode and operated over a temperature range −180 to +300 °C and frequency of 10 Hz. The samples used were ~1 mm thick, and E' the bending modulus and tan δ were measured.

■ RESULTS AND DISCUSSION

Dynamic Mechanical Thermal Analysis (DMTA). Samples 1 mm thick were subjected to DMTA analysis, and the bending modulus E' and tan δ were measured over a temperature range from 0 to 180 °C at 10 Hz (Figure 3). In the ethylene glycol and the 1,10-decanediol system the separation between urethane groups is relatively short, and extensive hydrogen bonding between urethane groups and the trifunctional nature of the PU creates a highly cross-linked network structure.

The high-temperature shoulder in the case of the 1,10-decanediol PU (Figure 3A) reflects heterogeneity in the sample and implies that the material is attempting to phase separate to create ordered regions. However, the relatively short chain of the ethylene glycol and the trifunctional nature of the isocyanate preclude the organized hard block structure type of MDI-based materials, and a broad single peak is observed (Figure 3B).

In the ethylene glycol PU, the dominate relaxation is a single peak located at ~120 °C; however, a second transition at about 150 °C can be seen which is typical of hard block structure in aromatic polyurethanes which have achieved phase separation. The glass transition temperatures and secondary peak temperatures are summarized in Table 1.

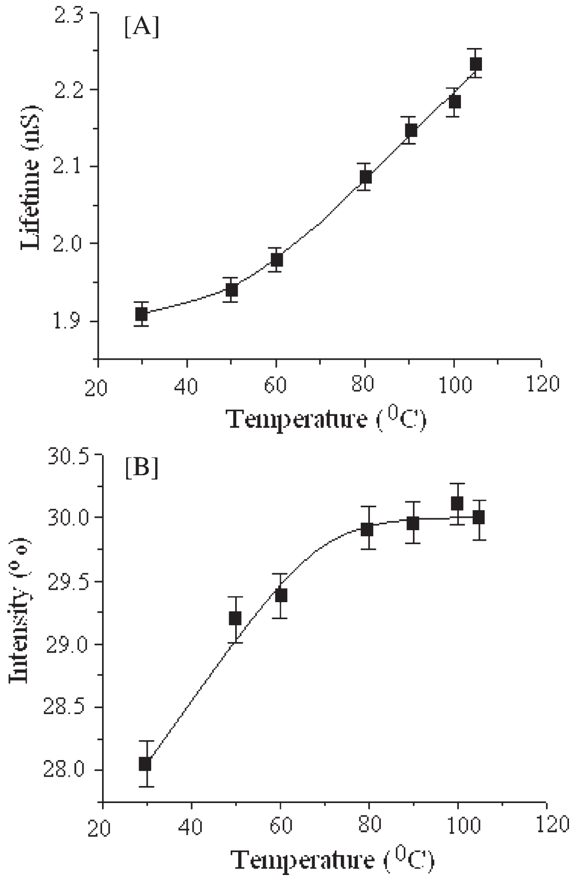

Figure 4. Variation o-Ps Lifetime versus temperature (A) and intensity (B) for 1,10-decanediol + Desmodur L75 polyurethane.

Table 2. **Free Volume Radii and Volumes for Desmodur L75 + 1,10-Decanediol and Desmodur L75 + Ethylene Glycol Polyurethane (Error Bars on Data ±2%)**

	Desmodur L751 + 10-decanediol PU		Desmodur L751 + ethylene glycol PU	
temp (°C)	hole radius (nm)	hole volume (nm^3)	hole radius (nm)	hole volume (nm^3)
30	0.2767	0.089	0.268	0.081
50	0.2800	0.092	0.2727	0.085
60	0.2836	0.096	0.2755	0.088
80	0.2933	0.106	0.2789	0.091
90	0.2987	0.112	0.2811	0.093
100	0.3018	0.115	0.2841	0.096
105	0.3061	0.120	0.2914	0.104

Measurements on the silicone resin are not reported as it had a rubbery modulus at 0° and 100 °C of ~6 × 10^6 Pa and exhibited no transitions between 0 and 180 °C.

Positron Annihilation Lifetime Spectroscopy PALS). PALS measurements were carried our on fully cured samples of the PU's. Data of Desmodur reacted with 1,10-decanediol and are presented in Figure 4, and the hole radius and volume are summarized in Table 2. The PALS lifetime rises linearly up to slightly above 70 °C and then changes its slope. The change in slope is indicative of the

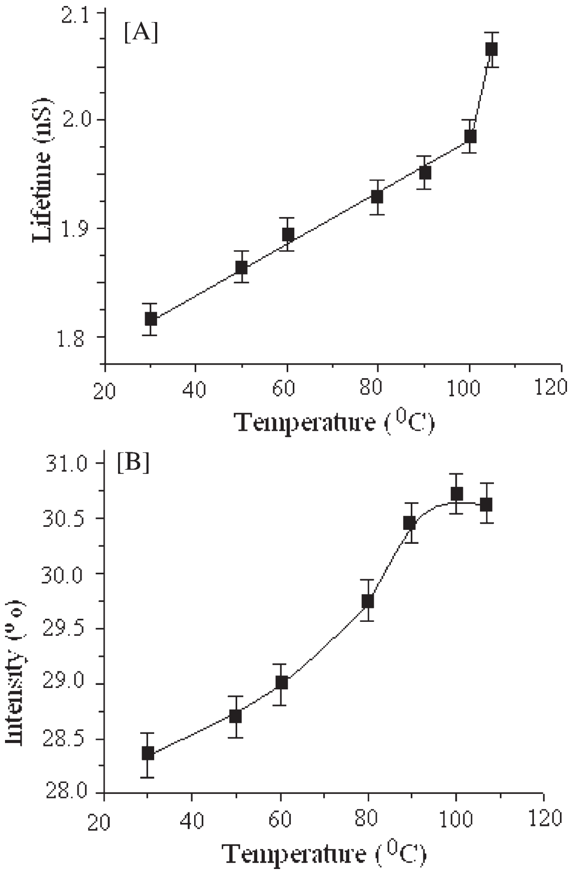

Figure 5. Variation of the o-Ps lifetime (A) and intensity (B) for Desmodur L75 + ethylene glycol polyurethane.

T_g process and is consistent with the DMTA data where the modulus starts to drop at 70 °C. The o-Ps senses the dynamics of the matrix on a time scale of nanoseconds, whereas the DMTA measurements are performed at 10 Hz, and therefore a shift in the apparent T_g is not unexpected. The intensity curves turn over at 10−20 °C above the glass transition temperature.

Measurements on the PU obtained with ethylene glycol are presented in Figure 5, and the calculated hole radius and volume are presented in Table 2. The oPs lifetimes are shorter and the calculated radius and free volume and smaller than for the ethylene glycol + Desmodur L75 PU. The shorted alkyl chain between the urethane linkages will be expected to reduce the radius and hence size of the voids. While these polymers will not be expected to show the ordered structure found when methylene diphenyl isocyanate (MDI) is used, hydrogen bonding between the urethane groups will tend to align the diol entities and allow some local order to be created. A number of studies of PALS on PU have been reported.[20−26] The radius and hole volumes reported in Table 2 are comparable to those reported by other workers on PU's. The hole sizes are smaller in the ethylene glycol chain extended PU compared with the 1,10-decanediol PU. The shorter bridging chain will allow a greater degree of hydrogen bonding to occur, and this leads to a reduction in the void size.

The smaller void size is reflected in a higher value of the T_g for the ethylene glycol chain extended material compared with the 1,10-decanediol extended material.

The oPs lifetimes and intensities were measured for Desmodur L75 + silicone, and the data are presented in Figure 6 and Table 3.

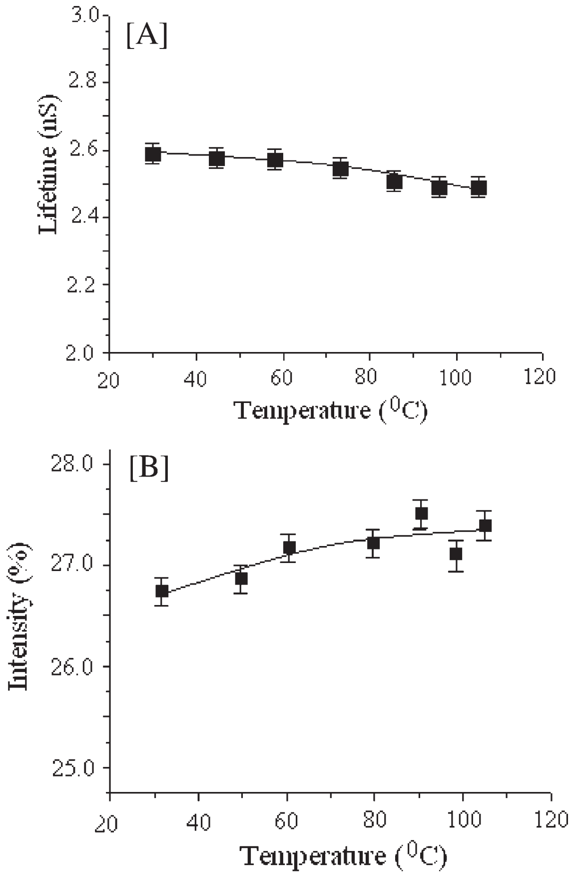

Figure 6. Variation of the o-Ps lifetime (A) and intensity (B) for Desmodur L75 + silicone.

Table 3. Free Volume Radii and Volumes for Desmodur L75 + Silicone A and Desmodur L75 + Silicone B Polyurethane (Errors Bars ±2%)

	Desmodur L75 + silicone	
temp (°C)	hole radius (nm)	hole volume (nm^3)
30	0.3372	0.161
50	0.3347	0.157
60	0.3352	0.158
80	0.3343	0.156
90	0.3353	0.158
100	0.3297	0.150
105	0.3305	0.151

The values for free volume obtained for the silicones polyurethanes are higher than the diol-cured systems. The incorporation of the polydimethylsiloxane copolyester block introduces a separate flexible phase into the polyurethane.

At room temperature this polymer is ∼60 °C above its glass transition temperature, and the weak temperature dependence in both the lifetimes and the intensities reflects the oPs occurring in a rubbery matrix (Figure 6). The surrounding polyurethane matrix will be stable up to ∼150 °C, the point at which the urethane hydrogen bonding will break up. Other studies of phase-separated polyurethanes have shown that in the region between the soft block glass transition and the higher temperature hard block

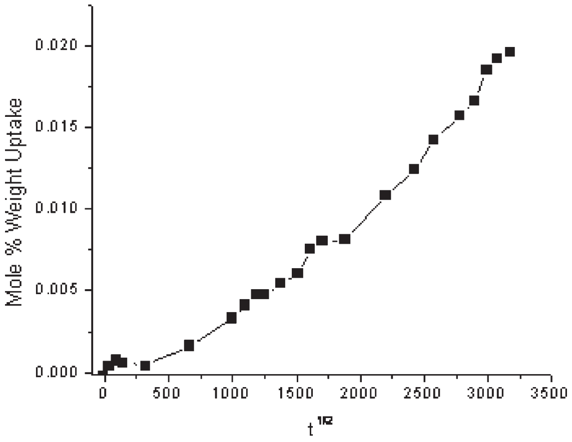

Figure 7. Mol % weight uptake data for Synperonic NP10 in 1,10-decanediol + Desmodur L75 polyurethane at 80 °C. Error bars: ±1.5%.

transition the oPs lifetime and intensity are weakly sensitive to temperature.

The o-Ps intensity rises linearly with temperature and shows the beginnings of a leveling off of the void density as the temperature is raised. The break up of the hydrogen bonding associated with the urethane entity is expected to occur in an aromatic containing systems at ~150 °C.

The rapid chain motions of the diol-based segments at this temperature allow free volume hole collapse to occur within the lifetime of the oPs and lead to an apparent reduction in the size of the voids with increasing temperature, which is contrary to the increase expected due to expansion of the PU as the temperature is increased. The molecular chain motion is able to occur faster than the lifetime of the oPs, and as a result the observed hole dimensions are smaller than would be expected. These effects have been observed previously in other glass-forming systems.[26−28]

Studies of polydimethylsiloxane indicate that at high temperatures starvation kinetics begin to operate.[29,30] The term starvation kinetics has been introduced by Eyring to explain deviations observed from simple thermal activation[30,31] and explains the weak temperature dependence in this system.

Starvation kinetics describes the change from a thermally activated to a process being controlled by the rate at which energy is supplied to the transition state. At high temperatures segmental motion in polydimethylsiloxane is weakly temperature dependent, and its rate is not controlled by an activation barrier but by the rate at which energy is supplied to the segments. Increasing the temperature will usually increase the rate at which segmental motion will occur which would be expected to produce a decrease in the lifetime of the oPs. While there is a decrease, this does not occur as dramatically as might be expected and implies that starvation kinetics may be beginning to become operative. The hole radius for the siloxane containing PU's are significantly greater than those for other PU's examined consistent with the rubbery nature of this material.

Gravimetric Weight Uptake. Experiments were carried out for 5 months on the three polymer systems (Figures 7 and 8). In the case of the 1,10-decanediol and ethylene glycol polyurethane materials, no detectable uptake of the permeants occurred over the temperature range 30, 40, 60, 70, and 80 °C, with the exception of nonylphenol ethoxylate which showed weight uptake at 80 °C (Figure 7). At the lower temperatures the weight uptake was within experimental error. A diffusion coefficient was calculated for nonylphenol ethoxylate at 80 °C: $D = 2.01 \times 10^{-9} \pm 1.92 \times 10^{-12}$ cm^2 s^{-1}.

In contrast, the permeants were absorbed by the silicone modified polyurethane at all temperatures.

Desmodur L75 + Silicone. Unlike the two diol polyurethanes, the silicone material proved to be a very poor barrier to these large molecule permeants (Figure 8). Sever plasticization of the matrix was observed, and in some case swelling occurred to 3 times their original size during the course the experiment and the samples became very sticky.

At the lower temperatures, the diffusion of all the permeants appears to be Fickian as would be expected of permeants entering a rubbery matrix well above its glass transition temperature. This silicon containing PU retains its structural stability up to the temperature at which hydrogen the hydrogen bonds between the urethane linkages are broken and this is ~150 °C. For higher temperatures, further weight uptake after equilibrium is observed and implies that the swelling has become sufficiently strong to disrupt the hydrogen-bonding structure. The diffusion coefficients are presented in Table 4. Above 60 °C the nonylphenol ethoxylate and oleic acid did not show an equilibrium value but simply kept swelling, and therefore no diffusion coefficients were calculated for these systems. Both these systems have the potential of disrupting the hydrogen bond structure of the PU.

The high permeability of the silicone polyurethane matrix reflects the high mobility of the polydimethylsiloxane segment in the polymer, and the urethane matrix does not significantly impede the segmental motion. The hydrophobic nature of the matrix also makes it compatible with the hydrocarbon-based materials and aids permeation.

The activation energy for diffusion was calculated using the data from Table 5. The error in the data is quite large, but the very low values reflect that the diffusion process is controlled to a large extent by the segmental mobility of the polydimethylsiloxane segments of the PU. The isopropyl myristate exhibits the highest rate of diffusion and at high temperatures is clearly able to swell the matrix. Although at 30 °C oleic acid has a lower diffusion rate at higher temperatures, the carboxylic acid function is able to effectively disrupt the matrix and uncontrolled swelling and disintegration of the material occurs. The dioctyl phthalate and 2-ethylhexylbenzene phthalate surprisingly show higher values than the nonylphenol ethoxylate and the oleic acid at 30 °C, reflecting a higher solubility of the molecules and hence the ability to penetrate the matrix. At higher temperatures these systems are clearly able to swell the polymer matrix as indicated in Figure 8E.

It is only at the highest temperatures that second stage diffusion associated with swelling of the matrix is observed. The phthalates, despite their relative large sizes, are able to diffuse relatively easily into the matrix, and the phenyl group will increase their compatibility with the urethane element and as a consequence 2-ethylhexyl; benzene phthalate and dioctyl phthalate both show second stage diffusion at the highest temperatures.

Theoretical Calculations on the Penetrants. *Molecular Modeling.* In an attempt to gain a greater insight into the relationship between the molecular sizes and the oPs measurements of the cavity size, quantum mechanical calculations were performed to determine the lowest energy conformations for the permeant molecules (Figure 9). The calculations were performed using Hyperchem Version 4.5. Using this conformation, it is possible to construct the volume which such a molecular structure would occupy (Table 6). The conformations and values of cross-sectional areas calculated correspond to the minimum-energy

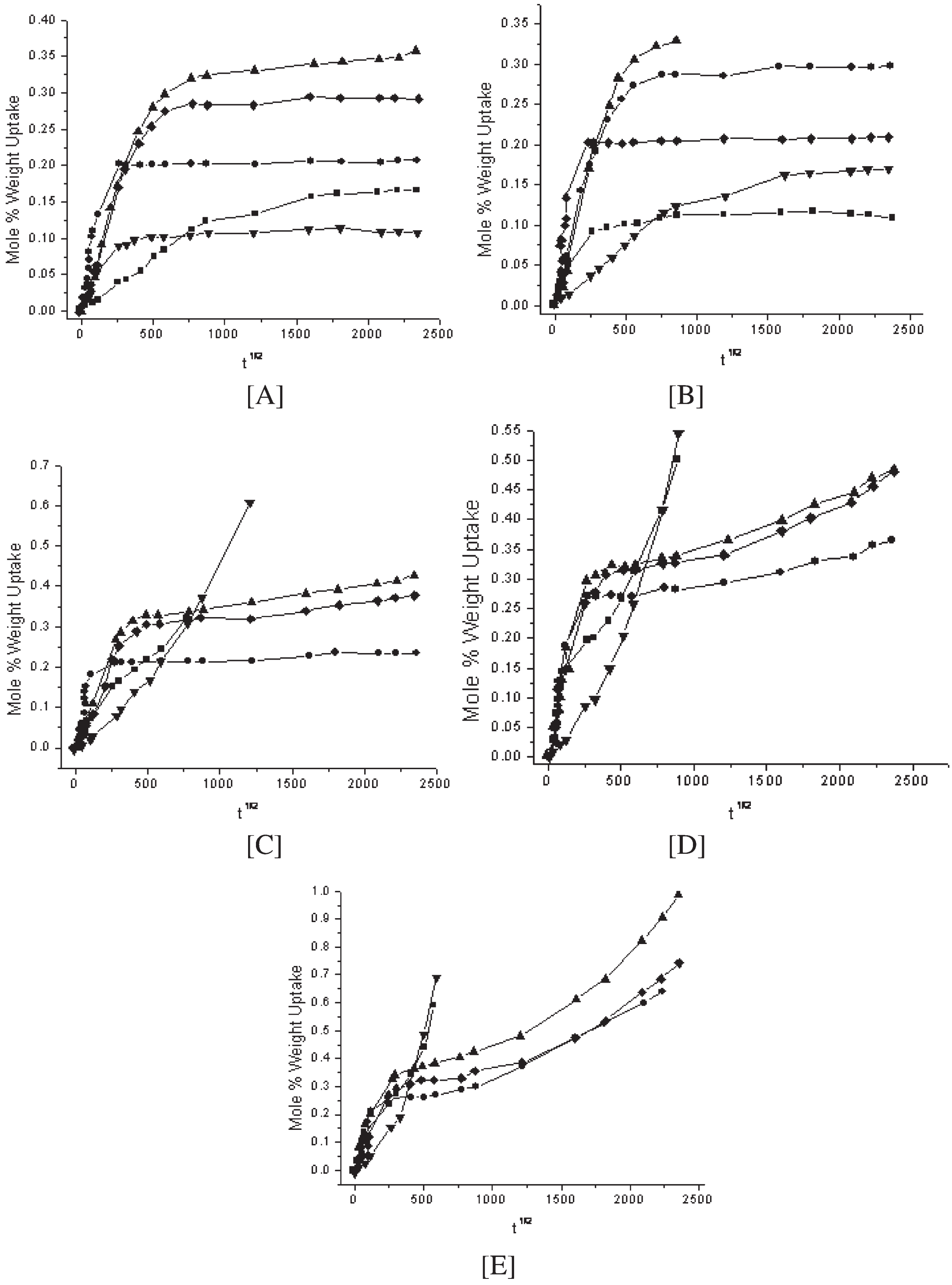

Figure 8. Mol % weight uptake data for permeant uptake in Silicone B + Desmodur L75 + silicone polyurethane at (A) 30, (B) 40, (C) 60, (D) 70, and (E) 80 °C. Key: ■, oleic acid; ▲, 2-ethylhexylbenzene phthalate; ▼, nonylphenol ethoxylate; ●, isopropyl myristate; ♦, dioctyl phthalate. Error bars ±3%.

state for the isolated molecule and do not take in to account any interactions which might occur with the polymer matrix.

Higher energy conformations will usually reduce the size of the molecule by the alkane chains adopting more gauche conformations. This "periodic box" is an upper estimate of the volume required, as it does not allow these high aspect ratio molecules to fit in between other molecular entities. Comparison of the data from the calculations and that from oPs studies indicates that the concept of a molecule hopping into a void is not consistent with the size of hole available in the polymer matrix. Looking at the permeants, the cross section of the alkane chain is comparable to that of the hole. The oPs is a measurement of the average void size measured on a time scale of 10^{-9} s, whereas the diffusion process is the integration of motions taking place over a considerably longer period of time. It is therefore obvious that the molecule rather than moving by a single jump must reptate or

Table 4. Diffusion Coefficients for Permeant Uptake in Silicone B + Desmodur L75 + Silicone Polyurethane

	diffusion coefficient D (cm^2 s^{-1})				
liquid	30 °C	40 °C	60 °C	70 °C	80 °C
dioctyl phthalate	105 ± 0.16	108 ± 0.17	260 ± 0.85	525 ± 0.30	603 ± 0.69
2-ethylhexylbenzene phthalate	63.0 ± 0.054	127 ± 0.162	250 ± 0.73	315 ± 48.4	611 ± 1.14
nonylphenol ethoxylate	21.8 ± 0.021	55.7 ± 0.02	n/a	n/a	n/a
isopropyl myristate	1050 ± 7.92	1280 ± 1.76	1630 ± 4.68	2970 ± 6.65	3960 ± 13.7
oleic acid	22.6 ± 0.88	391 ± 1.99	n/a	n/a	n/a

Table 5. Activation Energies of Diffusion of Permeants in Desmodur L75 + Silicone Polyurethane

permeant	E_D (kJ mol^{-1})	error
dioctyl phthalate	16.11	2.28
2-ethylhexylbenzene phthalate	17.55	0.58
nonylphenol ethoxylate	19.4	2.2
isopropyl myristate	11.08	1.71
oleic acid	81.95	n/a

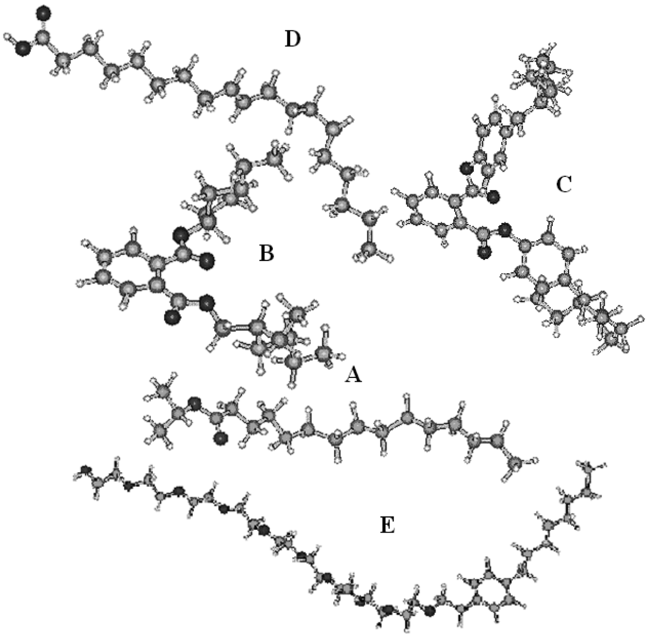

Figure 9. Equilibrium conformations for the permeant molecules at 30 °C: (A) isopropyl myristate; (B) dioctyl phthalate; (C) 2-ethylhexylbenzene phthalate; (D) oleic acid; (E) nonylphenol ethanoate.

slither through the polymer matrix. The oPs measurement of the void is a mean value and represents a cross section rather than a complete definition of the void. This problem has been discussed by Shantarovich,[33] who has attempted to rationalize the dimensions measured by oPs and those obtained by molecular simulation and other methods. It may be assumed that the oPs is essentially determining a mean cross section for the voids in the material and may not indicate the length of the void.

In the case of isopropyl myristate and oleic acid, the cross section which the molecule presents is comparable with the dimensions measured by oPs; however, the length dimensions are significantly greater than the measured cavity dimensions which indicates that the diffusion process must be rather like a snake entering a tube. In the case of dioctyl phthalate, 2-ethylhexylbenzyl phthalate, and nonylphenol ethoxylate their dimensions are all greater than the void size measured by oPs, which is consistent with the observation that these molecules must undergo significant interactions with the polymer matrix prior to diffusion occurring and consequent swelling increases the void size allowing diffusion. Since the polymer and permeant both contain phenyl groups, favorable $\pi-\pi^*$ interactions provides a mechanism for swelling the polymer matrix. On this basis, the dioctyl

Table 6. Values of the Periodic Box Volume and Dimensions Calculated for the Permeant Molecules

temp (°C)	periodic box volume (nm^3)	periodic box dimensions (nm)
	Dioctyl Phthalate	
30	0.906	1.06 × 0.77 × 1.11
40	0.901	1.06 × 0.78 × 1.09
60	0.912	1.11 × 0.74 × 1.11
70	0.976	1.16 × 0.61 × 1.38
80	0.987	1.13 × 0.74 × 1.18
	2-Ethylhexylbenzene Phthalate	
30	2.056	1.14 × 0.82 × 2.20
40	2.057	1.13 × 0.82 × 2.22
60	2.023	1.12 × 0.81 × 2.23
70	2.096	1.14 × 0.81 × 2.27
80	2.041	1.14 × 0.81 × 2.21
	Nonylphenol Ethanoate	
30	4.793	1.44 × 0.86 × 3.87
40	4.857	1.45 × 0.87 × 3.85
60	4.917	1.45 × 0.89 × 3.81
70	4.993	1.46 × 0.90 × 3.81
80	5.022	1.46 × 0.91 × 3.78
	Isopropyl Myristate	
30	0.514	0.59 × 0.40 × 2.18
40	0.558	0.59 × 0.45 × 2.10
60	0.607	0.79 × 0.39 × 1.97
70	0.650	0.67 × 0.48 × 2.02
80	0.647	0.69 × 0.47 × 2.00
	Oleic Acid	
30	0.655	0.82 × 0.36 × 2.22
40	0.679	0.83 × 0.37 × 2.21
60	0.702	0.87 × 0.37 × 2.18
70	0.707	0.88 × 0.37 × 2.17
80	0.716	0.90 × 0.37 × 2.15

phthalate with a structure which closely resembles that of the PU matrix will have a greater ability to swell the PU than 2-ethylhexylbenzene phthalate.

Molecules such as isopropyl myristate and oleic acids lack the ability to undergo strong interactions with the phenyl groups and rely on their ability to find a void in the siloxane diol segments of the matrix. Nonylphenol ethanoate, with a combination of phenyl and ether groups, will be able to swell the polymer and destroy the hydrogen-bonded structure in the PU.

■ CONCLUSIONS

The simple diol extended polyurethane exhibit surprisingly good barrier characteristics to the permeants used in this study. The incorporation of the polydimethylsiloxane copolyester segment into the polyurethane creates a rubbery phase into which relatively facile diffusion can occur. The positron annihilation data show surprising and important consequences of the high mobility of the silicone phase and provide an interest example of the effects of chain mobility on the o-Ps lifetime. The permeation characteristics of these large molecules are controlled not only by the available free volume but also by the solubility of the molecules in the PU matrix.

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