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The effect of structure on gas solubility and gas induced dilation in a series of poly(urethane) elastomers

B. J. Briscoe* and C. T. Kelly†
Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK
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This paper describes a study of the interaction of high pressure subcritical and supercritical carbon dioxide with a series of poly(urethane) elastomers of differing hard segment content. The extent of gas absorbed by each poly(urethane) type and also the corresponding dilation of each poly(urethane) have been measured under gas pressures of up to ca. 23 MPa at 42°C. The data indicates that, for this particular series of poly(urethanes), the extent of sorption and dilation are directly related to the structural properties of each polymer including the extent and characteristics of the soft phase component. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: poly(urethane); dilation; solubility; carbon dioxide)

INTRODUCTION

The solubility of foreign molecules in a polymer may be defined, as the state of equilibrium between the concentrations of molecules outside and inside the polymer, in terms of a sorption coefficient. Generally, the sorption coefficient for elastomers is either constant or increases with gas pressure. Sorption is usually assumed to take place homogeneously throughout the whole of the *amorphous* polymer phase. An increasing sorption coefficient with an increase in the extent of the sorption is generally attributed to the 'plasticization' and associated swelling of the amorphous component of the polymer, thus enhancing mobility and flexibility of the polymer chains. Hence, the extent of the gas sorption and the gas induced dilation will normally be directly interrelated, and also a function of the nature of the polymer system. The nature of these types of processes is invariably sensitive to changes in the polymer microstructure on a scale comparable to the size of the penetrant. The morphology of the polymer may be such that it inhibits or promotes sorption due to: (a) geometric constraints, which affect the available free volume and its distribution; and (b) specific interactions between the gas and polymer molecules. In semi-crystalline polymers it has been rationalized that the crystallites do not take part in the gas sorption process[1]. Similarly, in a study of the diffusion of some simple gases (oxygen, carbon dioxide and hydrogen) through poly(urethane) elastomers at a gas pressure of 4.25 psi, McBride *et al.*[2] have reported that the extents of hard segment content in the polymer directly influence the rate of diffusion of the gas, and deduced that hard segment domains may be impermeable to an imbibed solvent.

Poly(urethane)s provide an interesting subject material for studies of gas sorption and the related gas induced dilation. Poly(urethane) elastomer molecules are made up of 'soft' (mobile) polyol segments, which alternate along the polymer chain with highly polar, 'hard' (immobile) urethane segments. Hydrogen bonding interactions may occur between the hard segments, and this phenomenon, coupled with the fact that the soft and hard segments are incompatible, mean that an effective phase separation of the hard segments and soft segments may occur. Thus, the resulting structure of the poly(urethane) may be one where the relatively hard blocks separate into highly ordered regions or domains ('hard phase'), which may be para-crystalline, and are dispersed in a matrix of soft segments ('soft phase')[3]. It may also be the case that some specific interactions may exist between the hard and soft segments, and that not all of the hard segments will be located within the hard domains. In addition, some molecules may exist entirely within one phase. In general, the co-existing phases are now thought not to be completely pure[4]. *Figure 1* shows a schematic diagram of the supposed structure of a typical poly(urethane). The degree of phase separation is not only a function of the system thermodynamics, but also depends a great deal on the size, length and content of the hard segments, and also on the extent of hydrogen bonds of each type, i.e. hard segment–hard segment and hard segment–soft segment. This paper examines the effect of altering hard-segment content upon the extent of sorption of carbon dioxide and the corresponding dilation of the polymer, up to gas pressures of ca. 23 MPa. It will be seen that carbon dioxide is a particularly good solvent for poly(urethane)s, and induces

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* To whom correspondence should be addressed
† Present address: Department of Chemical Engineering, The University of Queensland, St Lucia, Brisbane, Queensland 4072, Australia

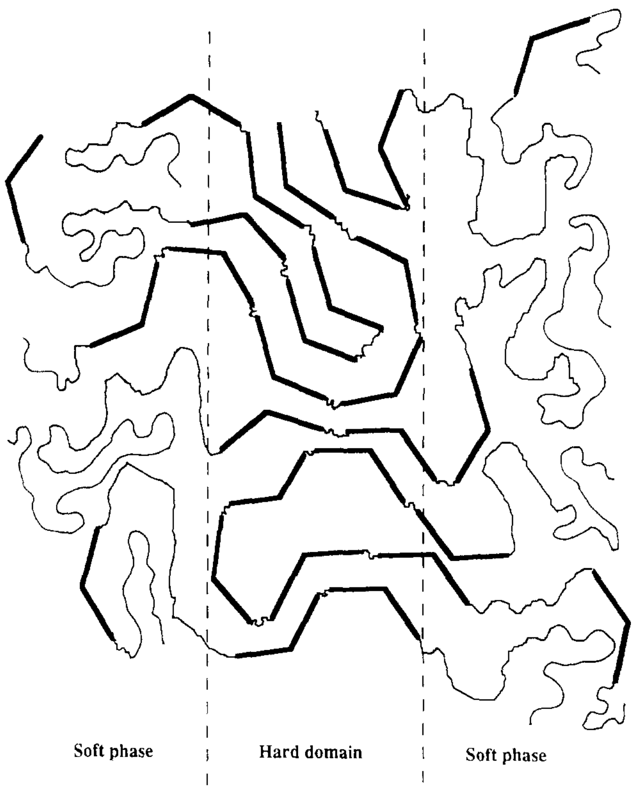

Figure 1 Schematic diagram of the arrangement of the hard segments (shown as bold stiff rods) and soft segments (shown as thick flexible lines) into domains, to indicate incomplete phase separation[4]. The major component of the hard domain is the hard segment and vice versa. Each domain may contain a complete molecular unity but this is not shown

significant dilation. The extents of the sorption and dilation are however shown to be a function of the nature of the predominantly soft segment phase as well as its volume fraction.

MATERIALS AND METHODS

Materials

The elastomeric materials used in this study were diphenylmethyl-4,4-diisocyanate (MDI) polyester based poly(urethane) elastomers, which were produced with a range of Shore A hardness values (Shore A hardness values 55 ('PU 55'), 70 ('PU 70') and 90 ('PU 90')) (Kemira Polymers, UK, Diprane 54 series). The hardness values were related to the hard segment content of the polymers, PU 55 having the lowest hard segment content. The carbon dioxide (CO_2) gas used was of 99.9% purity (BOC, UK).

High pressure equipment

The high pressure equipment consisted essentially of the gas feed (cylinder), an intermediate gas receiver, a reciprocating gas booster pump (Charles Madan, Altrincham) and the high pressure cell. Two pressure vessels were employed in this study. A conventional (non-optical) high pressure vessel was used to make measurements of the mass of gas absorbed by the polymers. An optical high pressure cell was designed and built to carry out direct visual measurements of the extent of the dilation of the polymers. *Figure 2* shows a schematic diagram of the optical cell. A more detailed description of the ancillary high pressure equipment may be found elsewhere[5]. The temperature of the vessels containing the prepared specimens was maintained above the critical temperature of CO_2 (31°C) at 42 ± 1°C.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) scans were obtained for each of the poly(urethane) specimens, using a Perkin Elmer DSC2 machine. The samples were scanned over the range -60 to $+120$°C, at a heating rate of 20°C min^{-1}, to determine both the glass transition temperature T_g and the also width of this transition for each of the polymers.

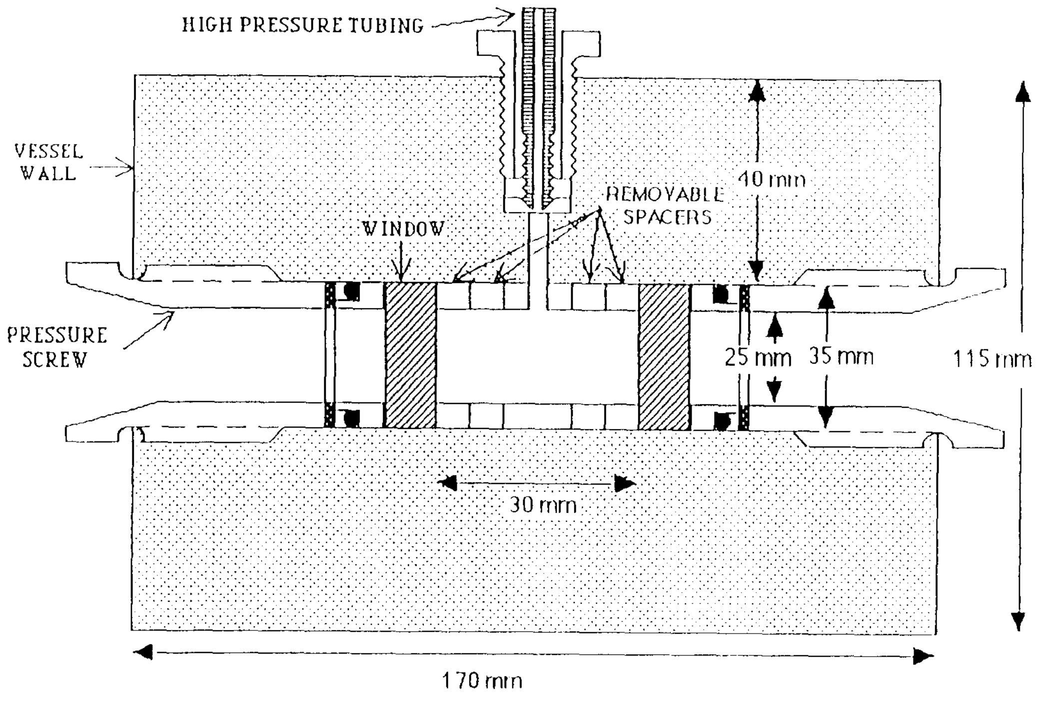

Figure 2 Schematic diagram of the high pressure optical cell

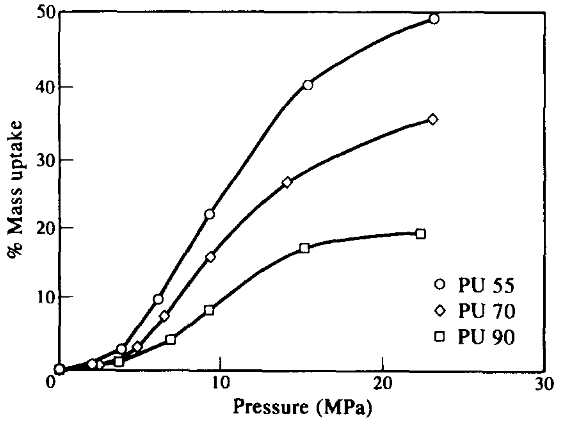

Figure 3 Percentage mass uptake for the three poly(urethane) specimens as a function of carbon dioxide gas pressure, 42°C

Mass sorption probe

The technique used to determine the mass of gas absorbed in the elastomeric specimens involved measuring the first harmonic frequency of a slender steel beam rigidly clamped at one end. The polymer specimen (ca. 28 × 28 × 8 mm) was attached to the free end of the beam. The change in the resonant frequency (period) of the whole assembly may be related to the effective mass change induced in the polymer[6]. The probe was placed inside the conventional pressure vessel, and the carbon dioxide pressure was subsequently raised in steps of ca. 5–6 MPa to a maximum of ca. 23 MPa. The gas–polymer system was allowed to equilibrate for 1 h at each pressure step. The changes in the period of vibration were measured continuously during each pressure step. The mass change sensitivity of this system was nominally better than 5 mg in samples of ca. 2.5 g.

Dilation studies

The optical high pressure cell was fitted with Sapphire windows (Goodfellows, UK), with dimensions 16 mm thick and 35 mm diameter. An 8 mm square poly(urethane) elastomer was placed in the cell cavity. A white light source was placed at one of the windows to illuminate the sample, and a CCD camera (Pulnix TM-90) placed at the other window. The camera was lined to a TV monitor/video recorder system (Pace) for collection of the data. The carbon dioxide pressure was raised in steps of ca. 5–6 MPa to a maximum of ca. 23 MPa. The gas–polymer system was allowed to equilibrate for 1 h at each pressure step and the subsequent changes in the specimen dimensions at equilibrium were recorded using the TV/video system. The recorded images of the dilation of the polymer at each pressure increment were then analysed using an Optomax (AMS, UK) image analyser. Using this method, an accuracy in the linear dimension of 0.1 mm was attainable. In order to compute the volumetric dilation the swelling was assumed to be isotropic.

RESULTS AND DISCUSSION

Gas mass sorption

The sorption of carbon dioxide in the three poly(urethane)s (PU 55, PU 70 and PU 90) was measured at 42°C and at pressures up to 23 MPa. The sorption isotherms for each of the polymers are given in *Figure 3*. Each data point represents the computed percentage change in the specimen mass after approximately 1 h following each pressure increment. For the 'softest' poly(urethane) specimen (PU 55), at a gas pressure of ca. 23 MPa, the mass uptake is ca. 50% (w/w). The percentage mass uptake in the intermediate hardness poly(urethane) (PU 70) is ca. 38% while in the 'hardest' poly(urethane) (PU 90), the mass uptake decreases to 20% under the same pressure and temperature conditions. Thus, the trend is for a decreasing equilibrium gas mass uptake with the increasing of the hardness (increasing hard segment content).

The sorption and diffusion of a penetrant are assumed to take place only in the soft segment rich phase of a poly(urethane); the dense, hard segment domains of these polymers are supposed to take little or no part in the gas uptake process[2,7]. The solubility of the gas in the polymer would therefore be expected to be dependent upon: (a) the volume fraction of the hard domains, and (b) upon the mobility of the soft segments in the soft segment rich phase. Soft segment mobility will be restricted by the presence of isolated individual hard segments mixed within the soft phase, and also the hard segment domain formations themselves; both the isolated hard segments mixed in the soft phase and the actual hard segment domains may act as 'tie-down' points or immobilization sources for the adjacent soft segments[2]. The relatively 'static' hard segments will restrict the mobility of soft segment species in their vicinity. PU 55 has the lowest hard segment content, and this will have the lowest degree of hard segment mixing in the soft phase and also the lowest percentage of hard domain formation. Thus, the overall soft segmental mobility should be relatively high, allowing for significant sorption of a permeant. The ratio of the hard segment content to the soft segment content in PU 70 and PU 90 increases (PU 90 having the highest ratio). This may mean that, in addition to an increase in the hard domain formation (which are believed to be impermeable to the gas), the 'purity' of the soft phase may be diminished. This supposition is confirmed by d.s.c. measurements of each of the poly(urethane)s. *Figure 4* shows the d.s.c. scans recorded for each of the specimens. The soft segment T_g was observed to increase as the hard segment content increased; this phenomenon is indicative of increased mixing of individual hard segments in the soft segment regions[8]. In addition, a notable broadening of the T_g peak is also observed as the hard segment contact increases. This is also indicative of an increased hard segment content within the soft domains. The relatively immobile hard segment species influences the mobility, as detected in the transition, of the soft segments and produces a wider spectrum of molecular relaxation processes[9]. The polymer with the highest volume fraction of hard segments mixed in the soft phase, and the largest percentage of hard segment domain formation (PU 90), absorbs the least amount of gas.

The shapes of the carbon dioxide isotherms are also worth noting. In the low pressure range (up to ca. 5 MPa) the isotherms are quite linear, following a Henry's law prediction that the concentration of the sorbed species is directly related to the ambient penetrant pressure. These

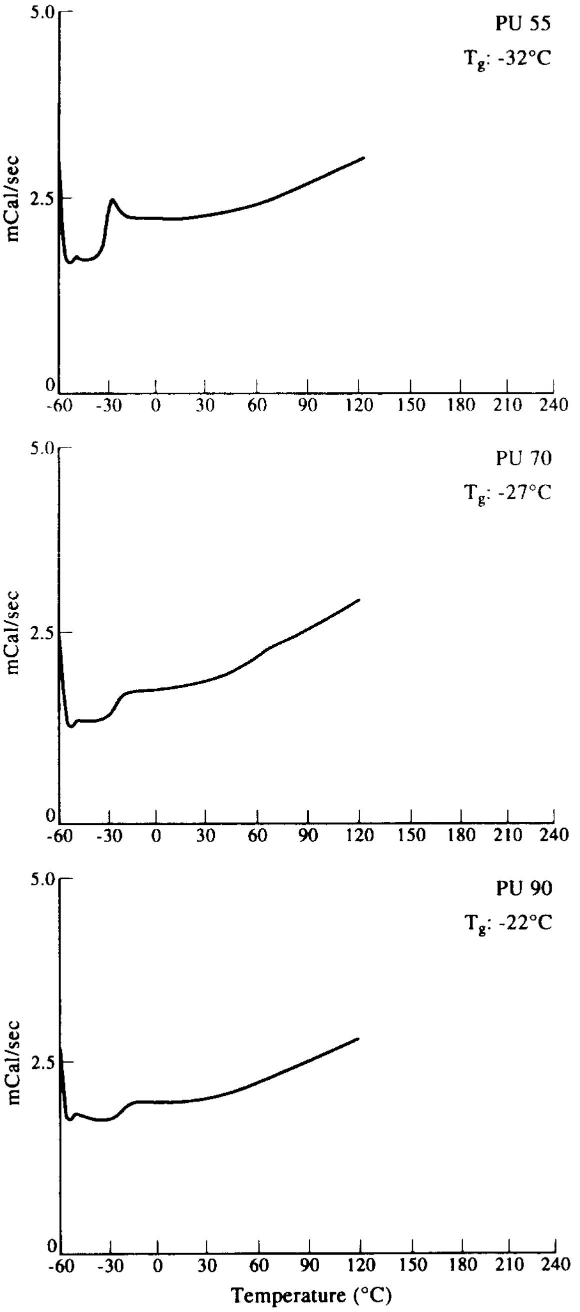

Figure 4 D.s.c. scans recorded for each of the poly(urethane)s (PU 55, PU 70 and PU 90)

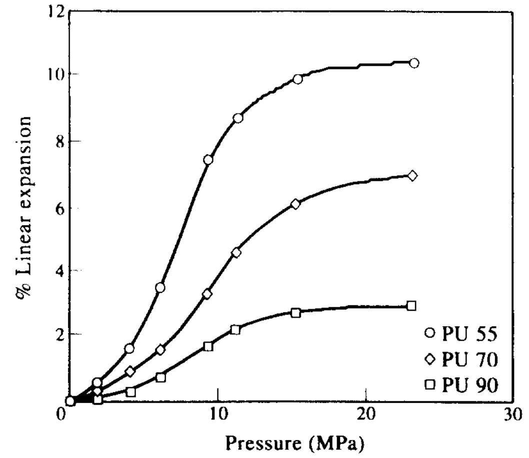

Figure 5 Percentage linear dilation of the three poly(urethane) specimens as a function of carbon dioxide gas pressure, 42°C

results are similar to those reported by Fleming and Koros[10] and Zakaria[11] for the sorption of carbon dioxide in silicone rubber, at gas pressures of 4–5 MPa. In the pressure range 6–13 MPa, a large increase in the solubility of the gas, in each of the poly(urethane)s, is observed, which is a process that is associated with the gas plasticizing, or swelling, of the polymers. This plasticizing effect of carbon dioxide occurs in a pronounced way at this point because the gas is in its supercritical state at pressures above 7 MPa[12,13].

The sorption isotherms for each poly(urethane) specimen (*Figure 3*) also display a significant decrease in their slopes at gas pressures above ca. 13 MPa; the sorption of carbon dioxide by the various specimens appears to be reaching a limiting value. At a gas pressure above 13 MPa, the hydrostatic component of the gas may begin to dominate over the plasticizing effect of the gas induced by the higher solute activity. This argument is consistent with the idea that a gas medium will act either as a plasticizing or a pressurizing medium[14,15], and that for any given gas–polymer system, the two effects will compete for dominance. With the carbon dioxide/poly(urethane) systems, the plasticizing effect appears to dominate at pressures up to ca. 13 MPa. At pressures above this value, the pressurizing effect of the gas seems to dominate, decreasing the available free volume, and thus reducing the molecular motions. As a consequence, the extent of the increase of gas sorption is reduced with the increasing of the pressure. This proposition is considered further in the next section.

Gas induced dilation

The carbon dioxide induced dilation of the three poly(urethane)s (PU 55, PU 70 and PU 90) was measured at 42°C and at pressures up to 23 MPa. The dilation isotherms for each of the polymers are given in *Figure 5*. For the 'softest' poly(urethane) specimen (PU 55), at a gas pressure of ca. 23 MPa, the percentage linear expansion is ca. 10.5%. The ultimate percentage linear expansion in the second poly(urethane) (PU 70) is ca. 7.1%, while in the 'hardest' poly(urethane) (PU 90), the linear expansion decreases to ca. 3.2% under the same pressure and temperature conditions. Thus, as the hardness (the hard segment content) of the polymer increases, there is a corresponding decrease in the dilation of the polymer. The trend reported earlier for the extent of the absorption of carbon dioxide, over the same pressure range, for the three poly(urethane)s was similar; increasing the hardness of the polymer resulted in a decrease in the capacity for gas absorption. Further, the shape of the dilation isotherm for each of the poly(urethane)s mimics the corresponding sorption isotherm. As may be seen in *Figure 5*, the shapes of the dilation *versus* pressure curves are linear in the low pressure region, where the gas sorption follows a Henry's law relationship. At carbon dioxide pressures above ca. 6 MPa, the rate of swelling increases quite significantly. This is associated with the increased solubility of the carbon dioxide as it enters its supercritical phase. The gas density increases rapidly with gas pressure[12], and now the solute acts as severe plasticizer for these polymeric matrices. In each of the dilation isotherms, at pressures

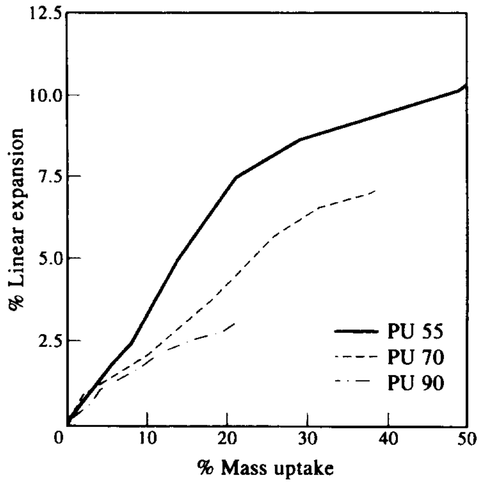

Figure 6 Relationship between gas mass sorption and gas induced dilation for the three poly(urethane) specimens

above 12–13 MPa, the rate of dilation is seen to decrease quite significantly. The measured dimensional change between ca. 12–13 MPa and 23 MPa is of the order of 0.5% to 1% in each of the poly(urethane) specimens. At these pressures, the rate of increase of the gas density with gas pressure is much lower. Thus, at higher pressures, the plasticizing effect of the gas may be dominated by the hydrostatic component of the gas, and the mobility of the polymer chains is reduced by the compressive stress exerted by the ambient gas. We have also studied the swelling of these poly(urethane)s at ambient temperature and pressure using a range of organic solvents including trichlorethane, xylene and methylethylketone. In these cases the ultimate extent of the swelling far exceeded the values noted for the carbon dioxide solvent. This indicates that the systems had not attained their full swelling potential and supports the notion of an imposed hydrostatic constraint at high pressures.

CONCLUSIONS

The solubility of the carbon dioxide was shown to decrease in the series of poly(urethane)s as the hard segment content increased. The results of the dilation measurements were similar to the solubility data in that the extent of dilation could be directly related to the morphology of the polymer.

Figure 6 directly illustrates a general trend for the interrelationship between the volume and sorbed mass for the three elastomers. The responses are qualitatively similar. There exists a rather linear relationship between volume change and mass sorption up to some pressure after which mass sorption increases more rapidly than the volume dilation.

It is notable however that the interrelationship between the extents of dilation and mass sorption are not quantitatively the same for each polymer. The softer the system the more dilation is evident per unit mass sorbed. Clearly, if the only factor involved was simply the extent of the amorphous phase, then comparable behaviour would be anticipated. As it turns out, the volume expansion per unit mass of gas sorbed is significantly less for the harder poly(urethane) (PU 90) than for the softer ones; for a 20% mass uptake there is a factor of almost three difference in the linear dilation between PU 55 and PU 90, as shown in *Figure 6*. A rather similar phenomenon has been reported by Briscoe and Zakaria[16] for glass particle filled silicone elastomers where the glass particles increase the hardness, but suppress mass sorption and volumetric dilation. Here too the harder (higher volume fraction of filler) systems showed comparatively less dilation per unit mass sorbed. It was argued by Zakaria that the fillers restrained dilation and hence sorption, the major trend, but also a 'sphere of influence' of modified elastomer existed around the filler where the sorption–dilation characteristics were altered. A similar argument may be offered for these poly(urethane) systems. This could occur at the hard segment–soft segment interface, as was proposed for the glass-silicone system, or because of changes in hard segment–soft segment interactions in the soft amorphous phase. The d.s.c. data are consistent with these speculations; the T_g of the soft phase increases and the peak broadens with the increase of the hard phase (hard segment) volume fraction.

These trends lead to a partial molar volume of the sorbate which decreases with the ambient pressure[5] and attains unusually low values. Recently, Kirchheim[17] and others[18] have speculated on the origin of this effect but currently no firm and unequivocal explanation of this trend is available. It appears that the nature of the amorphous phase, in particular its morphology, is an important factor in controlling this effect through the subtle variation of local free volume fluctuations. The present data, shown in *Figure 6*, and the d.s.c. data, clearly confirm that this may indeed be the case.

More generally, the data do illustrate that the solute sorption and the corresponding solute induced dilation are not simply a function of the hard/soft phase volume fraction ratio for these systems. The nature of the soft phase component, which is modified by the presence of hard segments, has a major influence upon the sorption and dilation behaviour. Thus in principle, these types of sorption and dilation studies provide a means to characterize the structure of the soft phase.

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