Transport–morphology relationships in segmented polybutadiene polyurethanes: 1. Experimental results

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The microphase-separated morphology in a series of well characterized polybutadiene polyurethanes with hydroxy-terminated polybutadiene (HTPBD) endcapped with 2,4-toluene diisocyanate (TDI) as the soft segment (SS) phase, and the combination of 2,4-toluene diisocyanate and 1,4-butanediol (BDO) as the hard segment (HS) phase, has been investigated by transmission electron microscopy (TEM) and sorption studies using N_2, O_2 and CO_2. This system constitutes a model segmented polyurethane copolymer composed of amorphous rubbery and glassy domains. Evidence for the presence of phase separation is inferred from the scattering and phase contrast mechanisms of imaging. However, it is not possible to assign specific domain morphologies such as spherical, lamellar or cylindrical, based solely on the results of TEM. Complementary evidence of the domain presence is provided from the transport results; in particular, phase inversion and domain connectivity. Incomplete phase separation was indicated from the combined transport–morphology results for samples with less than 33 wt% hard segment.

(Keywords: morphology; electron microscopy; polybutadiene polyurethanes; phase separation; transport)

INTRODUCTION

The understanding of the microstructure in phase-separated polymers constitutes an important area as a result of the enhanced mechanical and transport properties exhibited by those copolymers compared with the parent homopolymers and their blends. Copolymerization can provide a means of preparing new materials, with specific properties, by carefully selecting the chemical constituents, the synthesis method, and the sample processing history. In the context of transport, potential applications of tailor-made copolymers are: membranes for novel gas separations, transport of liquids as in the case of reverse osmosis, membrane reactors in biotechnology, selective gas permeabilities in the food packaging industries, and various biomedical applications.

Phase separation in regular diblock copolymers has been well characterized by electron microscopy and small-angle X-ray scattering (SAXS)[1–3]. Predictive thermodynamic theories are available for such well defined types of phase-separated block copolymers, and reasonable agreement between theory and experiment exists[4,5].

Segmented multiblock copolymers present a rich variety of phase heterogeneities of various length scales: molecular, domain and supermolecular structures[6]. Segmented copolymers are significantly different from the regular diblock copolymers in that they contain wide distributions of block sizes, sequence distributions and chain molecular weights. Polyurethanes are representatives of this type of phase-separated copolymer[7–9]. A wide range of end use properties can be realized by controlling the chain stiffness, interchain interactions, crystalline components, crosslinking and average composition[10,11].

Polybutadiene polyurethanes are, in particular, a model system for the investigation of transport and morphology relationships in segmented block copolymers. The rubbery component (soft segment, SS) is hydroxy-terminated polybutadiene endcapped with 2,4-toluene diisocyanate; the glassy (hard segment, HS) component is the reaction product of 2,4-toluene diisocyanate with 1,4-butanediol (*Figure 1*). Key features of this polyurethane include absence of hydrogen bonding between the hard and soft segment phases, amorphous soft and hard segments, and no chemical crosslinking. Phase separation is constrained to small scales without the presence of supermolecular (semicrystalline) structures. Moreover, enhancement of the transmission electron microscope (TEM) image contrast is feasible by using osmium tetroxide (OsO_4) as a selective stain for the polybutadiene phase.

Previous studies of bulk polymerized polybutadiene/T-DI/BDO polyurethanes by Xu *et al.*[12] showed that a major factor influencing the hard segment sequence length distribution was the initial reactant incompatibility. This hard segment length heterogeneity was responsible for the presence of two hard segment T_g's. Further evidence of the initial reactant incompatibility was presented by Chen *et al.*[13] by following the initial stages of polymerization by optical microscopy. Characteristic sizes for the phase separation were in the order of several microns.

Solution polymerized polybutadiene polyurethanes, where the presence of solvent overcomes the tendency of

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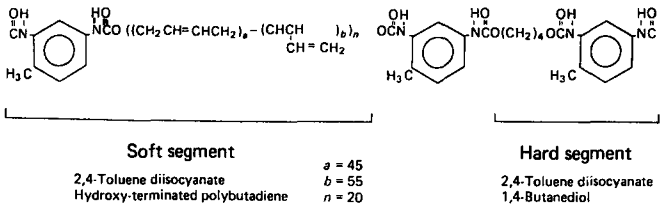

Figure 1 Solution-polymerized polybutadiene polyurethanes investigated

both reactants and products to macro-phase separate during the early stages of the reaction, can be contrasted with the above discussed bulk polymerized materials. These materials exhibit a single hard segment T_g reflecting the statistical nature of the homogeneous products. This type of solution-polymerized polyurethane is the one investigated here.

Transport of small molecules through segmented polyurethanes can reflect the underlying morphology, especially when the ratio of the diffusivities among the phase is very large (~100) and when there is no interaction between the permeant and the polymer[14].

One of the earliest transport studies in polyurethane elastomers compared the transport properties of four commercial polyurethanes with emphasis on the role of the soft segment component, i.e. polyether vs. a polyester. Ar, He, N_2 and O_2 were used as permeants and the hard segment domain morphology was assumed to be uniform spheres of 1 to 10 μm diameter dispersed in a soft matrix. The dispersed hard segment phase was considered impermeable as a result of the ratio of diffusivities between the soft and hard segment phase (~10). The transport (permeability) and mechanical (modulus) properties in a series of AB_n multiblock copolymers of polysulphone (PSF) and poly(dimethylsiloxane) (PSX)[15] were represented by a Maxwell type of model. Phase inversion for these copolymers was at about an equal ratio of PSF and PSX. The assumed morphology was spherical inclusions of the component with the lower composition. Crystallinity effects were evident at high concentrations of PSX; this implies a three phase copolymer system.

Regular diblock copolymer morphologies (cylinders and lamellae) in styrene–butadiene (S–B) allowed Odani *et al.*[16] to observe the effect of the domain shape on the transport properties. A reduction in diffusivity in the copolymer samples relative to homopolybutadiene was ascribed to a reduction in chain mobility in the polybutadiene matrix. Evidence for the presence of a diffuse domain boundary was provided from the results of solubility measurements. The simple linear additivity model of solubility measurements overpredicted the experimental results, and larger deviations were observed by increasing the styrene content.

The effect of varying the hard segment length, the hard segment composition, and the type of soft segment on the transport properties in polyether and polyester polyurethanes was considered by McBride *et al.*[17] For the range of hard segment compositions investigated (30 to 47% HS) increasing the soft segment length increased the diffusivities of O_2, H_2 and CO_2. The domain morphology was described as interpenetrating.

Combined transport–morphology studies have been rather scarce in the past 15 years. Some studies focussed on the morphological aspects while others emphasized transport aspects under a constrained set of compositions and assumed morphologies. In the present work both transport and morphological aspects are studied simultaneously in a series of well characterized polybutadiene polyurethanes.

ELECTRON MICROSCOPY OF DOMAINS

The domain characterization in segmented polyurethanes using electron microscopy has constituted a challenging problem since the original work by Koutsky *et al.*[18] in a 38 wt% HS (MDI/BDO) polyurethane with polyether/poly(tetramethylene oxide) and polyester/poly(tetramethylene adipate)/soft segments. The main interest lies in understanding the enhanced mechanical properties exhibited by segmented copolymers, ascribed to the presence of a microdomain morphology[19,20]. Specifically, the physical crosslinking from the hard segment domains and the improvements in material strength and toughness similar to a reinforced rubber account for the interest in understanding structure–property relationships in polyurethanes.

A complete description of the sample morphology comprises the determination of the phase volume fraction, sizes, shapes, orientation, connectivity and interfacial thicknesses as a function of the hard segment content, and sample history. The limiting factor in the domain characterization is the small scale of phase separation (order of 100 Å); hence, the preparation of thin films with approximately this thickness is necessary to minimize superposition of features in the 2-dimensional TEM image.

A chemically crosslinked polybutadiene polyurethane with 31 wt% hard segment was evaluated by TEM, WAXD and SAXS methods by Lagasse[21]. A 90 Å domain periodicity was found in a solvent cast sample. Additional morphological evidence for phase separation by TEM was presented by Dequatre *et al.*[22] in polybutadiene polyurethanes with 38 to 52 wt% hard segment (MDI/BDO). More recently, Chen *et al.*[23] investigated the present solution-polymerized polybutadiene polyurethanes by combination of SAXS, along with deformation studies, and TEM methods. Inconclusive evidence for phase separation by TEM was found in samples below 50 wt% hard segment. Cylinders of soft segment in a glassy matrix of hard segment was the proposed morphology in a 75 wt% hard segment, and a lamellar type of structure was established in the 52 wt% hard segment material. Additional supporting evidence for phase separation in samples of low and high HS content is provided in this work. Both amplitude (mass thickness) contrast and phase contrast images are presented for microtomed, and for solvent-cast thin films. The use of phase contrast is emphasized[24].

EXPERIMENTAL

Experimental materials

A series of solution-polymerized polybutadiene polyurethanes was synthesized by Bengston[25]. The corresponding mechanical and thermal properties have been presented elsewhere[26–28]. These polyurethanes should be contrasted with the previously bulk-polymerized polyurethanes which exhibited two hard segment glass transition temperatures which have been shown to be due to the presence of a bimodal hard segment length distribution. Soft and hard segment T_g's in these polyurethanes are indicative of a well phase-separated structure.

Sample preparation

Thin films were cast by dipping either glass slides or mica sheets into a 0.20 wt% of polymer in tetrahydrofuran solution followed by a quick removal of the substrate. Thin films were floated onto distilled water and recovered with TEM grids. Stained films were prepared by exposing these films to an atmosphere of osmium tetroxide vapours for three hours prior to the TEM characterization.

Ultracryomicrotomy

A Reichert–Jung Ultracut microtome with cryo-thin sectioning attachment and a diamond knife were used in the preparation of high hard segment content samples. The floating solvent was n-propyl alcohol and the films were cut at −90°C and recovered with TEM grids.

Electron microscopy

A JEOL 100CX transmission electron microscope at an accelerating voltage of 100 kV with 5000 to 33 000 magnifications was utilized with Kodak SO163 plates with an average exposure time of 2 s.

Visualization of microdomain morphology by TEM

Direct visualization of the domain morphology by TEM methods was attempted for a series of solution-polymerized polybutadiene polyurethanes with 33 to 75 wt% hard segment. Both solution casting and microtoming methods were applied for the preparation of thin films. In the following description of the electron micrographs the presence of organized regions in the thin areas has been used as an indicator of the presence of domain structures in both stained and unstained samples.

33 wt% hard segment

A through-focus series of micrographs of a solvent cast and stained sample is shown in *Figure 2*. There is no evidence for the presence of microphase separation. By defocussing the objective lens, structures appear with sizes of the order of 50 Å. Since the random noise fluctuations enhanced in these images by defocussing is approximately of the size of the 'structures' no reliable conclusion can be drawn from these micrographs about phase separation. If the observed image speckle is 'real', it represents a much smaller scale of phase separation than is present in the higher hard segment content samples.

44 and 51 wt% hard segment

Solvent cast, stained samples at these two compositions (*Figures 3* and *4*) clearly show phase separation. The black regions represent the stained rubbery phase since the more electron dense rubber material provides dark mass thickness and phase contrast in an underfocussed image. While phase separation is distinct, domain morphology is not well organized. A similar type of network morphology with HS domains of the order of 300 Å was also found in the 51 wt% hard segment sample (*Figure 4*) similar to the phase separation exhibited by PBD/MDI/BDO samples[21].

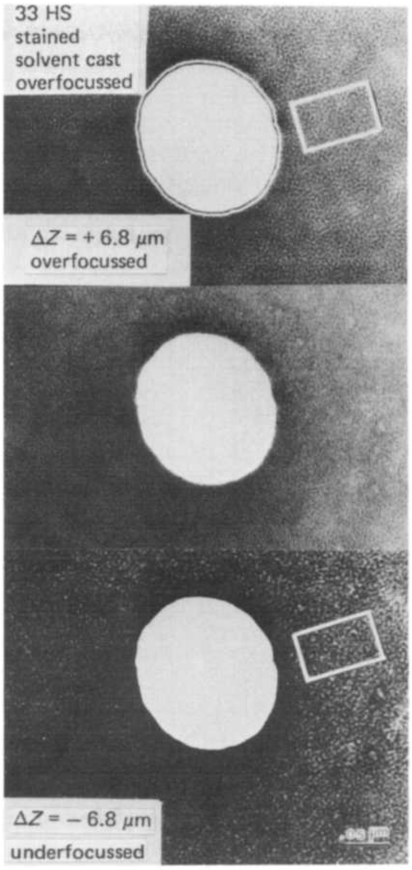

Figure 2 Electron micrograph for a through-focus series of a 33 wt% HS OsO_4 stained polybutadiene polyurethane. ΔZ is the amount of defocus. Note that dark regions in the overfocussed micrographs invert their contrast in the underfocussed micrograph (compare boxed areas) indicating image contrast is dominated by phase contrast

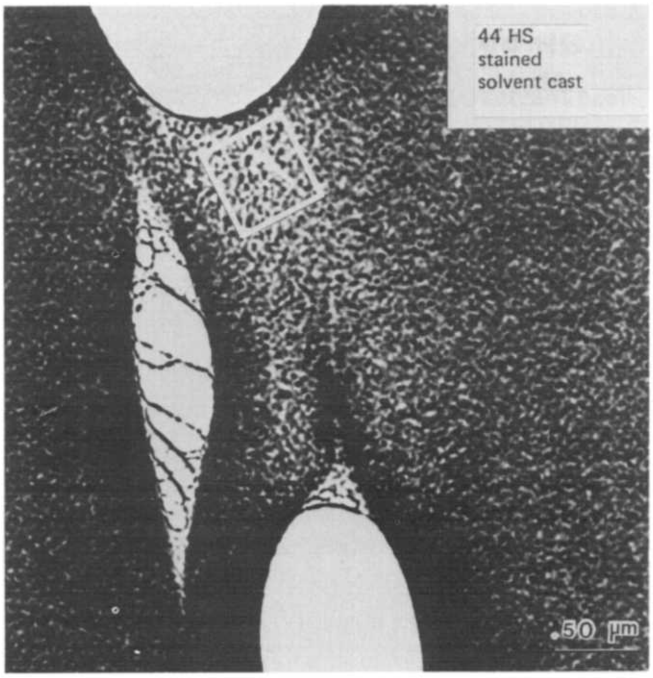

Figure 3 Electron micrograph of a solution cast 44 wt% HS OsO_4 stained polybutadiene polyurethane. The box indicates a thin section where the HS domain morphology is evident

55 wt% hard segment

This microtomed, *unstained* sample exemplifies the use of the phase contrast mechanism in the imaging of polybutadiene polyurethanes (*Figure 5*). In this case,

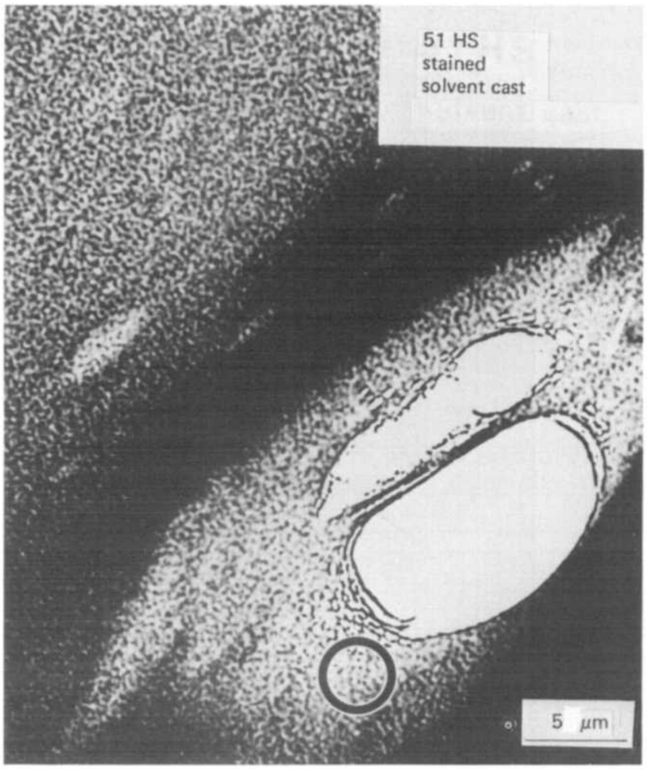

Figure 4 Electron micrograph of a solution cast 51 wt% HS OsO_4 stained polybutadiene polyurethane. The dark phase is the rubbery SS phase

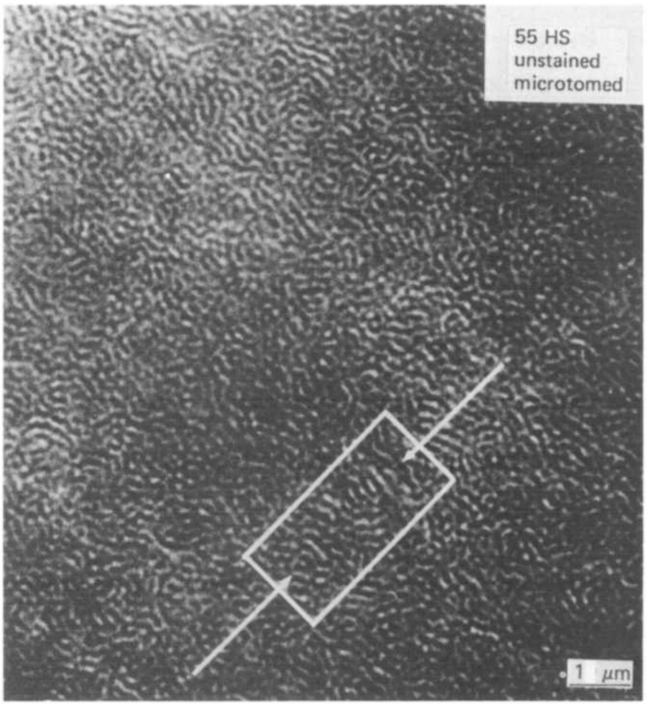

Figure 5 Electron micrograph of a microtomed unstained 55 wt% HS polybutadiene polyurethane. The arrows indicate the lamellar morphology. The black regions represent the HS phase in this underfocussed micrograph

underfocussing results in dark contrast for the more electron dense hard segment domains. A somewhat more ordered lamellar structure is present compared with the previously discussed solution cast samples (see the area inside the rectangle). This evidence supports the previously proposed lamellar morphology for this composition based on SAXS and TEM[23]. The shape and ordering of the domains is evidence that the image does not consist of 'random noise domains' introduced from the electron microscope optics. The size of the lamellar repeat is of the order of 100 Å compared with the 130 Å reported by Chen-Tsai *et al.*[23]

75 wt% hard segment

Figures 6 and *7* present the domain morphology of a continuous glassy hard segment matrix material with dispersed soft segment domains consistent with previous

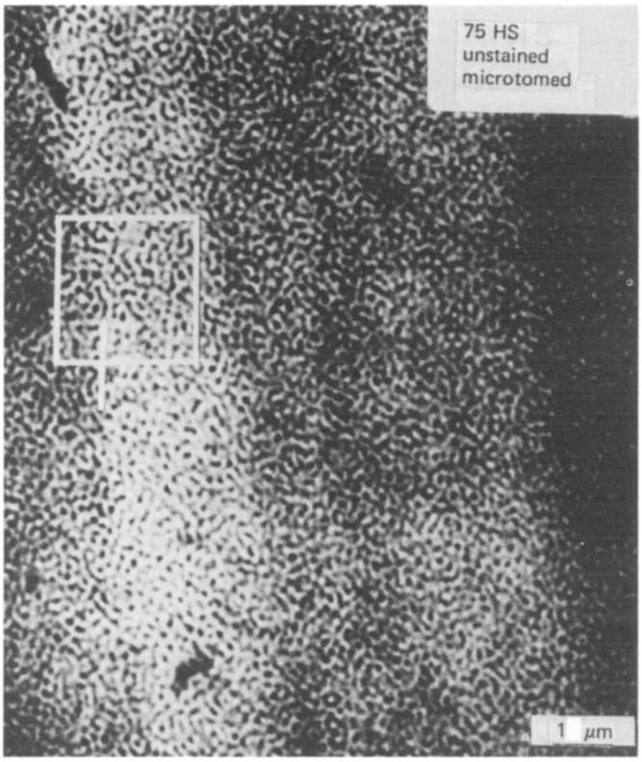

Figure 6 Electron micrograph of a microtomed unstained 75 wt% HS polybutadiene polyurethane. The black phase presumably represents the glassy HS phase

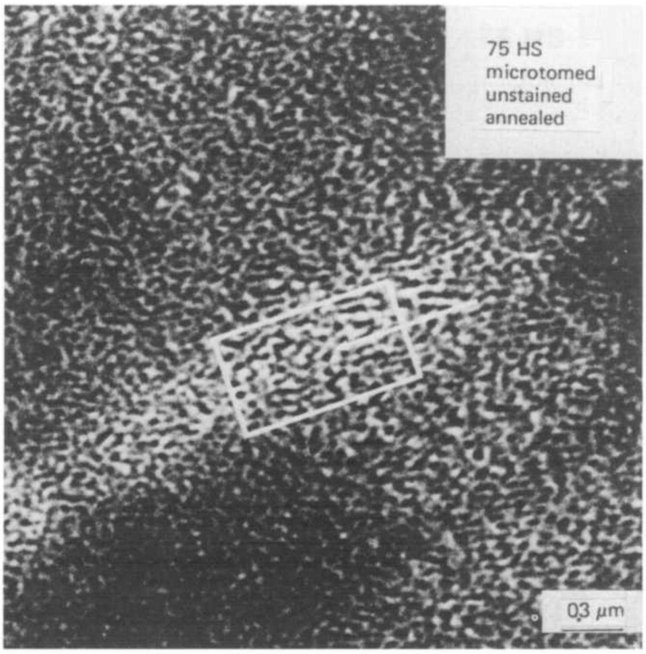

Figure 7 Electron micrograph of a microtomed unstained 75 wt% HS polybutadiene polyurethane. The black phase presumably represents the glassy HS phase

mechanical studies[25] and SAXS studies[23]. Both annealed and unannealed samples were microtomed (unstained) and, therefore, these morphologies represent the bulk morphology of polybutadiene polyurethanes. The size scale of the domains is about 100 Å. The presence of cylindrical domains of soft segment in a glassy hard segment matrix in similar samples was proposed from TEM and SAXS studies[23]. Annealing for three hours at 30°C above the hard segment T_g did not introduce significant changes in the observed morphology.

Sorption experiment

Sorption measurements are useful in the determination of solubilities, detection of sorption anomalies, and the analysis of slow transport processes[29]. The inherent difficulties in the direct characterization of polyurethane copolymers due to the small scale of phase separation suggest the use of alternative methods to probe the underlying morphology. Transport studies using N_2, O_2 and CO_2 were previously used in probing the structure of mechanically interspersed polymer blends[30–32].

Sorption and desorption experiments were conducted for both the hard segment and the soft segment homopolymers along with the series of polyurethane copolymer samples. The transport experiments with the soft segment involved the use of a thin mould to mimic a slab geometry with only one side exposed to penetrant, since this sample is a viscous liquid at room temperature ($T_g = -68$°C) and cannot be cast as a free standing film. Approximate Fickian behaviour was verified with all permeants in this sample by the superposition of the sorption and desorption curves and the linearity of the initial stages of diffusion with the square root of time. The hard segment sample was compression-moulded into a slab geometry. Non-Fickian two-stage sorption characteristics with CO_2 were identified in this sample. Less pronounced non-Fickian behaviour was also found with O_2. It was not detected with N_2. The diffusivity in this sample was computed from the initial slope of a desorption experiment. Greater scatter in the data with N_2 and O_2 was found among the various methods of calculating diffusivities due to the larger experimental error (very small weight gain) involved in these measurements.

Some of the copolymer (19 to 75 wt% HS) samples presented various degrees of non-Fickian characteristics, but for our analyses the diffusivities were computed from the first plateau of the pseudo two stage sorption curves. All four classical methods of Fickian analyses were considered: half time (HT), initial slope (IS), limiting slope (LS) and the moment method (MM). A graphical summary of the experimental results is displayed in *Figures 8* to *11*. The ratio of the SS to the HS diffusivities with CO_2 was 45 and 28 for both O_2 and N_2. This ratio was higher than that previously deduced with conventional polyurethanes[14].

The diffusivities attained by all four methods were consistent (*Figures 8–11*). Larger predictions of the diffusivity by the initial slope method were found in agreement with the results of polymer blends[31]. Modelling and analysis for the transport properties of these samples are described in Part 2 of this study.

The transport of small molecules in the high soft segment content samples (above 60% SS) is dominated by the rubbery component and there is a negligible effect of the HS domains on the overall transport properties. The 70% HS sample has a continuous glassy phase with transport properties close to those of the pure HS segment.

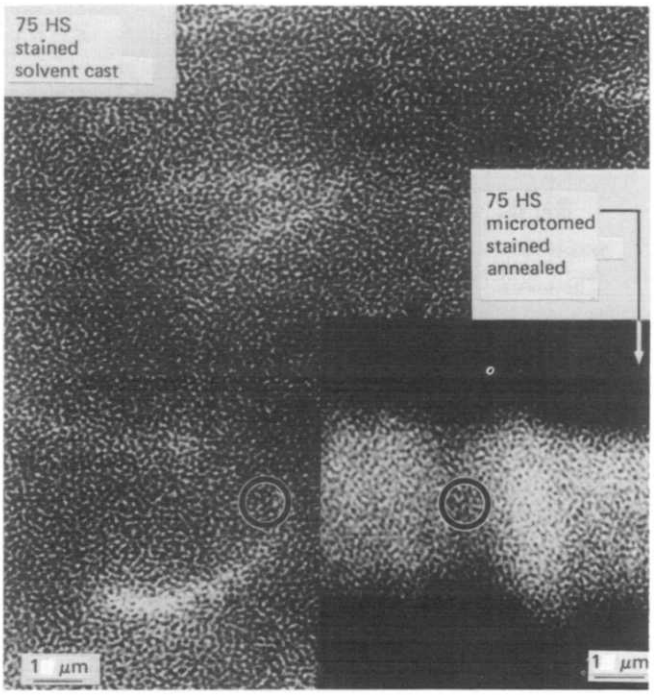

Figure 8 Electron micrograph of a microtomed unstained 75 wt% HS annealed polybutadiene polyurethane. The black phase presumably represents the glassy HS phase

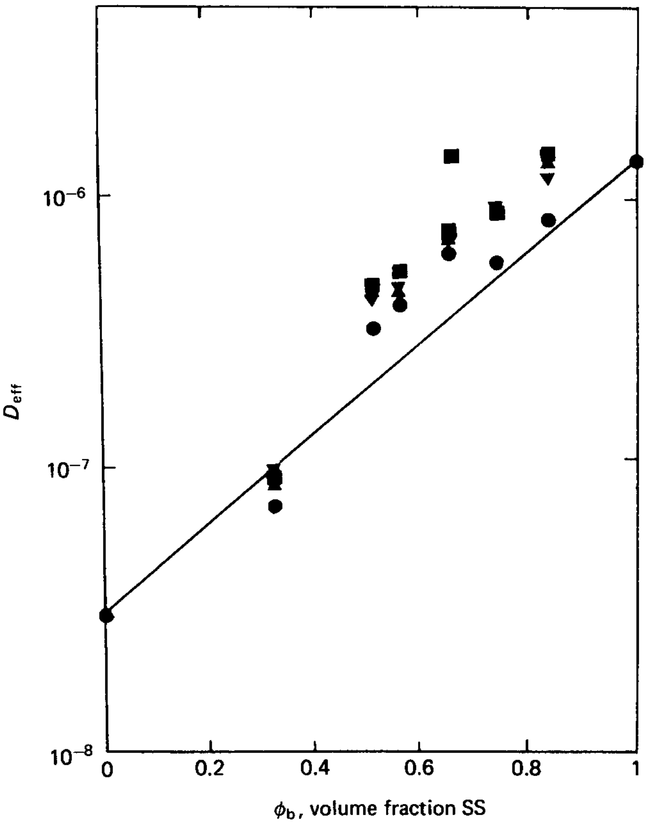

Figure 9 Transport properties (diffusion coefficients) of CO_2 ($cm^2 s^{-1}$) in solution-polymerized polybutadiene polyurethanes determined by the initial slope (IS, ■), half-time (HT, ●), moment method (MM, ▼) and limiting slope (LS, ▲) methods from sorption experiments. The hard segment is TDI/BDO and the soft segment is PBD/TDI

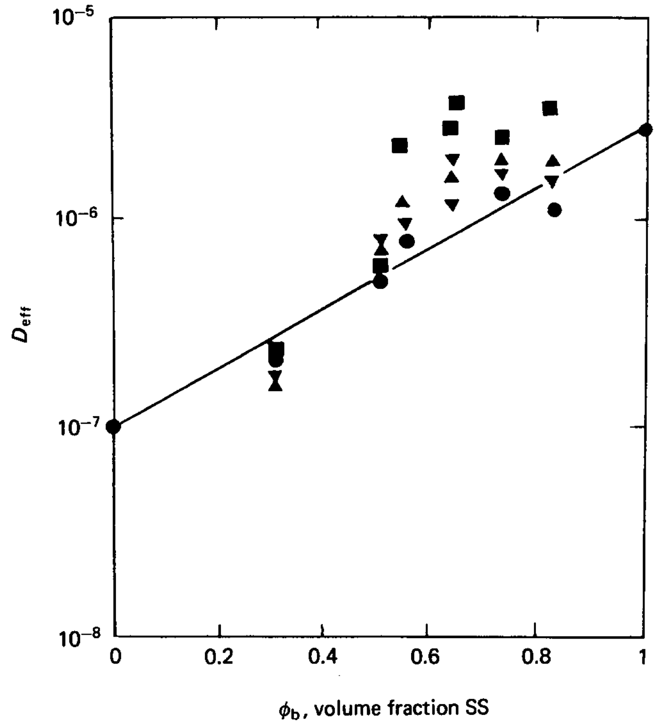

Figure 10 Transport properties (diffusion coefficients) of O_2 ($cm^2 s^{-1}$) in solution-polymerized polybutadiene polyurethanes. Symbols as in *Figure 9*

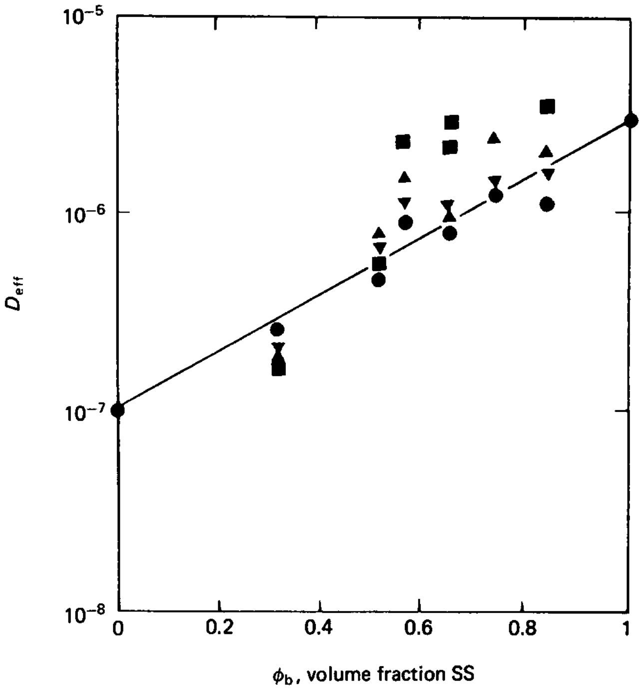

Figure 11 Transport properties (diffusion coefficients) of N_2 ($cm^2 s^{-1}$) in solution-polymerized polybutadiene polyurethanes. Symbols as in *Figure 9*

The solubility results (*Figure 12*) are similar to those obtained by Odani[16]. This type of behaviour has been carefully investigated by Mehta and Dole[33]. They also found a minimum in the solubility in diblock copolymers of styrene and butadiene using a quenching method. In our polybutadiene polyurethanes, CO_2 solubilities exhibit a distinct minimum around 75 wt% HS.

CONCLUSION

A series of well characterized solution-polymerized segmented polybutadiene polyurethanes has been investigated by transmission electron microscopy and sorption measurements. Both solution casting and microtoming methods of thin film preparation were employed. Micrographs provide additional experimental evidence for the presence of phase separation on the scale of 100 Å in samples with 44 to 75 wt% hard segment. However, microscopy data are not sufficient to assign specific morphologies, or to infer continuity of the phases, primarily as a consequence of the difficulty in the preparation of adequately thin films. At 33% hard segment composition, no clear indication by electron microscopy of phase separation was found, while the rest of the samples presented clear evidence of phase separation from both scattering and phase contrast mechanisms.

Transport studies of this model polyurethane sample show unique features not found in other phase-separated systems. A variable hard segment T_g and the distribution of domain type and size are complicating factors in the understanding of the transport properties in segmented copolymers. The domain connectivity and the phase inversion point were estimated at 60 vol% of hard segment. Incomplete phase separation was indicated from both the transport and morphological results in samples below 33 wt% HS.

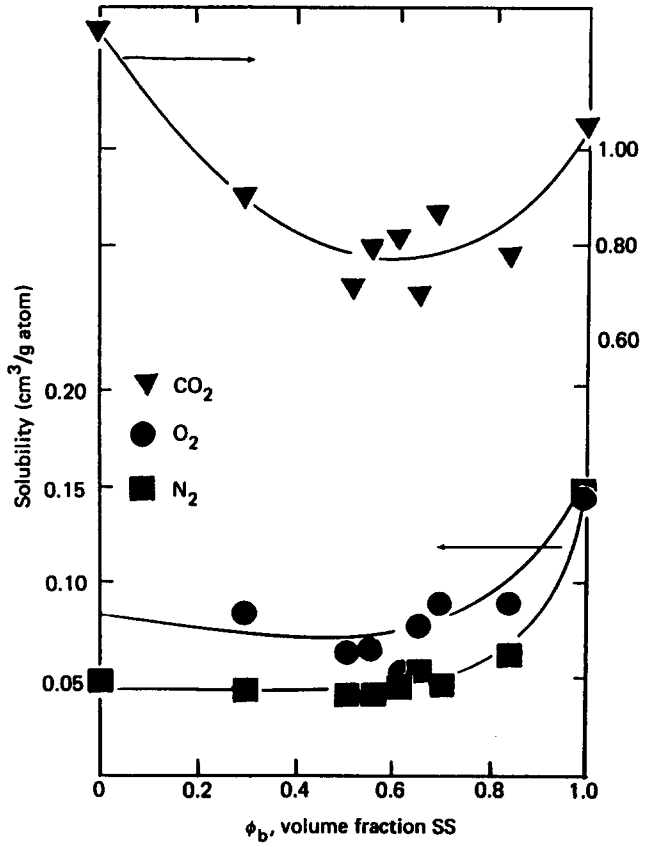

Figure 12 Solubility measurements of O_2, N_2 and CO_2 in polybutadiene polyurethanes from sorption experiments

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