

# Small-angle light scattering studies of macrophase separation in segmented polyurethane block copolymers

**Jeffrey T. Koberstein**

*Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA*

**and Richard S. Stein**

*Polymer Research Institute, University of Massachusetts, Amherst, MA 01003, USA  
(Received 22 October 1982; revised 5 February 1983)*

Quantitative small-angle light scattering (SALS) analysis is carried out on two similar segmented polyurethane block copolymers. The polyurethane prepared from toluene diisocyanate, is optically transparent, while a polyurethane prepared using the same soft segment, but with 4-4' diphenyl methane diisocyanate, scatters light appreciably. SALS investigation of the latter sample shows clearly that the scattering arises from the presence of long-range density fluctuations. Analysis of the density fluctuations is accomplished with the Debye-Bueche theory for random two-phase systems, incorporating a correction for the effects of multiple scattering. Application of this procedure leads to a correlation length of 4200 nm; corresponding well with the structure observed in optical photomicrographs. The occurrence of phase separation during polymerization is discussed as a possible origin for the observed macrophase structure.

**Keywords** Small-angle light scattering; macrophase separation; polyurethane; block copolymers

## INTRODUCTION

In recent investigations<sup>1,2</sup>, the microdomain morphology of two segmented polyurethane block copolymers and their interstitial composites was examined using the small-angle X-ray scattering technique. In these latter studies, small-angle light scattering (SALS) was also used to determine the macroscopic phase structure of the composites. In the course of the study, it was discovered that one of the polyurethane homopolymers itself gave appreciable SALS intensity while the other was optically transparent. The major difference between the two materials is the symmetry of the diisocyanate precursor that comprises the hard segment sequence. This paper presents initial SALS results for these materials and considers the reason for the difference in behaviour of the two systems and the origin of the apparent macroscopic phase structure that gives rise to SALS.

## EXPERIMENTAL

### *Samples*

The polyurethane block copolymers were kindly prepared by Dr. Robert Herold of the General Tire and Rubber Company of Akron, Ohio. Chemical compositions of the samples are shown in *Table 1*. The material denoted MDI/BD is based on a symmetric hard segment consisting of 4-4' diphenyl methane diisocyanate (MDI) chain extended with butane diol (BD), and a 10 000 molecular weight (number av.) soft segment of polypropylene ether triol end-capped with 10 wt%

ethylene oxide. The sample denoted TDI/EG contains hard segments formed from toluene diisocyanate (TDI) and ethylene glycol (EG). The TDI used is an 80:20 commercial mixture of the asymmetric 2,4-isomer and the symmetric 2,6-isomer. The soft segment for this material is a 50:50 mixture of number-average, 8300 molecular weight polypropylene ether diol and 7450 molecular weight polypropylene ether triol. The two samples have similar hard segment content and calculated hard segment sequence length distribution as shown in *Table 1*. Their preparation has been described previously<sup>1</sup>.

### *SALS*

Small-angle light scattering (SALS) measurements were recorded with a laser light-scattering apparatus equipped with a Princeton Applied Research Corporation Model 1205B Optical Multichannel Analyzer. This apparatus allows data to be recorded as many scattering angles simultaneously and is discussed in more detail in a previous report<sup>3</sup>. The light source was a Spectra Physics 4mW He-Ne laser with a wavelength of 632.8 nm. The incident radiation was monochromatized using an Oriel Optics Inc. laser line red filter and the incident intensity was regulated with neutral density filters. Regulation of the incident beam intensity was required to prevent flooding of the detector as a result of the limited dynamic range of the vidicon. This range is approximately two to three orders of magnitude. Samples were coated with refractive index fluid and placed between glass slides. As the MDI/BD material was very turbid, samples were cut

Table 1 Composition of polyurethanes

Sample designation	Diisocyanate	Chain extender	Soft segment	Number-average soft segment molecular weight	Number-average DI residues per hard segment	Reaction ratio <sup>a</sup>	Diisocyanate content (wt%)
MDI/BD	MDI	BD	Poly(propylene ether) triol end-capped with 10 wt% polyethylene oxide	10000	8.4	13.4 : 12 : 1	23.2
TDI/EG	TDI	EG	50% Poly(propylene ether) diol	8300	9.0	14.4 : 13 : 1	22.6
			50% Poly(propylene ether) triol	7450			

<sup>a</sup> Mol ratio of diisocyanate: chain extender: polyol

from mold flashing to minimize multiple scattering effects.

The SALS apparatus was interfaced to a cassette storage device to allow computer analysis and corrections of the scattering profiles. Experimental data was corrected for detector sensitivity and refraction, and computer smoothed using a progressive fit cubic smoothing routine. The apparatus was calibrated following a previously described procedure<sup>4</sup> such that scattering intensities could be expressed in terms of Rayleigh factors.

## RESULTS AND DISCUSSION

Turbidity measurements on MDI/BD resulted in  $\tau d$  values of  $\approx 2.1$ , where  $\tau$  is the turbidity and  $d$  is the sample thickness. The TDI/EG sample, however, was optically transparent. An explanation for the difference in behaviour of the two materials may be related to the difference in chemical structure between them; i.e., in the symmetry of the diisocyanate.

A first possibility that must be ruled out, however, is the presence of voids in MDI/BD. For this purpose, MDI/BD was lightly swollen in a variety of solvents after which the SALS behaviour was observed. If voids are present in a system, swelling leads to a large decrease in intensity as a result of the solvent filling the voids and drastically reducing the phase contrast. Swelling of MDI/BD, however, did not reduce appreciably the SALS intensity, indicating that voids were not the origin of the SALS.

A possible explanation for the difference of behaviour of the symmetric and asymmetric materials may reside in their respective abilities to crystallize. The asymmetric TDI/EG does not crystallize, while MDI polyurethanes have been shown to exhibit rodlike and spherulitic morphologies<sup>5,6</sup>. Polarized SALS measurements carried out in the latter study, showed that Maltese cross patterns typical of such morphologies were obtained under  $H_v$  or cross-polarization conditions, MDI/BD, however, did not show any detectable scattering intensity when placed between crossed polaroids. Furthermore, wide-angle X-ray scattering studies of MDI/BD provided no evidence for crystallinity in this material<sup>7</sup>. The turbidity in MDI/BD must, therefore, originate from the presence of density fluctuations rather than orientation fluctuations.

This observation implies that there is a macroscopic phase structure in MDI/BD because density fluctuations of the order of several micrometres are needed to scatter light. The optical photomicrograph shown in Figure 1

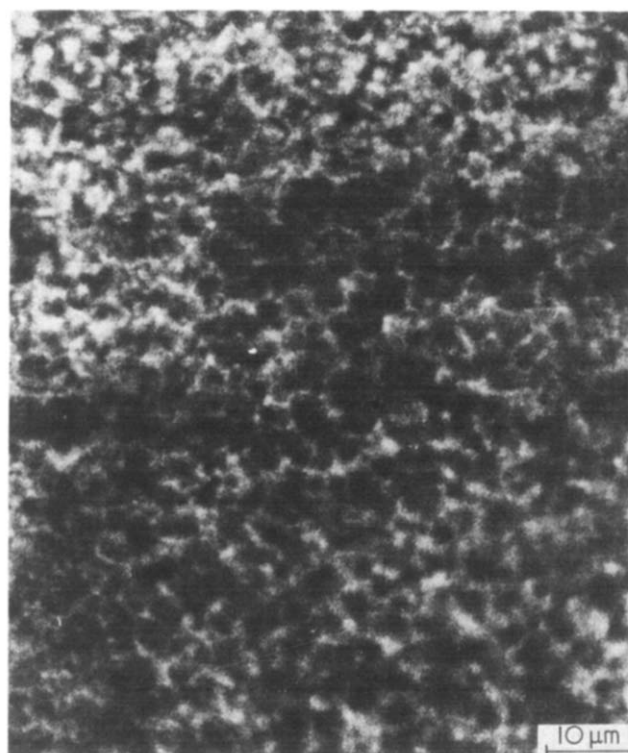


Figure 1 Optical photomicrograph of MDI/BD

confirms the presence of this macrophase structure. The structure is not well defined, but fluctuations are clearly visible with an average size of approximately 5  $\mu\text{m}$ .

Further characterization of the macroscopic phase structure in MDI/BD was accomplished by quantitative SALS measurements. The resulting  $V_v$  scattering profile is shown in Figure 2 as a function of the scattering angle  $\theta$ .

To interpret this scattering, a model for the phase structure must be chosen. Based on the photomicrograph in Figure 1, and the apparent absence of a maximum in Figure 2, the Debye-Bueche random two phase model<sup>8,9</sup> was applied. This model predicts that the Rayleigh factor for scattered radiation is given by:

$$R(h) = 8\pi(\omega/c)^4 \langle \eta^2 \rangle \frac{a^3}{(1+h^2 a^2)^2} \quad (1)$$

where  $\omega$  is the angular frequency of radiation of wavelength  $\lambda = 632.8 \text{ nm}$ ,  $c$  is the speed of light,  $\langle \eta^2 \rangle$  is the mean square fluctuation in polarizability,  $h$  is the

magnitude of the scattering vector ( $|h| = 4\pi/\lambda \sin\theta/2$ ), and  $a$  is the correlation length.

The correlation length is a measure of phase size and is determined from a plot of  $R^{-1/2}(h)$  versus  $h^2$ . The slope to intercept ratio of such a plot yields:

$$a = \left( \frac{\text{slope}}{\text{intercept}} \right)^{1/2} \quad (2)$$

The intercept of this plot may be used to calculate the mean square fluctuation in polarizability through the following relation:

$$\langle \eta^2 \rangle = \frac{(\text{intercept})^{-2}}{8\pi(\omega/c)^4 a^3} \quad (3)$$

A Debye–Beuche plot for MDI/BD is shown in Figure 3. The plot is rectilinear at intermediate angles but shows deviations at small  $h^2$  corresponding to a depletion of scattering intensity.

Similar behaviour is predicted from considerations of the effects of multiple scattering<sup>10</sup>. Direct analysis of the rectilinear linear asymptotic region in Figure 3 leads to apparent values of 2400 nm for the correlation length, and  $1.2 \times 10^{-6}$  for  $\langle \eta^2 \rangle$ .

An apparent correlation length may also be obtained through analysis of the density correlation function. The correlation function is obtained through Fourier transformation of the experimental scattering curve. The Debye–Bueche theory predicts a correlation function,  $\gamma(r)$  of form

$$\gamma(r) = e^{-r/a} \quad (4)$$

The experimental correlation function may then be fitted according to equation (4) to obtain a value for  $a$ . This analysis is shown in Figure 4 and leads to a value of  $a \approx 2200$  nm, in good agreement with the previous value. Again in this plot, however, deviations are obtained for

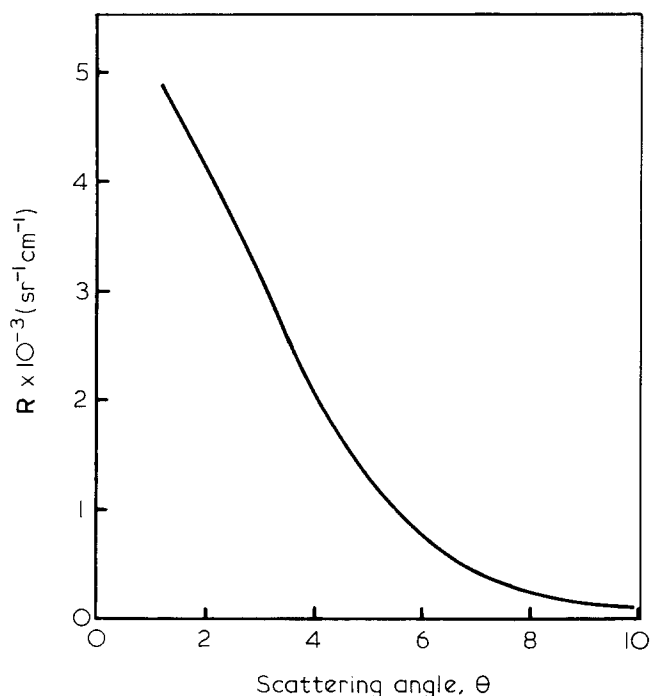


Figure 2 Rayleigh factor as a function of scattering angle for MDI/BD. Parallel polarization conditions

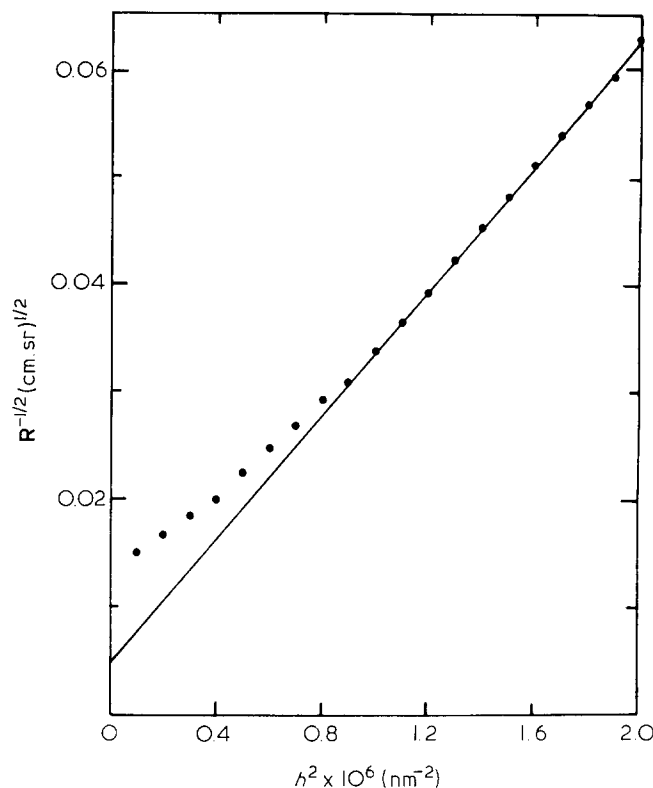


Figure 3 Debye–Bueche plot for MDI/BD. Solid line is fit of equation (1);  $a$ , 2400 nm

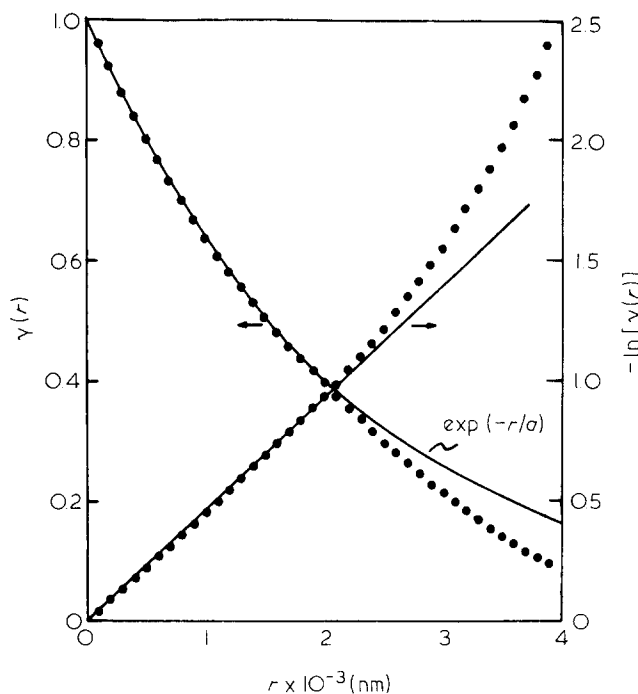


Figure 4 Analysis of exponential correlation function for MDI/BD. Solid lines are fits of equation (4);  $a$ , 2200 nm

large distance correlations (corresponding to deviations at small  $h$  as observed in Figure 3).

As mentioned previously, multiple scattering may be the cause of this deviation. Appreciable multiple scattering is expected in MDI/BD as a result of the high  $\tau D$  value of approximately 2.1. It should be noted that the film thickness employed was 0.06 mm, and that thinner films were not obtainable. Previous considerations of

multiple scattering<sup>10</sup> demonstrated that this effect leads to an overestimate in the apparent mean square polarizability fluctuation, and an underestimate of the apparent correlation length. Unfortunately, this work did not extend to values of  $\tau D = 2.1$ .

To estimate the effect of multiple scattering, the multiple scattering theory for the Debye-Bueche model<sup>10</sup> was used to generate theoretical intensity profiles that were fitted directly to the experimental scattering curve. This procedure was applied to fitting both the plot of the Rayleigh factor, and the Debye-Bueche plot. The best fit for the Debye-Bueche plot appears as the solid line in Figure 5. The parameters used to generate this fit are  $a = 4200$  nm,  $\langle \eta^2 \rangle = 5.5 \times 10^{-7}$ , and  $\tau D = 2.1$ . Values of  $\tau D$  in the range of 1.8–2.4 were examined, as this corresponds to a  $\pm 5\%$  precision in determination of the sample transmission. The fit was best, however, using the experimental value of  $\tau D = 2.1$ . The theoretical fit was not extremely successful, as seen in Figure 5. The experimental points oscillate around the theoretical fit, but deviate appreciably at small angles.

Similar behaviour is observed in the plot of the fitted Rayleigh factor in Figure 6. The best fit in this case is  $a = 3000$  nm. The criterion for best fit is very subjective in this case as a result of the wide range of Rayleigh factors, spanning two orders of magnitude. In fitting this profile, it was possible to fit either the high-angle or low-angle data well, but not both simultaneously. When the high-angle data were fitted, a value of  $a \approx 5000$  nm was obtained, whereas a value of  $a \approx 1400$  nm was obtained when the low-angle data were fitted.

The inability of multiple scattering considerations to account completely for the observed scattering profile may result from inapplicability of the Debye-Bueche random correlation function. Closer examination of Figure 4 suggests that there may in fact be more than one correlation length. This may also account for the observed inability to fit both the high- and low-angle data with a single correlation length. Similar observations have been made in light scattering studies of phase-separated polymer blends<sup>11,12</sup>. A number of model correlation

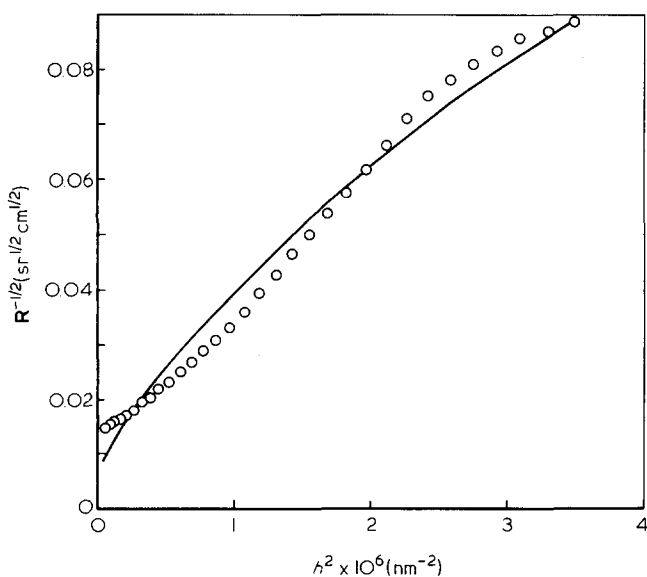


Figure 5 Debye-Bueche plot for MDI/BD. Solid line is theoretical best fit of equation (1) including for the effects of multiple scattering parameters obtained from this fit are  $a$ , 4200 nm;  $\langle \eta^2 \rangle$ ,  $5.5 \times 10^{-7}$ ; and  $\tau d$ , 2.1

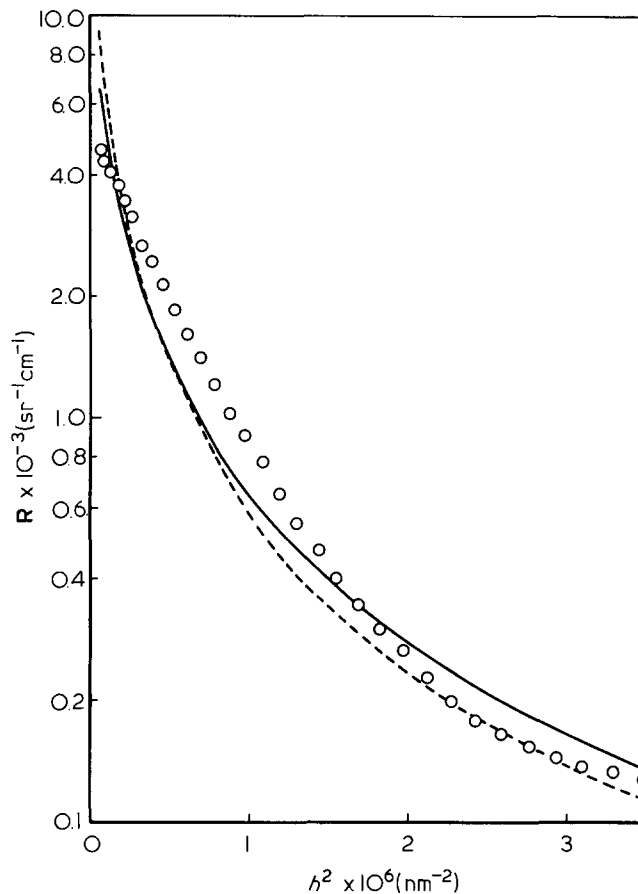


Figure 6 Semilog plot of Rayleigh factor as a function of  $h^2$  for MDI/BD. Dashed line is theoretical intensity accounting for multiple scattering;  $a$ , 4200 nm;  $\tau d$ , 2.1; solid line is theoretical intensity accounting for multiple scattering;  $a$ , 3000 nm;  $\tau d$ , 2.1

functions can be proposed that allow two or more correlation lengths<sup>12</sup>. The observation of two correlation lengths is generally attributed to contributions from both short- and long-range density fluctuations in the material.

It is possible that this type of macro-structure is also obtained in MDI/BD. These models, however, usually lead to a Debye-Bueche plot that curves down at low angles as a result of additional intensity arising from the long-range correlations. In the present case, the Debye-Bueche plot is found to curve up at low angles, corresponding to a depletion of scattering. A possible explanation for this may be obtained from closer examination of Figures 2 and 6. In these Figures a small shoulder is evident, indicative of perhaps a weak interference maximum in the scattering profile. The presence of maxima of this type have been detected previously in studies of phase separation of rubber-modified epoxies<sup>13</sup>. These materials are similar to MDI/BD in that the polymerization is in bulk, and that the phase separation occurs during polymerization. These authors applied the Debye-Bueche theory by extrapolating a smooth curve through the observed maxima. The correlation lengths obtained in this fashion corresponded well to the sizes of rubber domains observed by electron microscopy.

The observed oscillations in the Debye-Bueche plot for MDI/BD may arise from this same effect; i.e., amplification of the shoulder observed in the scattering profiles (Figures 2 and 6). The best fit traverses through the oscillations and, thus, is effectively extrapolating through the maximum as had been carried out in previous

work<sup>13</sup>. The observed fit is expected, therefore, to provide reasonable estimates of the correlation length and mean square fluctuation in polarizability. These parameters were given earlier as 4200 nm and  $5.5 \times 10^{-7}$ , respectively. This value of the correlation length corresponds well to the size of the fluctuations apparent in the photomicrograph in Figure 1.

The mean square fluctuation in polarizability can be examined to estimate a refractive index difference between phases by assuming a two-phase structure. In the absence of orientation fluctuations the two-phase model leads to<sup>8</sup>:

$$\langle \eta^2 \rangle = \phi_1 \phi_2 (\alpha_1 - \alpha_2)^2 \quad (5)$$

where  $\phi_1$  is the volume fraction of phase 1 and  $\alpha_1$  is its polarizability. The refractive index difference between phases is then calculated from the polarizability difference through application of the differentiated Lorenz-Lorentz equation:

$$(n_1 - n_2) = \frac{2}{3} \pi \frac{(n^2 + 2)^2}{n} (\alpha_1 - \alpha_2) \quad (6)$$

where  $n_1$  is the refractive index of phase 1 and  $n$  is the mean refractive index. Taking the volume fraction of phases as 0.5 and the mean refractive index as 1.5, application of this procedure yields a refractive index difference of 0.0125 for MDI/BD.

This value is reasonable considering the values of refractive indices of the polyurethane copolymer building blocks. The refractive indices of BD, MDI, and the polyether soft segment are approximately 1.45, 1.47, and 1.61, respectively. Based upon these values, a refractive index difference of 0.0125 may easily be obtained by assuming a composition variation within the sample. This provides support for the interpretation of the scattering in terms of macroscopic phase separation.

Several plausible explanations may be considered that account for macrophase separation in polyurethane elastomers. Gallacher and Bettleheim<sup>14</sup> observed similar SALS behaviour during the curing of polyesters. Their interpretation was that the curing was incomplete leading to the formation of microgel particles surrounded by partially cured material. The partially cured material provided the phase contrast. Incomplete curing for the polyurethanes could result from isocyanate side-reactions that would lead to non-stoichiometric reaction ratios. The drawback of this interpretation is that it does not clearly account for the difference in behaviour of MDI/BD and TDI/EG.

An alternative explanation for compositional variations in polyurethanes is that the initial mixing process is inhomogeneous or that the monomers themselves do not mix. This explanation has been invoked to explain the opacity present during the preparation of reaction injection molded polyurethanes<sup>15</sup> and has been proposed recently for polyurethanes containing polybutadiene soft segments<sup>16</sup>. The compatibility of monomer species dictates the degree to which this effect occurs.

Previous studies<sup>1</sup> suggest that the MDI/BD system possesses a higher degree of microphase separation than TDI/EG, and these ideas may apply to macrophase separation as well. In contrast to the polybutadiene systems, however, the monomer mixtures are transparent for these systems. The opacity in MDI/BD develops during the polymerization process. The same phenomena as seen by MacKnight *et al.*<sup>16</sup> is occurring, but in this case

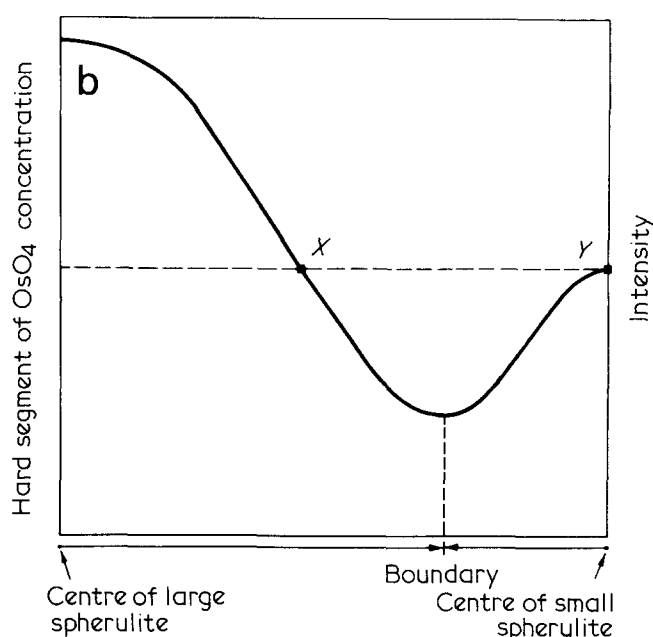
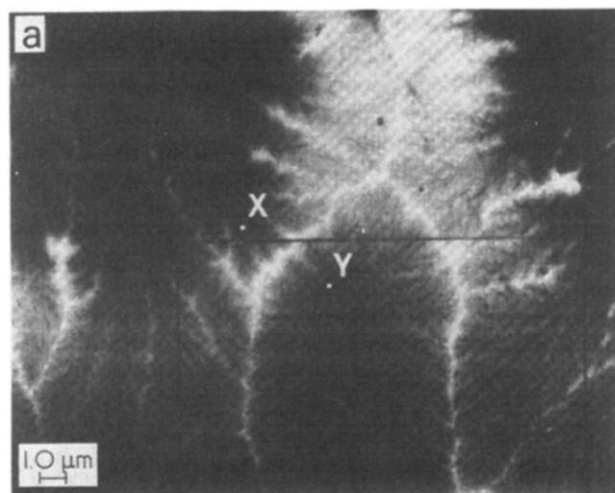


Figure 7 (a) Electron micrograph of  $O_3O_4$ -stained MDI spherulite; (b) corresponding hard segment concentration profile (axis drawn along points X and Y). Reprinted with permission from ref. 5

the mixture starts out compatible and goes through a critical point for phase separation during polymerization. That is, during polymerization, oligomers of a certain size may associate, become insoluble, and subsequently phase separate.

Buist and Gudgeon<sup>17</sup> have suggested that this effect provides an explanation for opacity differences in polyurethanes. They state that TDI polyurethanes are usually transparent even at high urethane concentration, whereas polyurethanes based on symmetric diisocyanates such as 1,5-naphthalene, 1,4-phenylene and MDI are usually opaque. They further state that the opacity develops gradually during polymerization and is believed to be the result of strong interactions between urethane segments. The interactions are stronger for the symmetric diisocyanates and provide a driving force for phase separation in addition to the intrinsic thermodynamic incompatibility.

Recent work by Castro *et al.*<sup>18</sup> has predicted phase separation during polymerization for MDI/BD. Based on

consideration of the reaction kinetics, a critical number-average polymerization index of approximately 1.5 hard segment units is obtained; i.e. hard segments phase separate when their polymerization index attains 1.5. Experimental observation of viscosity and turbidity changes were found to correlate well with their model. During polymerization, this effect would lead to depletion of the hard segment content of the monomer bulk as hard segment oligomers phase separate. Growing particles in the polymeric phase would then develop a radial hard segment gradient as a result of the monomer depletion.

Electron micrographs of bulk polymerized polyurethanes<sup>5</sup> provide evidence for this type of structure. In these studies, osmium tetroxide staining was darker in the central regions of spherulites and decreased with radial position as shown in *Figure 7*. The size of these regions is similar to the correlation length observed for MDI/BD. *Figure 7* also gives an approximate hard segment concentration profile as determined from the stain density. These authors proposed that the effect resulted from phase separation during the solvent casting procedure. A similar process of phase separation would be expected to occur during polymerization, and may lead to a similar superstructure. MDI/BD is not crystalline, however, a non-crystalline analogue of a spherulite, perhaps more appropriately an 'onion' morphology, is probable. In the case of MDI/BD, the thickness of the 'onion layers' or hard segment domains would be largest near the centre of the superstructure as a result of the previously described monomer depletion effect.

A distribution of hard segment domain thicknesses of this type corresponds well to results of small-angle X-ray scattering (SAXS) analyses of MDI/BD<sup>1</sup>. In these studies, the breadth of the scattering maximum and analysis of the correlation function revealed a broad distribution of interdomain spacings. Such a distribution is expected for the hard segment gradient shown in *Figure 7*. The hard segment domain thickness is approximately proportional to its concentration, while the soft segment domain thickness is relatively constant as its molecular weight is independent of concentration. The interdomain spacing is related to the sum of the domain thicknesses and, thus, would depend upon local hard segment concentration. The hard segment concentration gradient, therefore, leads to a distribution of interdomain spacings. SAXS studies of TDI/EG<sup>1</sup> showed that the distribution of interdomain spacings is very sharp for this material. This observation suggests that there are no hard segment concentration gradients in TDI/EG. The absence of experimental SALS intensity in TDI/EG is then expected.

It is evident that the occurrence of phase separation during bulk polymerization provides a reasonable explanation for the opacity in MDI/BD. The transparency of TDI/EG, however, indicates increased compatibility in this system as is also reflected in the poorer microphase separation seen by SAXS<sup>1</sup>. Considering only the 'aromatic' character of the diisocyanates, this result is expected, as TDI has only one phenyl residue while MDI has two per molecule. In addition, the greater enthalpy of association for the symmetric MDI hard segments provides an additional free energy contribution that favours phase separation. The critical molecular weight for phase separation, therefore, is larger for TDI/EG and may not be attained during the polymerization.

Finally, the difference in symmetry can also lead to different reaction kinetics for the two polymers. Data on reaction rates for TDI<sup>19</sup> show that the rate of addition to the first isocyanate in TDI is 25 times as fast as the rate of addition to the second isocyanate. The same data on MDI and other symmetric diisocyanates yield a corresponding factor of 2-3 for the ratio of rate constants. These values indicate that long sequences build up faster in the case of symmetric diisocyanates, thus favoring the onset of phase separation. In the asymmetric polyurethanes the build up of molecular weights is more homogeneous and they are perhaps not as susceptible to phase separation.

From the preceding discussion it is clear that arguments concerning the susceptibility for phase separation during polymerization provide a consistent explanation for the results of SALS, SAXS, and optical microscopy experiments on MDI/BD. Modelling of the light scattering with the simple random two-phase model with provision for a multiple-scattering correction yields reasonable estimates of the refractive index difference between phases and correlation length, but is only partially successful in quantitatively fitting the experimental scattering function. Quantitative analysis of the SALS of MDI/BD is limited by two factors: the sample is extremely turbid, leading to appreciable multiple scattering; little is known about the structure of the heterogeneities in MDI/BD, thus making specification of a more complete structural model difficult. The problem of turbidity may be overcome by microtoming samples. Specification of a more sophisticated model, however, is a much more difficult task with no obvious solution. Such a structural model must take into account the actual mechanism of phase separation during polymerization. Factors that would favour this process include increases in molecular weight, incompatibility, or symmetry (i.e. enthalpy of association). A structural model would have to take into account these factors as well as the kinetics of phase separation to describe the development of phase structure during polymerization. Considerations of this level of complexity are beyond the scope of this initial investigation. It is evident, however, that the occurrence of phase separation during polymerization will alter the sequence length distribution and influence greatly both the macroscopic and microscopic morphology. This phenomena effects directly the optical properties of polyurethanes, but at this time, little is known about the influence that this structural alteration may have on mechanical properties. The extensive use of bulk polymerized polyurethanes warrants further investigation in this area.

## CONCLUSION

SALS characterization of MDI/BD reveals the presence of long-range density fluctuations. A theoretical model assuming a random two-phase structure and taking into account the effects of multiple scattering is used to analyse the scattering profile. The model is found to fit the experimental results only qualitatively, but the resultant correlation length of 4200 nm is found to correspond well to the size of inhomogeneities observed in optical photomicrographs. The presence of the inhomogeneities are explained well by assuming that this system undergoes phase separation during bulk polymerization.

ACKNOWLEDGEMENTS

Supported by grants from the General Tire and Rubber Company, the National Science Foundation and the Materiale Research Laboratory of the University of Massachusetts. One of the authors (JTK) wishes to acknowledge partial support of this research under a National Science Foundation Grant (DMR-8105612).

REFERENCES

- 1 Koberstein, J. T. and Stein, R. S. submitted to *J. Polym. Sci. Polym. Phys. Edn.* 1983, **21**, 1439; 1983, *21*, 2181
- 2 Koberstein J. T. and Stein, R. S. submitted to *J. Polym. Sci. Polym. Eng. Sci.*
- 3 Wasiak, A., Peiffer, D. and Stein, R. S. *J. Polym. Sci. Polym. Lett. Ed.* 1976, **14**, 381
- 4 Russell, T. P., Koberstein, J., Prud'homme, R., Misra, A., Stein, R. S., Parsons, J. W. and Rowell, R. L., *J. Polym. Sci. Polym. Phys. Edn.* 1978, **16**, 1879
- 5 Fridman, I. D. and Thomas, E. L. *Polymer* 1980, **21**, 388
- 6 Kimura, I., Ishihara, H., Ono, H., Yoshihara, N., Nomura, S. and Kawai, H. *Macromolecules* 1974, **7**, 355
- 7 Koberstein, J. T. *Ph.D. Dissertation* University of Massachusetts, Amherst, MA, 1979
- 8 Debye, P. and Bueche, A. M. *J. Appl. Phys.* 1949, **20**, 518
- 9 Debye, P., Anderson, Jr., H. R. and Brumberger, H. *J. Appl. Phys.* 1957, **28**, 679
- 10 Koberstein, J. T. and Stein, R. S., *J. Polym. Sci., Polym. Phys. Ed.* 1980, **18**, 199
- 11 Moritani, M., Inoue, T., Motegi, M. and Kawai, H. *Macromolecules* 1970, **3**(4), 433
- 12 Yuen H. and Kinsinger, J. *Macromolecules* 1974, **7**, 329
- 13 Visconti, S. and Marchessault, R. *Macromolecules* 1974, **7**(6), 913
- 14 Gallacher, L. and Bettleheim, F. *J. Polym. Sci.* 1962, **58**, 697
- 15 Fridman, I. D., Thomas, E. L., Lee, L. J. and Macoski, C. W. *Polymer* 1980, **21**, 388
- 16 Xu, Mao and MacKnight, W. J. in preparation
- 17 Buist, J. M. and Gudgeon, H. (Eds.) 'Advances in Polyurethane Technology' McLaren and Sons, Ltd., London, 1968, pp. 105-106
- 18 Castro, J. M., Lopez-Serrano, F., Macosko, C. W. and Tirrell, M. *J. Appl. Polym. Sci.* 1981, **26**, 2067
- 19 Lenz, R. W. 'Organic Chemistry of Synthetic High Polymers' John Wiley and Sons, New York, 1967, 185