polymer papers

The thermal response of the polyether soft segment chain conformation in a polyurethane block copolymer measured by small-angle neutron scattering

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The conformation of the soft segment chains in a pair of polyether polyurethanes was studied as a function of temperature using small angle neutron scattering. The samples were synthesized from 3 moles of methylene bis(*p*-phenyl isocyanate), 2 moles of butanediol, and one mole of a poly(tetramethylene oxide) (PTMO) blend. The PTMO blend was composed of 0.325 moles of deuterated PTMO (d-PTMO) and 0.675 moles of hydrogenous PTMO. This degree of deuterolabelling was chosen so that there would be no interphase scattering in the final sample; only intrachain scattering from the labelled soft segments comprised the coherent part of the total scattering. At room temperature, the average soft segment was found to be in an extended conformation. As the temperature was raised from room temperature, the radius of gyration of the soft segments decreased. This was attributed to the stress exerted by the extended soft segments on the adjoining hard segments increasing as the temperature was increased. The increased stress causes some of the hard segments to pull out of the hard domain into the soft phase, thereby allowing the soft segments adjacent to the extracted hard segment to relax to a more compact conformation. As the temperature was increased above 160°C, the soft segment radius of gyration increased slightly. This behaviour is ascribed to an increased degree of mixing between the phases. The presence of substantial amounts of hard segment material in the soft phase causes the increase in the soft segment R_g due to the greater compatibility between the soft and hard segments in the soft phase at these elevated temperatures. This effect is similar to a homopolymer being swollen by a small amount of a good solvent, where the chain conformation is a random coil, but the radius of gyration is larger than that measured for the pure material.

(Keywords: polyurethane; block copolymer; small-angle neutron scattering; chain conformation)

INTRODUCTION

Polyurethane block copolymers have received a great deal of study during the last decade. This is primarily due to the two phase structure of these materials in the solid state which is responsible for their excellent mechanical properties. The soft phase of these materials is usually an amorphous, rubbery mixture composed of soft segments which can be either polyether-, polyester- or polyalkylglycols. Recently polydimethylsiloxanes have also been used as the soft segment for biocompatible polyurethanes. The soft phase also contains small amounts of the hard segment material due to incomplete phase separation and partial compatibility between the segment types. The hard phase consists mainly of hard segments, which are composed of alternating sequences of short diisocyanate units and diol or diamine units. The hard phase also includes some soft segments due to incomplete phase separation. The molecular weight of the hard and soft segments is on the order of several thousand. The hard phase acts as a multifunctional crosslink and as a reinforcing filler for the soft phase for polyurethane materials with a hard segment content between 30% and 70% by weight.

A number of techniques have been used to study the microstructure of polyurethane systems including dynamic mechanical studies, dielectric measurements, thermal analysis, electron microscopy, infrared dichroism, and small-angle X-ray and neutron scattering. The morphology observed by these techniques in polyurethanes containing between 30% and 70% by weight of hard segment material is one consisting of hard phase lamellae or pseudolamellae imbedded in a soft matrix phase[1]. The phase separation is not complete; hard segments are observed in the soft phase and *vice versa*[2]. A spherulitic superstructure can be seen in some systems, particularly those with a high hard segment content where the hard segments are crystallizable[3]. Small-angle neutron scattering results have shown that the poly(tetramethylene oxide) soft segment in a polyether polyurethane with a moderate hard segment content is in a somewhat extended conformation relative to the bulk oligomer[4].

Small-angle neutron scattering (SANS) has been used by several researchers to determine the chain conformation of one of the blocks in a two-phase block copolymer. Two principal methods are used to obtain this

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information. The first involves a sample where one of the phases has some of the chains labelled with deuterium and where the sample has a very regular microstructure. This regularity is needed so that when the sample is properly aligned with the incident neutron beam no interphase scattering results. Hadziioannou *et al.*[5] studied a diblock copolymer system of styrene and isoprene that exhibited a uniform lamellar morphology. The SANS data were acquired with the lamellar surfaces perpendicular to the incident beam which caused the interphase scattering to vanish. Only the scattering due to the partially labelled styrene chain segments was observed. Hadziioannou *et al.*[5] reported that the styrene blocks are in an extended conformation relative to the conformation in bulk polystyrene, with the long axis of the molecule being perpendicular to the lamellar surface.

The second method available for obtaining the single chain scattering from a two-phase material requires scattering data from two samples. The first sample has one of its phases partially labelled with deuterated chains. The second sample, which must have the same microstructure and chemical composition as the first, contains no deuterated chains. The single chain scattering from the partially labelled phase can be obtained by a weighted subtraction of the scattering from these two samples, as has been described by Koberstein[6] and Jahshan and Summerfield[13,14]. Bates *et al.*[7] investigated a diblock copolymer of styrene and butadiene using this method. The butadiene segments consisted of a mixture of labelled and unlabelled chains. The morphology of this material featured spherical butadiene domains within a styrene matrix. The butadiene chains were found to be in a random coil, or Gaussian, conformation, similar to that found in bulk polybutadiene.

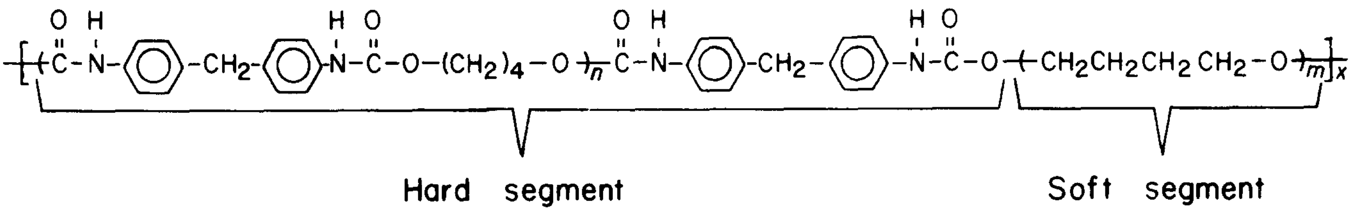
Miller *et al.*[4] investigated the conformation of the soft segment in a polyether polyurethane elastomer by this method. The average poly(tetramethylene oxide) segment was found to be somewhat extended when compared with the conformation of the segment in the bulk oligomer[8]. This study also established that the reliability of the SANS data in such an experiment can be improved by using a phase contrast matched sample. In such a sample, the degree of labelling of the appropriate segment type is such that no interphase scattering occurs. The necessary condition for this is that the coherent scattering length density of each of the two phases is equal. Miller *et al.*[9] applied this principle in determining the conformation of the polyether soft segment, the polyester hard segment, and the entire chain in an investigation of medium and high hard segment content polyether–polyester block copolymers. The change in the segmental and whole chain conformation in response to a rise in temperature was also studied. These materials exhibit a two-phase morphology similar to that of polyether polyurethanes. The authors reported that the soft segments are in a slightly extended conformation relative to the bulk oligomer. Upon heating, the soft segment conformation approached the bulk conformation due to a relaxation of internal stresses. The polyester hard segment was shown to be in a chain folded configuration at room temperature with a folding repeat of three to four hard segment units. As the samples were heated, the hard segments become more extended as some of the segments unfold into a more extended crystalline conformation. The radius of gyration of the whole polymer chain was reported to drop and then to rise as the temperature was increased. A two mechanism competitive process was proposed to explain these observations.

The objective of the present study was to examine the effect of heating on the conformation of the polyether soft segment in a polyurethane elastomer. It is well known that polyurethanes undergo morphological changes as they are heated. For example, Koberstein *et al.*[10,11] propose a phase mixing–demixing transition in segmented polyurethanes around 150°C in order to account for data obtained using small-angle X-ray scattering (SAXS) and differential scanning calorimetry (d.s.c.). By studying the conformation of the soft segment in response to changes in temperature, it is hoped that a better understanding of the changes in morphology that occur in polyurethanes at elevated temperatures can be obtained.

EXPERIMENTAL

The samples used in this study were prepared by a two-step solution polymerization. Methylene bis(*p*-phenyl isocyanate) (MDI, Eastman Kodak Co.) was purified by melt filtration followed by recrystallization in n-hexane at 0°C. 1,4-butanediol (Aldrich Chemical Co.) was vacuum distilled prior to use. The poly(tetramethylene oxide) (PTMO, DuPont Teracol 1000) was dried in a vacuum oven for 48 h at 50°C prior to use. The deuterated PTMO was prepared by a ring opening polymerization procedure. This material has been characterized by high performance liquid chromatography and neutron scattering[8]. The MDI, the PTMO and the deuterated PTMO (d-PTMO) were reacted in dimethyl acetamide (DMAc) solution (30% by weight) for 1 h at 70°C under a nitrogen purge. The butanediol chain extender was then added, and the entire mixture was allowed to react for an additional 3 h. The overall stoichiometry was 3 moles of MDI, 2 moles of butanediol, and one mole of the PTMO oligomers. The PTMO consisted of a blend of 32.5 mole per cent d-PTMO and 67.5 mole per cent hydrogenous PTMO. This ratio of d-PTMO to PTMO was chosen so that the sample would be phase contrast matched[4]. The polymer was precipitated from solution using distilled water. After several washings with distilled water, the samples were dried under vacuum for one week at 50°C. The polymer structure is shown in *Figure 1*. The scattering samples were prepared by compression moulding at 180°C and 20 MPa for 10 min, followed by cooling to room temperature over a time span of 5 min. The samples were stored under dessication until needed for the scattering experiments.

The small angle neutron scattering data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory on the Small Angle Diffractometer (SAD) instrument. This facility has been described in detail elsewhere[12]. The operating conditions for this set of experiments were as follows: Q range: 0.008–0.35 Å^{-1}, resolution: 0.004 Å^{-1}, flux at the sample: $\sim 4\times10^4$ neutrons s^{-1} cm^{-2}. The samples were heated and held at a fixed temperature inside a helium purged vacuum furnace while the scattering data were being gathered. Data were collected for about 4 h at each temperature level, giving a total count at the detector of ~200 000 neutrons. While it would be desirable to get more counts in order to improve the signal to noise ratio, the increased time required could cause an increase in the thermal degradation of the sample.



$$\cdots H_n - S_m - H_n - S_m - H_n \cdots$$

Figure 1 Polyether–polyurethane structure. In this study, $\langle n \rangle = 2$ and $\langle m \rangle = 14$

THEORY

The single chain scattering from the labelled segments in a two-phase partially labelled material can be obtained by a weighted subtraction. The equation describing this technique is described by Koberstein[6].

$$(R_L(q) - R_{\mathrm{inc,L}}) - \left[\frac{\beta_A - x\beta_{BD} - (1-x)\beta_{BH}}{\beta_A - \beta_{BH}}\right]^2 (R_U(q) - R_{\mathrm{inc,U}}) \tag{1}$$
$$= \frac{4\pi}{V_S}(b_{BD} - b_{BH})^2 N_{BT} Z_B^2 x(1-x) P_B(q)$$

In this expression, $R_L(q)$ and $R_U(q)$ are the total scattering contributions from a partially labelled sample and a completely unlabelled sample, $R_{\mathrm{inc,L}}$ and $R_{\mathrm{inc,U}}$ are the incoherent background scattering terms for the labelled and unlabelled samples, and $P_B(q)$ is the single chain scattering function for the chains in the labelled B phase. β_A is the coherent scattering length density of pure A segments, β_{BH} and β_{BD} are the coherent scattering length densities for pure protonated B segments and pure deuterated B segments, and x is the fraction of the B chains that are deuterated. V_s is the irradiated sample volume, b_{BH} and b_{BD} are the monomeric coherent scattering lengths for the protonated and deuterated B monomers, N_{BT} is the total number of B chains present in the scattering volume, and Z_B is the average degree of polymerization of the B segments. $P_B(q)$ is the single chain scattering function, also known as the structure or form factor for the B segments or as the intramolecular interference function. An expression equivalent to equation (1) has also been derived independently by Jahshan and Summerfield[13,14].

At a particular value of x, the interphase scattering from the labelled sample vanishes. This is known as the phase contrast matched condition.

$$\beta_A - x\beta_{BD} - (1-x)\beta_{BH} = 0 \tag{2}$$

The advantage of having a phase contrast matched sample is that there is no need to perform a subtraction in order to obtain the single chain scattering. This eliminates the difficulty in making two samples with exactly the same microstructure. The overall error in the measurement of the single chain scattering is also reduced. In the present investigation the samples are phase contrast matched. Approximately 30% of the PTMO segments are deuterated, which may cause problems with the data analysis since this is not a dilute system. However, Ackasu *et al.*[15] and Wignall *et al.*[16] have shown that the degree of deuteration does not affect the radius of gyration as measured by neutron scattering experiments. It has also been shown that there is little correlation between pairs of deuterated segments, and hence there is little contribution to the scattering from such a correlation[9]. In other words, PTMO–MDI–PTMO subsequences where both of the PTMO segments are deuterated do not contribute significantly to the scattering.

Equation (2) may not be applicable over a wide temperature range because of the differences in the thermal expansion coefficients of the hard and soft phases. The linear thermal coefficient of expansion is 1.6×10^{-4}°C for the poly(tetramethylene oxide) oligomer as determined from density measurements at a variety of temperatures[24]. The linear coefficient of thermal expansion was measured at 2.2×10^{-4}°C for the polyurethane samples used in this investigation. The difference between the hard and soft phase coefficients is therefore fairly small. This leads to a difference in the coherent scattering length density of about 5% in the worst case. This implies that the interphase scattering contribution to the total scattering will be less than 0.5% of the interphase scattering in an unlabelled sample based on the coherent scattering length densities of the protonated soft and hard phases and the phase contrast matched soft phase[4]. The interphase scattering contribution due to a difference in the thermal expansion coefficients between the two phases is therefore negligible, even at the highest temperature studied.

For a phase contrast matched sample, only intrachain scattering and incoherent scattering occur, so we can write

$$R_{\mathrm{coh}}(q) = \frac{4\pi}{V_S}(b_{BD} - b_{BH})^2 N_{BT} Z_B^2 x(1-x) P_B(q) \tag{3}$$

In this expression, $R_{\mathrm{coh}}(q)$ is the coherent part of the scattering from the phase contrast matched sample. The incoherent portion of the scattering is not considered here. It can be expressed as a constant, and will be included as such in the modelling process to be discussed. Equations (1)–(3) were derived on the assumption that no phase mixing occurs. For polyurethane materials, this is not a valid assumption, since a substantial amount of intersegmental mixing occurs. However, the condition for phase contrast matching remains the same[9], so that if equation (2) is valid for a pure phase material, then it is also true if there is phase mixing in the material. This allows one to design phase contrast matched materials when the densities of the pure hard and soft phases are known. Knowledge of the composition of the individual phases is not required. A phase contrast matched sample exhibits only chain scattering regardless of the degree of phase separation.

The labelled soft phase in this investigation consists of a blend of hard segments, protonated soft segments, and deuterated soft segments. Hadziioannou and Stein[17] have expressed the neutron scattering from such a single phase, two component blend, where one of the components consists of labelled and unlabelled chains, as

$$R_L(q)=\frac{4\pi}{V_S}(b_{BD}-b_{BH})^2N_{BT}Z_B^2x(1-x)P_B(q)+\frac{4\pi}{V_S}\left[xb_{BD}+(1-x)b_{BH}-b_A\left(\frac{V_B}{V_A}\right)\right]^2N_{BT}Z_B^2(P_B(q)+N_{BT}Q_{BB}(q)) \quad (4)$$

where V_A and V_B are the molar volumes of the repeat units for A and B. $Q_{BB}(q)$ is the intermolecular interference function and $P_B(q)$ is the intramolecular interference function. An equivalent expression was derived by Warner *et al.*[18]. The factor that is shown in square brackets for the second part of the right hand side of equation (4) is zero whenever the phase contrast matched condition applies. Since this factor multiplies the intermolecular interference term, the only coherent scattering that occurs when the sample is phase contrast matched is due to the labelled and unlabelled B segments. No chain scattering occurs due to the presence of phase mixing. In a phase contrast matched material, the only coherent scattering that occurs is due to correlations between labelled and unlabelled segments of the same type. There is no contribution due to interphase scattering or due to correlations between different segment types.

Once the single chain scattering data have been obtained, they must be fit to some physical model. For random particle shapes, Guinier's law is often used[19].

$$\lim_{q\to 0}R(q)=K\mathrm{e}^{-q^2R_g^2/3} \quad (5)$$

In this equation, R_g is the radius of gyration of the particle. Guinier's law is only applicable at low values of q, where the product qR_g is less than one. A number of researchers have applied this equation with some success to SANS data beyond the normal upper limit on q, but this is not the best method of data analysis. A more sensible approach is to fit all of the scattering data to a model, not just the lowest angle data. For bulk amorphous polymers, the random coil model is usually used. The scattering from a random coil is given by the Debye function.

$$F(q)=\frac{2}{z^2}(\mathrm{e}^{-z}+z-1) \quad (6)$$

where $z=q^2R_g^2$ and R_g is the radius of gyration of the coil. When using such a modelling approach, the numerical results obtained tend to be model dependent, although the trends observed are usually correct. For this experiment, the data was modelled to

$$I(q)=AF(q)+I_{\mathrm{inc}} \quad (7)$$

where A is a constant of proportionality and I_{inc} is the incoherent scattering, which is taken to be a constant that accurately reflects the background scattering contribution[6]. $F(q)$ is the form factor for a Gaussian coil defined in equation (6). A least squares nonlinear regression routine that generates best fit parameters as well as error estimates was used to fit the single chain scattering data.

The value of the radius of gyration of the soft segment obtained by the fitting of equation (7) to the whole scattering curve is a z-average value. To correct for the polydispersity of the soft segment, the distribution of segment lengths must be known along with knowledge of how the radius of gyration changes as a function of the molecular weight. The applicable polydispersity equations are

$$\frac{\langle R_g^2\rangle_z}{\langle R_g^2\rangle_w}=\frac{\sum_{i=1}^{\infty}N_iM_i^2R^2(i)}{\sum_{i=1}^{\infty}N_iM_i^2}\,\frac{\sum_{i=1}^{\infty}N_iM_i}{\sum_{i=1}^{\infty}N_iM_iR^2(i)} \quad (8a)$$

$$\frac{\langle R_g^2\rangle_z}{\langle R_g^2\rangle_n}=\frac{\sum_{i=1}^{\infty}N_iM_i^2R^2(i)}{\sum_{i=1}^{\infty}N_iM_i^2}\,\frac{\sum_{i=1}^{\infty}N_i}{\sum_{i=1}^{\infty}N_iR^2(i)} \quad (8b)$$

where the n, w and z subscripts refer to the particular average being taken, N_i is the number of species that are i monomer units long, M_i is the molecular weight of a segment that is i monomers long, and $R(i)$ is the radius of gyration of a segment that is i monomers long. The distribution of soft segment lengths was obtained from high performance liquid chromatography data[8]. $R(i)$ is taken to be of the form

$$R(i)=KM^a \quad (9)$$

where K is a constant. The value of a is taken to be one half. This is the value one would find for a chain in an amorphous homopolymer. It is also a good approximation here[4].

RESULTS AND DISCUSSION

The radius of gyration measured as a function of temperature for each sample is listed in *Table 1*. Samples 1 and 2 have the same chemical and isotopic composition, but they were synthesized in separate procedures. The redundancy provides a check on the validity of the data. *Table 1* also includes an error parameter which is the 95% confidence limit established by the nonlinear regression routine. *Figure 2* illustrates a typical fit of equation (7) to the single chain scattering data obtained. The agreement with the Debye model of equation (6) is seen to be quite good, as the error estimates listed in *Table 1* imply.

Figure 3 graphically depicts the change in the soft segment R_g as a function of temperature. The error bars

Table 1 Soft segment R_g vs. temperature

Sample	Temperature (°C)	R_g (Å)	Error[a] (± Å)
No. 1	25	15.6	0.27
	65	15.5	0.42
	95	15.2	0.32
	125	14.4	0.34
	160	14.6	0.43
	190	15.1	0.42
	215	18.4	0.39
No. 2	25	14.9	0.21
	50	14.8	0.47
	80	14.1	0.44
	110	13.8	0.50
	140	13.6	0.50
	170	14.2	0.49

[a] The error estimates listed are 95% confidence limits established by the nonlinear regression routine

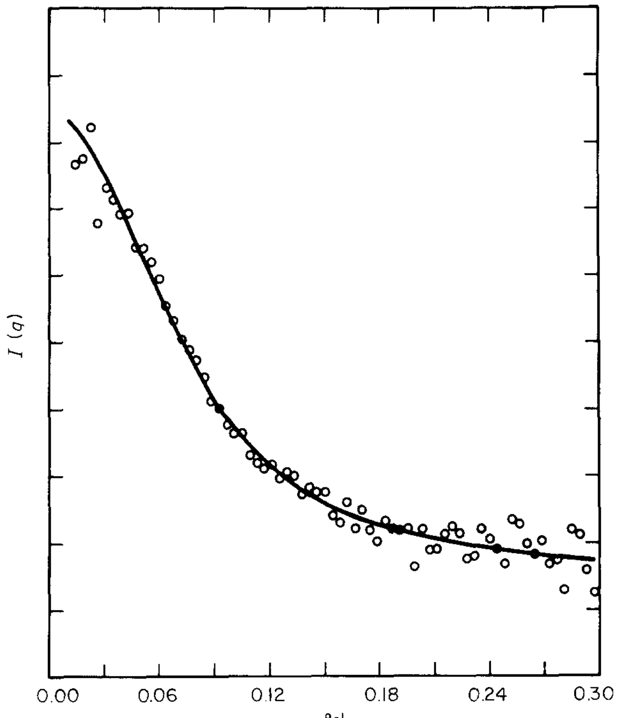


Figure 2 Model fit of the Debye function (equation (6)) to single chain scattering data for sample 1 at room temperature

are drawn at the 95% confidence limits discussed previously. At room temperature, the radius of gyration of the average soft segment is approximately 15.3 Å, which is in agreement with the value measured previously by Miller *et al.*[4], within experimental error. This value compares with a value of 12.1 Å for this same oligomer measured in the bulk state[8]. Values from 11.5 Å–12.3 Å are obtained when high molecular weight viscosity data for PTMO are extrapolated down to a molecular weight of 1000.[8] This implies that the soft segment chains are somewhat extended at room temperature, as shown in *Figure 4*. This conclusion is in agreement with previous results[4] and is similar to results obtained for polyether polyester block copolymers with a similar hard segment volume fraction and a lamellar microstructure[9]. The average soft segment is found to be somewhat extended, but since neutron scattering measures an average of many chain segments, there is a range of segment extensions. One possible case would be a bimodal distribution of random coil chains and fairly taut chains. The presence of soft segments which are taut tie molecules has been used to rationalize the thermal mechanical behaviour of polyether polyesters[20,21]. It would not be unreasonable to expect to find such taut tie molecules in polyurethanes since the microstructure, chemical architecture, and thermal mechanical properties are similar for the two families of materials.

As the temperature increases, the radius of gyration of the soft segments initially decreases. This is associated with the increased chain mobility at higher temperatures. Chee and Farris[22] have proposed a model for the kinetics of phase separation in two phase polyurethane systems that states that as the temperature rises, the retractive force arising from the extended soft segment chains increases. This is especially true for the taut tie molecules that may be present in the material. The increased force facilitates the pulling of hard segments out of the hard phase into the soft phase. The result of pulling a hard segment out of the hard phase would be to reduce the radius of gyration of the adjacent soft segments since after the hard segment is pulled from the hard domain, the soft segment is free to relax into a more nearly random coil conformation. This model, based only on phase separation kinetics, supports the SANS results in the

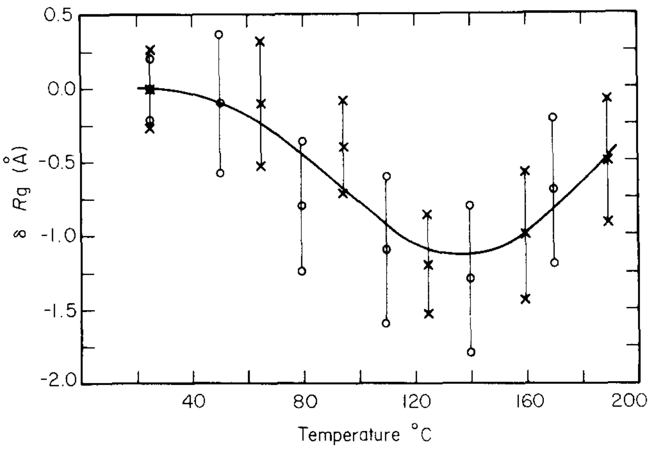


Figure 3 Change in the soft segment radius of gyration as a function of temperature for sample 1 (×) and sample 2 (○)

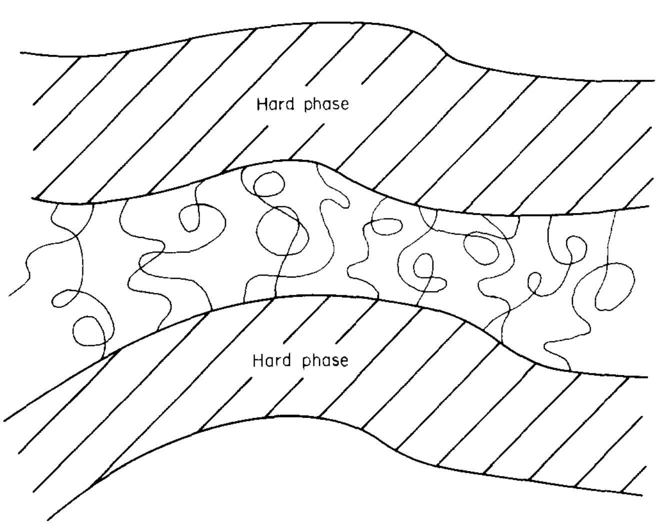


Figure 4 Soft segment conformation at room temperature. The segments are somewhat extended relative to the bulk oligomer

present experiment. This model also predicts that the degree of phase mixing will increase as the temperature increases. This has been observed by a number of researchers using SAXS[23,24].

As the temperature is raised to 160°C and above, a slight upturn in the soft segment radius of gyration is measured. It should be noted that above 160°C, some sample degradation did occur, since the samples were yellowed after removing them from the test chamber. The heating chamber was kept in a helium vacuum atmosphere during the test to partially alleviate the degradation problem. The degradation that did occur probably has no effect on the measured radius of gyration. The upturn in R_g above 160°C may be due to the presence of substantial phase mixing at higher temperatures, as has been reported by Wilkes and Emerson[23], and by Schneider and Paik Sung[24]. Koberstein *et al.*[10,11] have proposed a phase mixing–demixing transition in polyurethanes around 150°C based on d.s.c. and SAXS studies of the multiple endothermic properties of these materials. The SANS data of our experiment support this model, although the data do not prove the validity of the hypothesis. Initially on heating the dominant process is the relaxation of internal stresses caused by hard segments being pulled out of the hard phase which leads to a decrease in the soft segment value of R_g. As the temperature increases further, more phase mixing occurs, either gradually as the taut tie molecules pull the hard segments out of the hard domain or as a phase mixing transition occurs[11]. The interaction between the mixed hard and soft segments within the soft phases dominates any relaxation processes that may occur. This interaction causes the soft segment chains to have a larger radius of gyration than when there are few hard segment chains present. The chain conformation is still a random coil, but it is expanded somewhat, much as a homopolymer chain would be upon swelling by a small amount of solvent. The increase in the soft segment radius of gyration is probably not caused by an increase in the hard domain crystallinity. Such an increase in crystallinity would tend to reintroduce stress on the soft segments and lead to a larger value of R_g. In addition, the average hard segment length in the materials studied in this experiment is not large enough for substantial crystallinity to be present.

CONCLUSIONS

The soft segment radius of gyration was measured as a function of temperature in a polyether polyurethane comprising a 3/2/1 mole ratio of MDI, butanediol, and poly(tetramethylene oxide) using small angle neutron scattering (SANS). The two samples studied contained a mixture of 0.325 moles of d-PTMO and 0.675 moles of hydrogenous PTMO. These samples exhibited no interphase scattering because of the degree of deuteration used. Only intrachain scattering from the soft segments appeared in the coherent part of the scattering. At room temperature, the soft segments are in a somewhat extended conformation relative to the conformation in the bulk oligomer[8], in agreement with previous studies on polyether polyesters[9] and an identical polyurethane system[4]. As the samples were heated, the soft segment radius of gyration was initially found to decrease. Above 160°C, the measured R_g increased slightly. Two processes are occurring. The first predominates at lower temperatures. As the temperature rises, the retractive force associated with the extended soft segments increases, thus causing some hard segments to be pulled out of the hard domains. Once this occurs, the soft segments attached to this hard segment can reduce the stress associated with being extended by contracting to a less extended, more random coil conformation. As this process proceeds, the degree of phase mixing increases, either by a gradual process or fairly quickly through a phase mixing transition above a critical temperature, as has been proposed by Koberstein[11]. Eventually the favourable interaction between the mixed hard and soft segments in the soft phase causes an expansion of the soft segment coil, much as a homopolymer is swollen by a good solvent.

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