Small Angle X-ray Scattering Study of Phase Separation Kinetics in Segmented-Polyurea

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Thermoplastic elastomers based on diisocyanate chemistry like polyurethanes and polyurea compounds constitute a unique class of materials with domains of hard segments (HS) in a matrix of soft segments (SS).^{1, 2} The domain structure in these segmented materials is known to be temperature sensitive.³ The numerous variables associated with the structure of these materials like molecular weights of the segments, the HS content, the nature of the HS and SS (compatibility, crystallization potential etc.) offers many possibilities of tailoring the properties arising from the resulting structure.^{1, 2} This has lead to many potential applications of these materials in the field of tissue regeneration⁴ electronic materials,⁵ surface engineering,⁶ and as elastomeric materials.⁷ Micro-phase separation between the HS and SS components has an important bearing on the interfacial properties and hence is a critical aspect in the structure-property relationship window in such segmented systems. In this communication we present results from a kinetic study following the evolution of phase separation in a non-chain extended segmented polyurea system using small angle x-ray scattering (SAXS). The kinetics of structural evolution was also concurrently characterized using Fourier transform infra-red spectroscopy (FTIR).

Phase separation kinetics was monitored in HDI-polyurea (hexamethylene diisocyanate (HDI) reacted with diamine terminated poly(tetramethylene oxide) (PTMO)). A stoichiometirc amount of diamine terminated PTMO, molecular weight 1100 g/mol, was reacted with HDI in the synthesis of HDI-polyurea. The strong bidentate H-bonding in polyurea is known to promote phase separation even in the absence of chain extended HS.² The sample was heat treated to erase the existing morphology, so as to follow the re-developing microstructure as a function of

time. Phase separation in this material is consistent with a confined spinodal-like decomposition mechanism and resembles phase separation seen in other segmented systems.^{8,9}

Small angle x-ray scattering (SAXS) machine used in this work uses a Rigaku Rotoflex rotating anode X-ray generation equipment, operating at 40 kW and 30 mA. The collected sample data is corrected for appropriate background scattering. The 2-D data obtained is radially averaged to obtain 1-D plots of scattering intensity versus the scattering vector, q, which is given by,¹⁰

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{1}$$

where λ is the wavelength of the radiation used and θ is the scattering angle. Ultra small angle xray scattering (USAXS) runs were performed on the sample prior to the heat treatment cycle. The USAXS data was obtained at the Advanced Photon Source, Argonne National Laboratory, Chicago. SAXS and USAXS data on the untreated samples are shown in Figure 1. Both the data sets show a peak at q = 0.065 Å⁻¹. As can be seen from the USAXS profile, the curve at low-q is essentially featureless, indicating the SAXS q-range probed in this work is sufficient to capture the structural features associated with the HDI- polyurea sample.



Figure 1. Ultra small and small angle x-ray scattering data from HDI-polyurea samples prior to heat treatment. USAXS data obtained at APS, ANL, Chicago. The USAXS intensity has been scaled down for comparison with the SAXS profile. The peak in both the SAXS and USAXS runs occurs at q = 0.065 Å⁻¹.

The HDI-polyurea sample was heat treated in a vacuum oven at 175 °C for 7 minutes. Time resolved SAXS measurements were performed on the sample after the heat treatment, with zero time indicating the run immediately after heat treatment.

SAXS data at different times following heat treatment is shown in Figure 2. It is evident that there is a shift in the peak position from 0.065 Å⁻¹ in the untreated sample to around 0.1 Å⁻¹, (4 hours after heat treatment). This indicates a reduction in the domain size between the untreated and heat treated sample. The scattered intensity at this peak increases with time, as can be seen in the upward shift in the intensity values with increasing time. SAXS runs were performed till 118 hours, where no further increase in the peak intensity value was observed. The position of this peak in intensity remains constant with time ($q \sim 0.1$ Å⁻¹) and does not approach the original value ($q \sim 0.065$ Å⁻¹) prior to heat treatment.

This evidence is consistent with a spinodal-like decomposition mechanism of phase separation in network polymers, where the evolving phases are locked in due to the network structure, as has been seen in some other systems.¹¹ This indicates that late stage ripening of the phases analogous to Ostwald ripening and increase in domain size is not seen (peak does not shift to lower-q values). What follows is an analysis of spinodal decomposition kinetics based on this SAXS data.



Figure 2. Small angle x-ray scattering intensity plotted as a function of the scattering vector, q, for different times after heat treatment. Inset shows an expanded view in the q-range of interest.

The early stages of spinodal decomposition are described by the linearized Cahn-Hilliard-Cook theory¹²⁻¹⁵ which predicts that the rate of growth of concentration fluctuations, R(q) during early stages of spinodal decomposition is given as,¹²⁻¹⁴

$$R(q) = D q^{2} \left(1 - \frac{q^{2}}{2q_{m}^{2}} \right)$$
(2)

where *D* is the apparent diffusion constant, and $q_m = \zeta^{-1}$, where ζ is the correlation length of these fluctuations. The relaxation rate of the concentration fluctuations is related to the structure factor by the following relationship,¹²⁻¹⁴

$$S(q,t) = S(q,\infty) + \left[S(q,0) - S(q,\infty)\right] \exp\left[2R(q)t\right]$$
(3)

The rate of phase separation, R(q), can be calculated from slopes of the linear fits to the natural logarithm of intensity versus time plots as shown in Figure 3.



Figure 3. Natural logarithm of scattering intensity plotted as a function of time at scattering vector, $q = 0.12 \text{ Å}^{-1}$. The initial slope of scattered intensity is used to calculate the rate of phase separation R(q).

The rate of phase separation, R(q), obtained at different q values are plotted as a function of the scattering vector q in Figure 4a. The maximum rate of phase separation occurs at q^* , and as can be seen in the fit to the data in Figure 4a, q^* is equal to 0.086 Å⁻¹. According to the linearized Cahn-Hilliard-Cook theory,¹²⁻¹⁵ $R(q)/q^2$ decreases linearly with q^2 . It is expected to change from positive to negative extrapolated values, for q values greater than $\sqrt{2}$ (q^*). The behavior of the $R(q)/q^2$ versus q^2 as seen in Figure 4b is similar to the one noted by Bansil et al.¹⁶ in case of N-isopropylacrylamide gels. Cahn-Hilliard-Cook theory¹²⁻¹⁵ predicts the observed linear behavior (decrease) of $R(q)/q^2$ which is expected down to $q^2 \sim (q^*)^2 [(q^*)^2 = 0.0074 \text{ Å}^{-2}]$.

The intercept on the abscissa is the critical wave vector, q_c^2 , and a test of the initial stages of spinodal decomposition is given by,

$$q_c^2 = 2q^{*2}$$

$$q_c^2 = 0.012 \text{ Å}^{-2} \sim 2q^{*2} = 0.014 \text{ Å}^{-2}$$
(4)

The correlation distance (ξ) between the phases formed from this phase separation mechanism is calculated as,¹⁵

$$\xi = \frac{2\pi}{q^*} \approx 7.3 \,\mathrm{nm}$$

and we could expect the phases to be of the order of 7-8 nm. The ordinate intercept of the linear fit to the $R(q)/q^2$ versus q^2 plot (Figure 4b) gives an apparent diffusion coefficient, *D*, for the phase separating system of 6.84 Å² hr⁻¹. The apparent diffusion coefficient for the HDI-polyurea studied here is compared with previous studies in other systems^{15,16} undergoing spinodal decomposition in Table 1. The time scale of phase separation in these systems is related to apparent diffusivity of the phase separating system.

Table 1. Apparent diffusion coefficient, D, from N-isopropylacrylamide gels,¹⁶ polystyrene-poly(vinyl methyl ether),¹⁵ and current study on HDI-polyurea (PU).

#	Study	System Studied	$D (\mu m^2 s^{-1})$	Time Scale
1	Bansil et al. ¹⁶	NIPA gel	0.04	seconds
3	Hashimoto et al. ¹⁵	PS-PVME	0.0585 x 10 ⁻³	minutes
4	Current work	PU	0.019 x 10 ⁻⁹	hours



Figure 4 (a) Rate of phase separation R(q) as a function of wave vector, q, with a maximum at $q^* = 0.086 \text{ Å}^{-1}$ and, (b) $R(q)/q^2$ plotted as a function of q^2 , the critical wave vector obtained from this plot has a value of $q_c^2 = 0.0012 \text{ Å}^{-2}$.

Time resolved FTIR studies were performed on the HDI-polyurea samples after similar thermal treatment and the spectra are shown in Figure 5a (carbonyl region) and 5b (amine region). The carbonyl groups in the HDI-polyurea immediately following the heat treatment exist as either free or disordered hydrogen bonded carbonyls from the peaks seen at 1690 cm⁻¹ and 1650 cm⁻¹ respectively.¹⁷ With the progress of phase separation the carbonyl group absorption peak shifts to 1630 cm⁻¹, which corresponds to highly ordered hydrogen bonded carbonyls.¹⁷ Similarly, the spectra covering the amine absorption region (Figure 5b), shifts from free or disordered H-bonded amine groups (3340-3450 cm⁻¹)¹⁷ to highly ordered H-bonded amine groups (3320-3340 cm⁻¹)¹⁷ following the heat treatment. This confirms that H-bonding in the HS of the HDI-polyurea is the main driving force for phase separation in this system. The spectra shown in Figure 5 range from t = 0 minutes to t = 1150 minutes. The SAXS signature of phase separation thus follows the evolution of strong bidentate H-bonding in the HS component.



Figure 5. Time resolved FTIR spectra from a) the carbonyl region of HDI-polyurea and, b) amine region of the HDI-polyurea. Blue curve (t = 0 minutes), Red curve (t = 1150 minutes).

Figure 6 shows a schematic representation of the possible morphology of this system based on the SAXS and FTIR data presented here. The dark lines represent the hard segment component of polyurea, and the soft segments are indicated by the lighter broken lines. As shown in the schematic, we could expect the formation of hard phase rich and soft phase rich domains. These domains are represented by A and B in Figure 6 respectively. Such hard phase rich and soft phase rich domains could then be globally interconnected to like phases throughout the system.



Figure 6. Schematic representation of the possible morphology of the phase separated polyurea with distinct hard phase rich (A) and soft phase rich (B) domains. The hard phase is represented by the solid lines and the soft phase by the lighter broken lines.

We have presented evidence that the HDI-polyurea polymers micro-phase separate by a spinodal decomposition-like mechanism. This should result in the signature spinodal decomposition morphology of a co-continuous interconnected web. This result could be pivotal in establishing the microstructure of these important thermoplastic elastomers. The phase separation does not exhibit late stage phase ripening, similar to other systems where the presence of a network structure is responsible for locking in the phases.¹¹ The formation of strong bidentate H-bonds in the HS component of the HDI-polyurea could be potentially responsible foe this observed behavior. The kinetics of the phase separation process in HDI-polyurea is much slower than those observed in other polymeric systems. The network structure of these materials could again be an explanation for this observation.

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