



Influence of mixed soft segments on microphase separation of polyurea elastomers



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ABSTRACT

This paper describes the influence of mixed poly(tetramethylene oxide) (PTMO) soft segments on microphase separation and morphology, hydrogen bonding, and polymer transitions for a series of alternating polyurea copolymers prepared from a single modified diphenylmethane diisocyanate. The fraction of two PTMO soft segments [with molecular weight = 1000 and 250 g/mol] was systematically varied and incorporated during bulk polymerization. ATR-FTIR spectroscopy confirmed that the intended polymers were synthesized and was used to determine the state of the local hydrogen bonding in these copolymers. Systematic changes in hard domain microstructure as a function of soft segment composition were clearly observed in AFM tapping mode phase images: the polyureas become progressively disordered with increasing content of the shorter PTMO. This was confirmed in a quantitative fashion using small-angle X-ray scattering. Results from dynamic mechanical analysis experiments reveal rather significant changes in dynamic segmental relaxations and storage moduli at 25 °C for this series of polyureas, which are in keeping with the findings from other experiments.

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1. Introduction

Elastomeric polyurea copolymers can be readily synthesized by the reaction of di- (or higher functionality) isocyanates with oligomeric diamines having molecular weights ranging from several 100 to several 1000 g/mol. Thermodynamic incompatibility of the unlike segments and strong bidentate hydrogen bonding between urea moieties promote microphase separation into a continuous low glass transition temperature (T_g) soft phase and high T_g (in some cases semi-crystalline) hard domains. Polyureas are well known to form mechanically robust elastomers, with the hard domains providing physical crosslinks and mechanical reinforcement. Particular polyurea elastomers have been recently demonstrated to exhibit outstanding blast and ballistic penetration resistance [1,2], and as such have been proposed as candidates for preventing fracture of steel plates and armor [3–6] and for protection against traumatic brain injury (TBI) [6–8].

The nanoscale-segregated phase separation of segmented polyurethanes and polyureas is well known to be key to

determining their performance [9–15], and their properties can be manipulated by molecular design of the soft and hard segment chemistry [15–21], fabrication process [22,23], and thermal treatments [24–27]. The demixing of polyurea hard and soft segments on solidification has been found to be relatively incomplete [21,27], similar to segmented polyurethane and poly(urethane urea) multiblock copolymers. However, although polyurea elastomers have been utilized in a number of applications, an understanding their fundamental structure–property relationships needed to tailor this class of materials for advanced applications is relatively limited.

In a recent investigation, we demonstrated that soft segment molecular weight has a rather pronounced influence on phase separated microstructure, the state of hydrogen bonding, and molecular dynamics for polyureas synthesized from a modified MDI and poly(tetramethylene oxide) (PTMO) soft segments [21]. The hard segments in the polyurea containing 1000 g/mol PTMO self-assemble into continuous nanoscale ribbon-like texture, whereas the comparable polyurea with 250 g/mol soft segments exhibits a single-phase structure. In an effort to design materials with characteristics between these two ‘extreme’ cases, we report in the present paper our investigation of microphase separation of bulk-polymerized polyureas synthesized with various ratios of 250 and 1000 g/mol PTMO soft segments.

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2. Experimental

2.1. Materials

The polyurea copolymers in this study were prepared by bulk polymerization at room temperature from a uretonimine-modified 4,4'-diphenylmethane-diisocyanate (mMDI, Rubinate® 1680, Huntsman) and two polytetramethyleneoxide-di-*p*-aminobenzoates having PTMO molecular weights of 1000 g/mol and 250 g/mol (Versalink® P1000 and P250, Air Products) (Scheme 1). The average isocyanate (NCO) functionality of Rubinate 1680 provided by the manufacturer is 2.12. Accordingly, di- and triisocyanate fractions are estimated to be 0.88 and 0.12, respectively. Note that the polyureas synthesized herein are alternating copolymers, in contrast to the multiblock nature of segmented polyurethanes.

Diamines were degased at 40 °C and mMDI was degased at room temperature for 8 h prior to the polymerization. As a representative example, for the polyurea containing a P1000/P250 ratio of 75/25, the P1000 (29.4 g, 75% mole of total diamines) and P250 (4.0 g, 25% mole of total diamines) diamines were mixed and degased at room temperature for 2 min. The diamines and mMDI (10.0 g, 5% excess isocyanate) were mixed, degased for 1–2 min, and cast on Teflon sheets by using a film applicator to control sample thickness. The melt cast film was allowed to cure at ambient temperature for 48 h. Similarly, other polyureas were prepared in the same manner but using different molar ratios of P1000/P250, i.e., 50/50 and 25/75. The corresponding polymers containing only P1000 and P250 were prepared using procedures reported previously [21]. After curing, all samples were maintained at room temperature and with relative humidity controlled at <30% for at least 2 weeks prior to analysis. The polyureas in the present study are network polymers: from Flory's theory of network formation, assuming that all reactive units have the same reactivity and no intramolecular reaction occurs [28], the probability of network formation (the probability that each branch unit is connected to another branch unit through chain segments) for these systems is approximately 0.77. The characterization of the P1000 and P250 polymers were reported in our previous work [21] and are shown herein for comparison purposes.

2.2. Characterization

2.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded using 200 scans and resolution of 2 cm⁻¹, with a Nicolet 6700 FTIR spectrometer (Thermo Scientific).

Measurements were performed at room temperature using diamond attenuated total reflectance (ATR) cell from 4000 to 600 cm⁻¹.

2.2.2. Atomic force microscopy (AFM)

Tapping mode AFM measurements were performed on a Bruker Icon atomic force microscope at ambient temperature. The cantilevers used in this study were Nanosensors PPP-NCH AFM probes with spring constant 10–130 N and resonance frequency 204–497 kHz. The tip radius of curvature was reported to be less than 10 nm. All phase images reported are from scan areas of 500 × 500 nm² and acquired using tapping forces, r_{sp} (set point amplitude/free amplitude of oscillation) between 0.7 and 0.9.

2.2.3. Wide angle X-ray diffraction (WAXD)

WAXD profiles were determined at room temperature using a Rigaku DMAX-Rapid micro-diffractometer equipped with curved image plate detector. The X-ray beam was generated from a Cu point-focused source ($\lambda = 0.154$ nm) at 50 kV and 40 mA. 2D isotropic scattering patterns were integrated to give 1D profiles in a 2θ range from 5 to 35°.

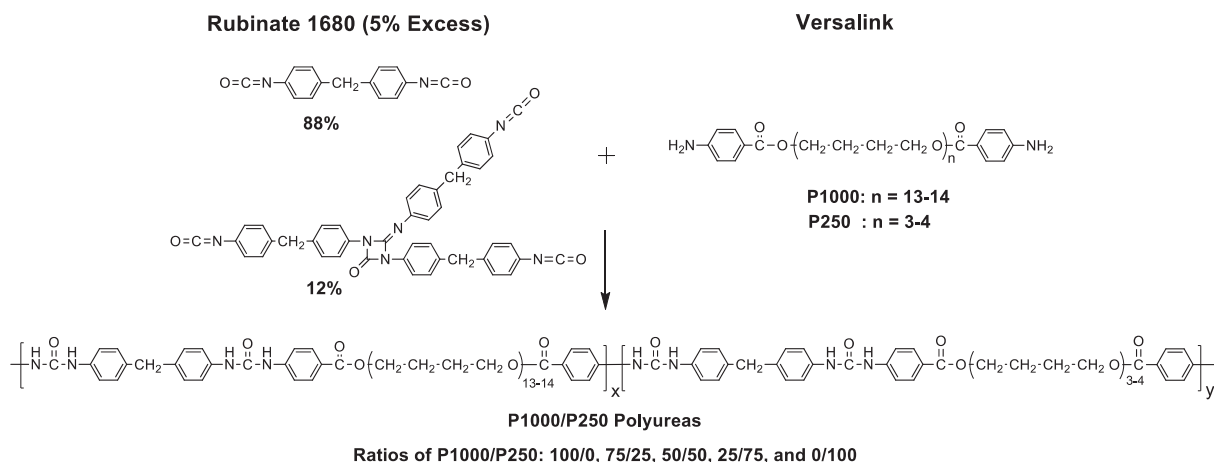
2.2.4. Small angle X-ray scattering (SAXS)

SAXS measurements were carried out at room temperature on a Molecular Metrology (Rigaku) SAXS equipped with a 2D multi-wire detector. Cu K α radiation ($\lambda = 0.154$ nm) was used as the X-ray source. The sample-to-detector distance was 1.5 m, resulting in a q (scattering vector) range between 0.07 and 1.7 nm⁻¹, where $q = (4\pi\sin\theta)/\lambda$ and 2θ is the scattering angle. The exposure time was 1 h for each sample. The measured isotropic 2D patterns were corrected for sample transmission, thickness, scattering background, mask and detector flat-field. Scattered intensities were put on an absolute scale by comparison to the scattering of a pre-calibrated crosslinked polyethylene (S-2907) secondary standard [29], prior to azimuthally averaging the data to obtain 1D absolute intensity profiles.

Degrees of phase separation (DOPS) were quantified from the absolute SAXS intensity using the ratio of the experimental to 'theoretical' electron density variance, according to the method of Bonart and Müller [30]:

$$\text{DOPS} = \frac{\overline{\Delta\eta}^2}{\Delta\eta_c^2} \quad (1)$$

where $\overline{\Delta\eta}^2$ is the experimental electron density variance (influenced by diffuse phase boundaries and segment intermixing) and $\Delta\eta_c^2$ is the theoretical electron density variance for the hypothetical



Scheme 1. Synthesis of P1000/P250 polyureas.

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