Polymer 55 (2014) 906–913

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The role of diisocyanate structure on microphase separation of solution polymerized polyureas

Yong He [a,b], Xinya Zhang [b,**], James Runt [a,*]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form
29 December 2013
Accepted 1 January 2014
Available online 8 January 2014

Keywords:
Polyurea
Phase separation
X-ray scattering

ABSTRACT

Three diisocyanates with different symmetry and planarity (2,6-TDI, 2,4-TDI and MDI) were used to synthesize polyureas with the same oligomeric polyetheramine having a molecular weight of ~1000 g/mol. The influence of diisocyanate symmetry on the phase separated morphology, hydrogen bonding behavior, and molecular dynamics were investigated. Symmetric diisocyanate structures facilitated self-assembly of hard segments into ribbon-like domains, driven by strong bidentate hydrogen bonding. The hard domains for the 2,6-TDI polymer appear to be continuous in AFM images, while the persistence length of the hard domains in the 2,4-TDI and MDI polymers gradually decrease, and fewer hard domains are apparent with decreasing hard segment symmetry. The extent of hard/soft segment demixing, assessed from small-angle X-ray scattering, was very incomplete for all of the polyureas and is significantly influenced by hard segment structure. For the 2,4- and 2,6-TDI polyureas, two segmental relaxations were observed using dielectric relaxation spectroscopy; one arising from relatively unrestricted motion in the soft segment rich phase, and a slower process associated with segments in the soft phase constrained by their attachment to hard domains.

1. Introduction

Polyurethanes are well-known thermoplastic multiblock copolymers, in which a fraction of the relatively high glass transition temperature (T_g) hard segments microphase separate into domains dispersed into a continuous low T_g matrix. Microphase separation is typically driven by the chemical immiscibility between the unlike segments, despite the relatively low molecular weight of the blocks [1]. Polyureas are generally similar to polyurethanes, but are formed from the reaction of diisocyanates and oligomeric diamines yielding alternating copolymers. It is well known that the properties and performance of both polyurethanes and polyureas are strongly dependent on their phase separated morphologies and the degree to which the unlike segments segregate [2]. Both families of materials have proven to be highly versatile, having applications as foams [3,4], elastomers [5,6], coatings [7], adhesives [8], and biomaterials [9]. More recently, polyureas with strong bidentate hydrogen bonding have received increasing attention for the mitigation of blast-induced shock waves [10,11].

A number of investigations have been carried out to understand the degree of microphase separation in polyurethanes and its effect on physical properties [12–16]. Compared to the monodentate hydrogen bonding in polyurethanes, bidentate hydrogen bonding in polyureas leads to quite strong hard domain cohesion [17,18]. Unfortunately, polyurea elastomers suffer from some disadvantages, such as poor melt processibility and incomplete solubility in organic solvents. However, polyureas synthesized without chain extenders and having relatively low hard segment contents (lower than ca. 20 wt%) exhibit excellent physical properties, compared to many other elastomers with higher hard segment content [19–23]. One issue that remains unclear is what role diisocyanate structure plays in determining the microstructural characteristics as well as the dynamics of polyureas [7,24,25].

In the present study, we investigate the phase separation behavior and molecular dynamics of a series of polyureas based on an oligomeric polyetheramine and three diisocyanates having varying geometries: 2,6-toluene diisocyanate (TDI), 2,4-TDI and 4,4′-diphenylmethane diisocyanate (MDI). The two aromatic rings on the central methylene unit of MDI are neither coplanar nor linear [26,27], while symmetric 2,6-TDI and asymmetric 2,4-TDI are both coplanar (Fig. 1). It has been proposed that the use of 2,6-TDI in polyureas may facilitate the formation of compact hard domains, resulting in stronger hydrogen bonding. Microphase separated

---

[*] Corresponding author. Tel.: +1 8148632749.
[**] Corresponding author. Tel.: +86 2087112047.
E-mail addresses: cexyzh@scut.edu.cn (X. Zhang), runt@matse.psu.edu (J. Runt).

0032-3861/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2014.01.001

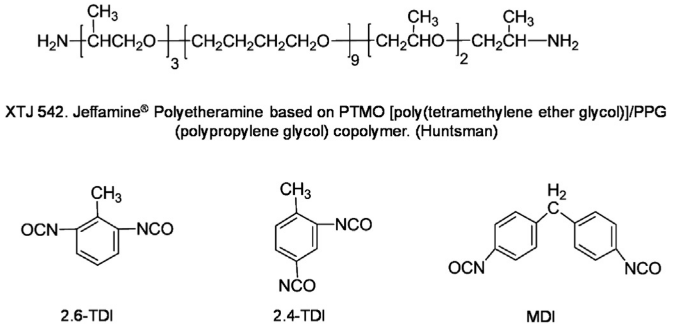

Fig. 1. Chemical structures of XTJ 542, 2,6-TDI, 2,4-TDI and MDI.

morphology, phase transitions and polymer dynamics are studied herein to elucidate the structure–property relationships in these model polyureas.

2. Experimental

2.1. Materials

2,6-TDI, 2,4-TDI and MDI were purchased from Aldrich. The oligomeric polyetheramine ($M_n \sim 1000$ g/mol) XTJ 542 was purchased from Huntsman (Fig. 1). The diamine was purified by rotary evaporator at 50 °C. Dimethylformamide (DMF) was purchased from Aldrich and purified on activated alumina columns.

2.2. Solution polymerization

Polymerization was conducted in a three-neck, round bottom flask equipped with a magnetic stirrer, addition funnel and argon gas inlet. All polyureas were solution synthesized using the XTJ 542 diamine and a slight excess of diisocyanate. The excess diisocyanate was used to compensate for some NCO group consumption arising from the reaction with residual moisture in the diamine, solvents, reactors and atmosphere. Excess water can perturb the desired stoichiometric balance necessary to obtain high molecular weight polymers. The solution of XTJ 542 and DMF was prepared first and then was slowly added dropwise to the diisocyanate solution at ambient temperature. An argon atmosphere was maintained during polymerization. The solids content was approximately 5–15 wt %. Completion of the reaction was determined by monitoring the disappearance of the isocyanate FTIR absorption peak at ~2270 cm^{-1}.

The polyureas synthesized from the TDI monomers contain ~15 wt% hard segments, while the MDI-based polymer contains ~20 wt% hard segments. Films of all polymers were obtained by solution casting into Teflon molds and heated at 50 °C for 24 h, followed by drying under vacuum at 50 °C for another 24 h.

2.3. Tapping mode atomic force microscopy (AFM)

The AFM tapping mode phase images of all samples were obtained by performing analysis on the free-air side of the solvent cast films at ambient temperature. AFM images were collected using a Bruker Icon AFM with Nanosensors PPP-NCH AFM probes (spring constant 10–130 N/m, resonance frequency 204–497 kHz). Tapping forces were in the range of 0.5–0.9 [defined as $r_{sp} = A/A_0$ (the set point amplitude/the free amplitude of tip oscillation)], which constitutes hard to soft tapping, respectively. Data were analyzed with NanoScope Analysis software.

2.4. Wide angle X-ray diffraction (WAXD)

WAXD data were collected on a Rigaku DMAX/Rapid microdiffractometer and Cu-K_α radiation ($\lambda = 1.54$ Å), operating at 50 kV and 40 mA. The sample thickness was in the range of 0.3–0.4 mm.

2.5. Small angle X-ray scattering (SAXS)

SAXS patterns were collected under vacuum at room temperature using a Molecular Metrology (Rigaku) SAXS with Cu-K_α radiation ($\lambda = 0.154$ nm) at 45 kV and 65 mA. Two-dimensional data sets were collected using a 2-D multiwire detector, located approximately 0.5 m from the sample. Absolute intensities were calculated using a pre-calibrated polyethylene secondary standard (S-2907) [28] and a silver behenate standard was used to calibrate the scattering vector.

In order to determine the degree of phase separation between two phases, we compare the theoretical variance calculated assuming complete segment demixing, $\overline{\Delta\eta_c^2}$, with the experimentally observed variance, $\overline{\Delta\eta^{2'}}$, using the method of Bonart and Muller [29]. The theoretical variance for the hypothetical case of complete segment demixing is defined as:

$$\overline{\Delta\eta_c^2} = \phi_{hs}\phi_{ss}(\eta_{hs}-\eta_{ss})^2 = \phi_{hs}(1-\phi_{hs})(\eta_{hs}-\eta_{ss})^2 \tag{1}$$

where ϕ_{hs} and ϕ_{ss} are the volume fractions and η_{hs} and η_{ss} are the electron densities of the hard and soft segments, respectively. The experimental variance $\overline{\Delta\eta^{2'}}$ is calculated from the SAXS invariant, Q (i.e., the experimental total scattering intensity) using the background and absolute intensity corrected SAXS intensities:

$$\overline{\Delta\eta^{2'}} = cQ = c\int_0^\infty [I(q)-I_b(q)]q^2 dq \tag{2}$$

where q is the scattering vector and c is a constant defined by,

$$c = \frac{1}{2\pi^2 i_e N_{av}^2} = 1.76\times10^{-24}\left(\text{mol}^2/\text{cm}^2\right) \tag{3}$$

and i_e is Thompson's constant for the scattering from one electron (7.94×10^{-26} cm^2), and N_A is Avogadro's number. The ratio of the experimental to ideal variance $\overline{\Delta\eta^{2'}}/\overline{\Delta\eta_c^2}$ provides a measure of the overall degree of phase separation. This ratio yields a value between 0 and 1, ranging from complete mixing to complete phase separation with infinitely sharp phase boundaries.

2.6. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was conducted using a Nicolet 6700 FTIR spectrometer (Thermo Scientific). The polyureas were dissolved in DMF (2 wt %) and the solutions were cast onto KBr windows. Specimens were dried overnight under ambient conditions and further dried for 2 h at 50 °C under vacuum. Samples were scanned 200 times at a resolution of 2 cm^{-1}.

2.7. Differential scanning calorimetry (DSC)

Polyurea phase transitions were determined using a Seiko 220 differential scanning calorimeter. Each sample was measured over a temperature range of −100 °C to 240 °C on heating, subsequently cooled at a rate of 10 °C/min to −100 °C, then reheated at 10 °C/min. All experiments were conducted under a nitrogen flow of 50 mL/min. The soft phase T_g was taken as the inflection point from the first DSC heating scan.