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Understanding the influence of hydrogen bonding and diisocyanate symmetry on the morphology and properties of segmented polyurethanes and polyureas: Computational and experimental study

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ABSTRACT

Quantum mechanical calculations (QMC) and dissipative particle dynamics (DPD) simulations were utilized to understand the nature of the short and long-range hydrogen bonding and its influence on the microphase morphology in segmented polyurethanes and segmented polyureas prepared without chain extenders through the stoichiometric reactions of hydroxy or amine terminated poly(tetramethylene oxide) (PTMO-1000) with 1,4-phenylene diisocyanate (PPDI) and 1,3-phenylene diisocyanate (MPDI). The possibility of long-range connectivity due to a network of well-ordered hydrogen bonds between symmetrical PPDI and kinked MPDI based model urethane and urea compounds were also investigated. Special emphasis was given on the understanding of the influence of diisocyanate symmetry and nature of the hydrogen bonding between hard segments on the morphology development. QMC results obtained clearly indicated the possibility of long-range ordering of hydrogen bonds between PPDI based urethane and urea groups, while MPDI based systems did not display such a behavior. DPD results strongly supported the QMC studies and clearly demonstrated the possibility of long-range connectivity of hydrogen bonds between urethane and urea groups in PPDI based segmented copolymers, leading to the formation of microphase separated morphologies in these systems, which was not observed in the kinked MPDI based segmented urethane and urea copolymers. Computational results obtained strongly supported the experimental observations reported on the morphology and thermal and mechanical properties of these segmented polyurethanes and polyureas based on PPDI and MPDI.

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1. Introduction

Segmented, thermoplastic polyurethanes (TPUs) are composed of covalently bonded, alternating hard and soft segments along a linear macromolecular backbone. Conventionally TPUs are synthesized by a two-step process called the *prepolymer method*. In the first step soft segment oligomers are reacted with a controlled excess of diisocyanate to form the *isocyanate terminated prepolymer*, which in the second step is reacted with stoichiometric amounts of short chain diols or diamines called the *chain extender*, to form high molecular weight TPUs. Utilization of diols as chain extenders lead to the formation of *urethane* hard segments, whereas diamine chain extenders form *urea* hard segments. Microphase morphologies of TPUs, which determine their ultimate properties, are strongly dependent on the morphological structure, molecular weight and the type and the content of the hard and soft segments in the copolymer. Numerous studies and a large number of publications, which discuss the structure–morphology–property relations in TPUs are available [1-12].

Although the conventional methods of TPU preparation involves the use of low molecular weight chain extenders, about 30 years ago preparation of novel segmented polyurea copolymers based on the stoichiometric reactions of α,ω -aminopropyl terminated polydimethylsiloxane (PDMS) oligomers and bis(4-isocyanatophenyl) methane (MDI) was reported [13,14]. Later on, the synthesis of

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Table 1	
Various structural properties of PTMO-1000, PPDI and MPDI based segmented polyurethanes and polyureas [2	5].

Polymer code	Hydrogen bonding	Symmetry	Interdomain spacing (Å) by SAXS	Modulus (MPa)	Tensile strength (MPa)	Elong (%)
PPDI-urea	S	+	55	76 ± 4	19.4 ± 1.8	540
PPDI-urethane	w	+	185	29 ± 8	8.4 ± 1.2	940
MPDI-urea	S	-	61	63 ± 8	5.4 ± 0.9	700
MPDI-urethane	w	_	_	_	_	_



Fig. 1. Ambient temperature tapping-mode atomic force microscopy phase images of copolymer films. (A) PPDI-Urethane, (B) PPDI-Urea, (C) MPDI-Urea (Scale bar 150 nm) [18]. Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

silicone-urea copolymers based on a cycloaliphatic diisocyanate, bis(4-isocyanatocyclohexyl)methane (HMDI) was also reported [15,16]. Urea hard segment contents of these copolymers were determined by the average molecular weight of the PDMS oligomers. Since no chain extenders were used, urea hard segments obtained consisted of the reaction product of the diisocyanate backbone and the aminopropyl end groups of PDMS oligomers and as a result had very uniform segment lengths. The PDMS soft segments which had very low solubility parameters when compared to the highly polar urea hard segments [17], resulted in copolymers with well separated microphase morphologies [15–17]. These copolymers obtained without the use of any chain extenders, very interestingly displayed composition dependent elastomeric properties comparable to those of crosslinked PDMS elastomers highly filled with silica. As a follow up to the PDMS-urea copolymers, during the last decade various research groups investigated the synthesis and structure-morphology-property behavior of poly(tetramethylene oxide) (PTMO) based polyurea and polyurethane copolymers obtained by stoichiometric reactions with different diisocyanates, i.e., no chain extenders were utilized [10,18-27].

One of the most fundamental studies, which clearly showed the dramatic effect of hydrogen bonding and hard segment symmetry on the morphology and properties of segmented copolymers was performed on PTMO-1000 ($M_{\rm p} = 1000$ g/mol) and 1,3-phenylene (MPDI) and 1,4-phenylene diisocyanate (PPDI) based segmented polyurethanes and polyureas [18]. Segmented copolymers were synthesized by the stoichiometric reactions between hydroxy and amine terminated PTMO-1000 and the respective diisocyanate without using any chain extender. As a result all copolymers had identical chemical compositions and uniform hard segments, which were obtained through the reactions of the diisocyanate backbone and the hydroxybutyl and aminopropyl end groups of PTMO. Quantum mechanical calculations have clearly shown that bidentate hydrogen bonding between urea groups (58.5 kJ/mol) are much stronger when compared with that between the urethane groups (46.5 kJ/mol) [28]. On the other hand PPDI is very symmetrical when compared with MPDI, while the latter is kinked. Table 1 provides various structural characteristics and properties of the copolymers obtained.

As summarized on Table 1, the four copolymers investigated had all possible combinations regarding the hard segment symmetry (symmetrical (+) kinked (-)) and the intermolecular hydrogen bond strength (weak (w) or strong (s)). Interdomain spacing values obtained by room temperature SAXS studies indicated the presence of a microphase morphology in all copolymers, except for the MPDI-



Fig. 2. Modulus-temperature and tan δ -temperature curves for segmented polyurethanes and polyureas prepared through stoichiometric reactions between hydroxy or amine terminated PTMO-1000 and 1,3-phenylene diisocyanate (MPDI) or 1,4phenylene diisocyanate (PPDI) [18]. (A) MPDI-urethane, (B) PPDI-urethane, (C) MPDI-urea, and (D) PPDI-urea. The weight content of hard segments for each sample is only about 14%. Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

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