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# Role of chain symmetry and hydrogen bonding in segmented copolymers with monodisperse hard segments

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**Abstract**

Thermoplastic segmented polyurethane and polyurea copolymers whose monodisperse hard segments are based on only a single diisocyanate molecule are discussed. The solid-state structure-property behavior of these materials demonstrates that a proper selection of the level of symmetry and/or cohesiveness of the hard microdomains may allow elimination of the traditional requirement of chain extension to obtain melt processable segmented urethanes, and more specifically, urea copolymers with useful structural properties.

*Keywords:* Polyurea; Polyurethane; Segmented copolymers

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## 1. Introduction

Segmented copolymers consist of alternating hard and soft segments along their backbone. The ability to develop microphase separation is one of their most defining features because such a microphase morphology imparts many useful properties for commercial applications [1]. Under appropriate conditions for microphase separation and when the relative hard segment (HS) volume or weight fraction of the copolymer is low, the HS generally segregate into isolated microdomains that are randomly dispersed in the continuous matrix of the soft segment (SS) phase. It is well established that the appropriate conditions for microphase separation of less strongly secondary bonded block copolymers are determined by the parameters $\chi N$ and $f$, where $\chi$ is the Flory–Huggins interaction parameter, $N$ the overall degree of polymerization, and $f$ the volume fraction of a block or segment [2]. This approach, however, is not easily applicable to the types of segmented copolymers addressed in this report. As the HS content is increased, the long-range connectivity of the HS improves, which in turn is thought to promote hard phase percolation through the soft matrix. The hard domains, irrespective of the extent of the hard phase percolation, act as physical cross-link sites and reinforce the soft matrix thereby enabling the copolymer to display useful structural properties in its 'service window'. In block and segmented copolymers the service window is defined by the region of the storage modulus, $E'$-temperature space within which $E'$ is relatively temperature insensitive above the SS $T_g$ (or $T_m$, if it can crystallize) and below the softening point of the copolymer's hard phase. In addition to the copolymer's HS content, the extent of the HS percolation and the potential crystallizability of the hard phase greatly influence the mechanical and thermal response of the material [1]. In segmented copolymers resulting from the isocyanate chemistry, namely polyurethanes, polyurethaneureas, and polyureas, the cohesiveness of the hard domains is further enhanced by the ability of the HS to establish a hydrogen bonded network.

The step-growth copolymers noted above, of which polyurethanes and polyurethaneureas are extensively used commercially, are generally synthesized by a two-step route, commonly referred to as the 'prepolymer' method [3]. In the first step, a prepolymer is made by end-capping a difunctional oligomer with excess diisocyanate. In the second step, the HS are formed by reacting the prepolymer mixture with stoichiometric amounts of a difunctional chain

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extender. Over the years consensus has developed amongst practitioners in the field that lengthening the HS, which of course also increases the HS content, is necessary to produce segmented copolymers that display useful structural properties in their service window. Therefore, few reports in the literature have addressed segmented copolymers that are non-chain extended, the most noteworthy being the report by Tyagi et al. [4] on polydimethylsiloxane based polyurea copolymers. In the present report, however, a percolated hard phase, such as could be produced by hard segment crystallinity or hydrogen bonding, was not observed visually or reconfirmed by any other method irrespective of the hard segment content (6–22 wt%) investigated. Segmented copolymers in which crystallizable HS of uniform (monodisperse) length are synthesized before condensing them with a selected SS generally require multistep synthesis and are expensive to produce. Therefore, they have also received limited attention [5–8].

As is well documented, hydrogen bonding and crystallization are two factors that strongly influence the morphology and properties of natural polymers, such as poly(nucleic acids) (e.g. DNA, RNA), proteins (e.g. spider silk), cellulose, polysaccharides, lipids, etc. [9–11]. Thus, inspired by such observations in natural materials, we hypothesized that a proper choice of the type of hydrogen bonding and the level of chain symmetry may potentially produce, without chain extension, segmented polyurethane and polyurea copolymers that would still display strong microphase separation. Furthermore, we also hoped to demonstrate that the service window behavior comparable to the traditional chain extended systems could be obtained, particularly for our materials that possessed urea linkages that allow for the capability of promoting strong bidentate hydrogen bonding. To confirm the hypothesis we synthesized copolymers using a one-step procedure. Equimolar amounts of a selected diisocyanate were reacted with dihydroxy terminated poly(tetramethylene oxide) of $\langle M_n \rangle$ 975 or diamine terminated poly(tetramethylene oxide) of $\langle M_n \rangle$ 1100 g/mol, thereby promoting either segmented polyurethane or polyurea segment copolymers, respectively. Thus, the resulting segmented copolymers had PTMO as the SS and a uniform length (monodisperse) HS based upon only a single diisocyanate molecule. We utilized the diisocyanates, *para*-phenylene diisocyanate (*p*PDI), *meta*-phenylene diisocyanate (*m*PDI), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), diphenyl methane diisocyanate (MDI), hydrogenated MDI (HMDI), and 1,4-*trans*-cyclohexyl diisocyanate (CHDI) to fully examine the role played by the level of HS symmetry. Only those segmented polyurethane and polyurea copolymers based on *p*PDI and *m*PDI are addressed in this communication. A full-length manuscript addressing materials based on the remainder of the diisocyanates is currently in preparation. The dihydroxy and diamine terminated poly(tetramethylene oxide) (PTMO) allowed us to synthesize analogous polyurethanes and polyureas, respectively. The synthesis strategy presented in Fig. 1 resulted in copolymers with ca. 14 wt% HS content.

## 2. Experimental

### 2.1. Materials

1,4-Phenylene diisocyanate (*p*PDI) and 1,3-phenylene diisocyanate (*m*PDI) were purchased from Aldrich. The diisocyanate *m*PDI was used as received, while *p*PDI was sublimed at 70 °C. Purities of diisocyanates were better than 99.5%. $\alpha,\omega$-Aminopropyl terminated poly(tetramethylene oxide) (PTMO) with $\langle M_n \rangle$ 1100 g/mol was purchased from Aldrich. Poly(tetramethylene oxide)glycol, with $\langle M_n \rangle$ 975 g/mol was kindly provided by DuPont. Reagent grade dimethylformamide (DMF) was purchased from Aldrich and used as received.

### 2.2. Polymer synthesis

Polymerizations were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and PTMO oligomer. No chain extenders were utilized. Segmented polyurea copolymers were prepared at

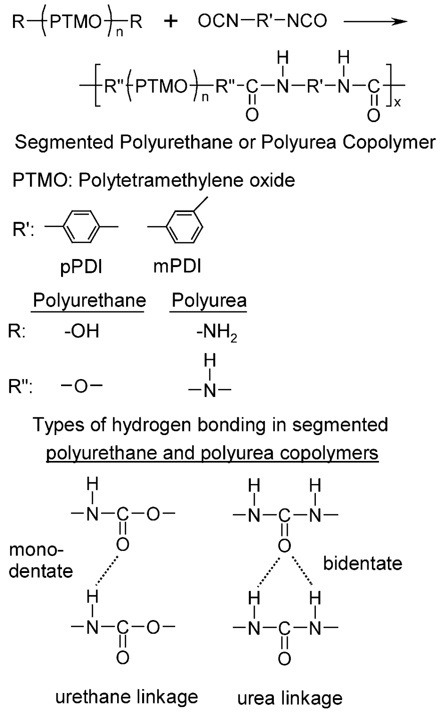

Fig. 1. Reaction scheme for the synthesis of segmented polyurethane and polyurea copolymers consisting of HS based on only a single diisocyanate. The –OH and –$NH_2$ terminated PTMO have $\langle M_n \rangle$ of 975 and 1100 g/mol, respectively. Monodentate and bidentate hydrogen bonding, which arise from urethane and urea linkages, respectively, are also shown.

room temperature in DMF by the dropwise addition of PTMO solution onto the diisocyanate solution, under strong agitation. The reaction precursors constituted 20 wt% of the solution. Polyurethanes were prepared in DMF at 60 °C. Completion of reactions was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 $\mathrm{cm}^{-1}$ with a FTIR spectrophotometer.

Polymer films ca. 1 mm thick were obtained by pouring the solutions into teflon molds. The molds were covered with a glass Petri dish to slow down the solvent evaporation and placed in an oven maintained at 60 °C. After evaporation of the solvent, the molds were placed in a vacuum oven at 60 °C for complete drying, which was monitored gravimetrically. The resulting films were then removed from the teflon molds and stored under vacuum at room temperature until needed for testing. Portions of these films were also compression molded in order to check their melt processability and to compare their solid-state behavior with that of their solution cast analog.

Also shown in Fig. 1 are the two principal types of hydrogen bonding that result from urethane and urea linkages. The former give rise to monodentate hydrogen bonding, which has a reported bond energy of 18.4 kJ/mol, whereas the latter result in bidentate hydrogen bonding with higher bond energy of 21.8 kJ/mol [12].

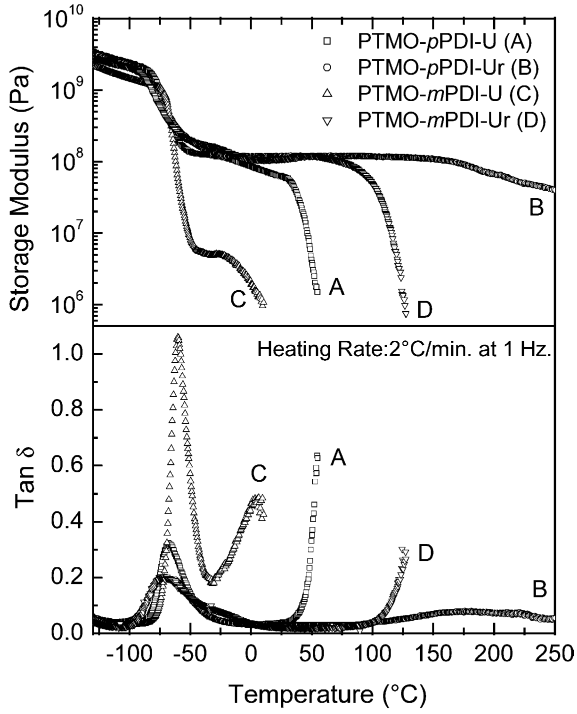

Fig. 2. Dynamic mechanical analysis behavior of copolymer films cast from 20 wt% solution in DMF. The tests were conducted under a nitrogen blanket by quenching the samples from ambient temperature to −130 °C and thereafter heating them at 2 °C/min at 1 Hz.

## 3. Results and discussion

The temperature dependent storage modulus, $E'$ and $\tan\delta$ responses of *p*PDI and *m*PDI based segmented polyurethane copolymers and their polyurea counterparts are presented in Fig. 2. The dynamic mechanical analysis was conducted on films cast from 20 wt% solutions in DMF. The samples are identified by the nomenclature: soft segment-diisocyanate-copolymer type, U for polyurethane or Ur for polyurea. Focusing on $E'$, as expected, below the SS glass transition, between −75 and −60 °C all four samples behave as rigid solids. Following this transition is a rubbery plateau whose breadth, average plateau modulus value, and temperature sensitivity depend upon the level of HS symmetry and the type of hydrogen bonding network within the hard phase. The rubbery plateau of PTMO-*p*PDI-U, although narrow and temperature sensitive, displays an average $E'$ value of ca. $10^8$ Pa. Such high $E'$ values above the SS $T_g$ are more commonly exhibited by conventional chain extended polyurethanes with a distinctly higher HS content [13] than the 14 wt% present in our copolymers. The high average $E'$ value strongly alludes to the presence of long-range connectivity of the HS and the percolation of the hard phase through the soft matrix. The tensile behavior of this material (Fig. 3) provides indirect support for this argument. When stretched uniaxially at ambient temperature this sample distinctly necks and displays a yield point, which must arise due to the break-up of the percolated hard phase. Consequently, when the applied load is released, it displays large permanent set and mechanical hysteresis. However, during the subsequent cyclic deformation, immediately following the first, the sample displays typical elastomeric behavior due to the inability of the microstructure to fully 'heal' before another deformation cycle is initiated. This elastomeric behavior further strengthens our argument that this system displays good microphase separation because a mixed SS–HS material would certainly

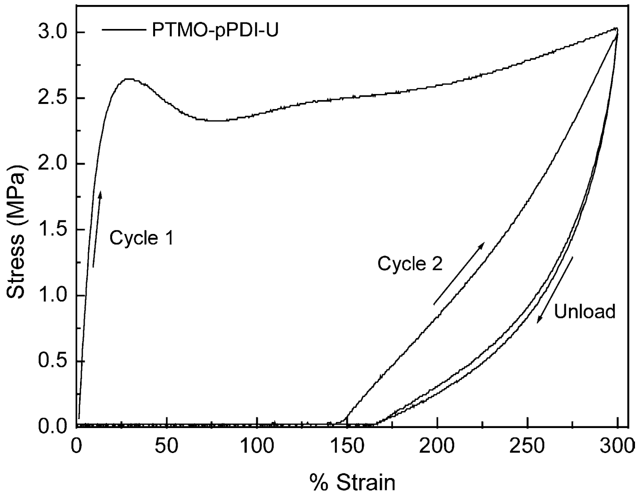

Fig. 3. Mechanical hysteresis behavior of the sample PTMO-*p*PDI-U. The test was conducted at a crosshead speed of 25 mm/min on a dog-bone shaped sample having a gauge length of 10 mm. The second cycle was initiated immediately upon the completion of the first.

not be expected to display good recovery following the second or higher deformations at this temperature [14,15]. Tapping mode atomic force microscopy (AFM) provides direct confirmation of the HS phase morphology. This sample's phase image (Fig. 4(A)) clearly displays a well-defined percolated HS phase that has developed in the form of ribbon-like hard domains of high aspect ratio. These ribbons are randomly dispersed throughout the SS phase, which dominates the composition and hence forms the continuous matrix. In addition to the HS connectivity, crystallization of the symmetric *p*PDI based HS phase also contributes towards elevating the average value of the rubbery plateau $E'$. The crystallization of the symmetric *p*PDI based HS phase was confirmed by DSC as well as WAXS (not shown). The DSC heating scan of PTMO-*p*PDI-U. exhibited a somewhat bimodal endothermic peak, centred at 50 °C, corresponding to the melting transition of the *p*PDI based HS phase. The melting point of pure *p*PDI is 97 °C. In addition, the 2D WAXS of PTMO-*p*PDI-U indicated an azimuthally independent reflection at 4.1 Å.

When the monodentate hydrogen bonded network is replaced by the stronger bidentate network, thereby resulting in the polyurea copolymer PTMO-*p*PDI-Ur, the upper limit of the rubbery plateau extends to considerably higher temperatures as expected. In addition, it also exhibits a Young's modulus of 75 MPa and a tensile strength of 26 MPa, which are, respectively, a factor of three and two higher than of the polyurethane counterpart, PTMO-*p*PDI-U. Similar to its polyurethane analog, the polyurea, PTMO-*p*PDI-Ur also exhibits neck formation and a yield point in its stress–strain response at ambient temperature. Another important advantage conferred by the low HS content in PTMO-*p*PDI-Ur is that the copolymer can be easily remolded (at 210 °C) without degradation or chemical cross-linking to generate a transparent homogeneous film that possesses comparable physical property behavior and morphology. We conducted tensile tests of the sample PTMO-*p*PDI-Ur before and after compression molding. The samples exhibited comparable Young's modulus, tensile strength, and elongation at break, thereby indicating that degradation or chemical cross-linking upon remolding was limited, if any. In contrast, under similar thermal molding conditions, the well-known commercial spandex, which is a segmented polyurethaneurea with greater than 80 wt% elastomeric component, begins to lose structural integrity and is not moldable. For this reason spandex, which possesses much more extensive bidentate hydrogen bonding, requires solution processing.

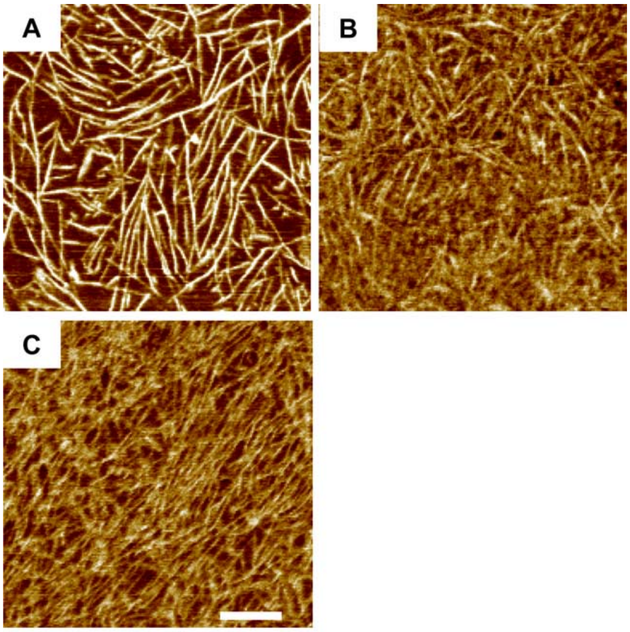

Fig. 4. Ambient temperature tapping-mode atomic force microscopy phase images of copolymer films cast from 20 wt% solution in DMF. (A) PTMO-*p*PDI-U; (B) PTMO-*p*PDI-Ur; and (C) PTMO-*m*PDI-Ur. The above images were captured at a set point ratio of 0.6. Note: the imaging tip in tapping mode AFM probes not just the free surface of a given sample but also the region a few nanometers underneath the free surface. This is the reason why the above phase images possess a higher percentage of bright regions than might be expect in a sample with 14 wt% hard segment content.

An understanding of the influence of the HS symmetry on the $E'$ response can be gained by comparing PTMO-*p*PDI-U with PTMO-*m*PDI-U. In the latter copolymer, the SS glass transition results in a precipitous drop in its $E'$. A very narrow rubbery plateau extends thereafter and its average plateau modulus is approximately an order of magnitude lower than that of PTMO-*p*PDI-U. Such an inferior service window response of PTMO-*m*PDI-U can be attributed to the absence of symmetry in the *m*PDI based HS which hinders their long-range connectivity. We also did not observe any hard phase crystallinity in this sample by either WAXS or DSC. In fact, the solution cast film of PTMO-*m*PDI-U is tacky at ambient temperature whereas that of PTMO-*p*PDI-U is distinctly non-tacky. Moreover, the solution cast film of the copolymer synthesized by utilizing an equal weight fraction mixture of *m*PDI and *p*PDI is also very tacky. This observation further confirms the importance of HS symmetry in enabling their long-range connectivity in copolymers having low HS content. Substitution of the monodentate hydrogen bond network in PTMO-*m*PDI-U with its bidentate counterpart in the segmented polyurea PTMO-*m*PDI-Ur raises the average plateau modulus of the copolymer nearly up to the level of the symmetric *p*PDI based samples. DSC analysis demonstrated that the hard phase of this sample was also able to crystallize. Moreover, its rubbery plateau is much broader than the polyurethane, PTMO-*p*PDI-U. Such behavior indicates that in addition to HS symmetry, the nature of the hydrogen bonded network within the hard phase distinctly influences HS long-range connectivity (see below) and hard phase crystallizability. Not surprisingly, PTMO-*p*PDI-Ur, which has both bidentate hydrogen bonding and a symmetric HS, exhibits the most enhanced service window response amongst the series addressed in Fig. 1.

The HS structure and its type of hydrogen bonding strongly influence the potential crystallizability and cohesiveness of the hard domains formed. This fact is evident from the tan $\delta$ response (Fig. 2). Here we note that with the exception of PTMO-*m*PDI-U, the peak value of tan $\delta$ is maintained between 0.2 and 0.3, whereas that for the remaining sample is above 1.0. While at first the higher tan $\delta$ value of the sample might be thought to imply better microphase separation, this is not the case based of the obvious clear sharp microphase separated AFM images of the other three materials to be discussed shortly. Indeed, WAXS, SAXS, and DSC data, not shown here, directly support the AFM results. Furthermore, one observes that PTMO-*m*PDI-U exhibits a very short rubbery plateau and then undergoes viscous flow below room temperature, thereby suggesting that it has relatively little microphase separation or if it does, the HS phase is not cohesive enough to enable an extended rubbery plateau before the HS softens and flow occurs. In addition, SAXS and DSC also did not indicate any microphase separation. On the other hand the cause of the surprisingly depressed tan $\delta$ peak of the three samples that display sharp microphase separation is believed to be due to the strong restrictions placed on the mobility of the SS phase by the rigid percolated HS that are covalently bonded to the relatively low MW (ca. 1000 g/mol) SS.

As indicated above, we also utilized tapping-mode AFM to confirm our hypothesis regarding the presence of a percolated HS phase in some of the copolymers (Fig. 4). As noted above, the sample PTMO-*p*PDI-U (Fig. 4(A)) exhibits long ribbon-like bright regions that are the hard domains. Furthermore, there appears to be little to no sign of branching by the HS ribbon phase. The average width of these ribbons determined by AFM is ca. 30 Å. Such morphology strongly suggests that the HS, which consist of only a single diisocyanate-derived moiety, pack perpendicular to the long axis of the ribbons. Aneja and Wilkes have also noted similar packing in PTMO based polyurethanes with uniform HS length [7]. The hard domains in PTMO-*p*PDI-U are semicrystalline (see earlier discussion) and their connectivity is facilitated by the HS's ability to establish a hydrogen bonded network; such connectivity in turn results in the percolation of the HS through the soft matrix. In fact, the calculated molecular length of the HS, which includes the two urethane linkages and the link between them, in PTMO-*p*PDI-U is ca. 10 Å. The difference between the observed width of the ribbons and the calculated HS length, we strongly believe, arises because portions of the SS at the interface with the hard phase experience considerable restrictions to their mobility. Therefore, in this more rigid interfacial region the portions of the included SS also appear bright in the phase image. The general morphology of the segmented polyurea PTMO-*p*PDI-Ur (Fig. 4(B)) is similar to that of its polyurethane counterpart (Fig. 4(A)).

In our earlier discussion we noted that the copolymer, PTMO-*m*PDI-U was tacky and its dynamic mechanical response suggested greater microphase mixing than in the other samples within the series. This conclusion is supported by AFM because we did not observe the presence of hard and soft regions in the phase image of this sample. On the other hand, its polyurea counterpart, namely PTMO-*m*PDI-Ur (Fig. 4(C)) clearly exhibits ribbon-like hard domains. This implies that the more cohesive bidentate hydrogen bonding of the urea groups can overcome the decreased symmetry of the mPDI diisocyanate in promoting HS connectivity. As an aside, the morphologies of both polyurethane and polyurea copolymers based on the aliphatic CHDI and HDI, just like their *p*PDI counterparts, also consist of ribbon-like hard domains that percolate through the soft matrix.

## 4. Conclusions

These results undermine the widely held belief that it is necessary to employ chain extension to produce segmented polyurethane and polyurea copolymers with useful structural properties. In particular, we have demonstrated that non-chain extended segmented urea copolymers in which the HS is based on only a single diisocyanate molecule may well exhibit properties, such as the breadth of the service window, the average plateau modulus, stiffness, tensile strength, and elongation at break that are similar to chain extended segmented copolymers that possess distinctly higher HS content. However, careful control of the HS symmetry and the nature of the hydrogen bonding are necessary to achieve such improved performance in non-chain extended systems. Thus, this report particularly provides strong evidence for the controlling role played by the symmetry of the hard segment in morphology development in polyurethanes and new direction for the production of thermoplastic segmented urea copolymers that display a considerable thermal range for their service window yet be solution as well as melt processable.

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