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ARTICLE

Novel Synthetic Approach for the Preparation of Poly(urethaneurea) Elastomers

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ABSTRACT: Novel segmented poly(urethaneurea) elastomers (TPUU) were prepared through the reaction of poly(tetramethylene oxide)glycols (PTMO-1000 and PTMO-2000) with excess aromatic diisocyanates (TDI and MDI), followed by *in situ* chain extension with water, through the formation of urea linkages. High molecular weight TPUU polymers with high urea hard segment (HS) contents of up to 44% by weight were obtained. FTIR analysis of the carbonyl region clearly showed the presence of strongly hydrogen bonded urethane and urea groups in the system. Dynamic mechanical analysis indicated the formation of microphase separated morphologies with well-defined PTMO glass transitions, followed by a composition dependent rubbery plateau extending well beyond 200 °C. Tapping mode AFM studies clearly indicated the formation of microphase morphology with hard urea domains dispersed or percolated through soft polyether matrix. Stress–strain tests demonstrated the formation of very strong elastomers with tensile strengths of up to 50 MPa. Tensile properties also showed a strong dependence on the soft segment molecular weight, structure of the diisocyanate used and HS content of the copolymer.

Introduction

Thermoplastic segmented poly(urethaneurea) elastomers (TPUU) are an important class of polymeric materials, which has extensively been investigated by both academic and industrial research groups for over 5 decades.[1–7] These copolymers are typically prepared by a two step process, called the “prepolymer method”, in which an oligomeric polyether or polyester glycol is reacted with an excess of diisocyanate followed by chain extension with stoichiometric equivalent of an organic diamine. One of the best known examples of TPUU is Du Pont’s Lycra.[3] Because of thermal instability of urethane and urea groups above about 200 °C, TPUUs are usually prepared in solution in highly polar solvents, such as dimethylformamide (DMF) and dimethylacetamide (DMAC).[3,8] Even in such polar solvents, due to extremely strong hydrogen bonding between the urea groups, physical gelation is a serious problem. This may effectively be avoided (i) by limiting the average molecular weight of the TPUU through the use of monofunctional end blockers such as butanol or dibutylamine and (ii) through the employment of alcohols (such as 2-propanol) as a cosolvent during chain extension reactions.[8,9]

Water is a key reactant in the preparation of high resilience flexible and rigid polyurethane foam formulations,[6,10,11] where it is used to generate carbon dioxide and produce urea groups in the system. As shown below, it is well-known that water reacts with an isocyanate group to produce an amine and carbon dioxide. The amine formed immediately reacts with another isocyanate to form a urea group. In this reaction scheme formation of the amine (reaction 1) is the rate-determining step.

$$\mathrm{R-NCO + H_2O \rightarrow R-NH_2 + CO_2\uparrow} \qquad \text{(reaction 1)}$$

$$\mathrm{R-NH_2 + R-NCO \rightarrow R-N(-H)-}C\mathrm{(=O)-N(-H)-R} \qquad \text{(reaction 2)}$$

Interestingly the use of water as an *in situ* chain extender in TPUU has not been investigated until very recently. Hilborn and co-workers recently demonstrated the preparation of various segmented TPUUs based on aliphatic diisocyanates, through the use of water vapor as an *in situ* chain extender.[12,13] For this purpose they first prepared a prepolymer in DMF solution and then slowly bubbled nitrogen gas through a water reservoir to carry the water vapor into the reaction system. Since aliphatic diisocyanates were employed, significant amounts of triamine catalysts had to be used in order to push the reactions to completion. However, through the use of this technique they demonstrated the preparation of TPUUs with very high urea contents, which is always problematic due to gelation of the polymer solution because of very strong hydrogen bonding between urea groups formed during the chain extension process. In order to avoid gel formation, it is necessary (i) to limit the overall molecular weight of the polymer, and/or (ii) to use an alcohol, such as 2-propanol as a cosolvent.[8,9] As a comparison they also used liquid water as the chain extender, which was added slowly through an addition funnel in a DMF solution. We have also used water as an *in situ* generator of urea linkages for the preparation of model branched poly(urethaneurea)s.[14]

We have been investigating the preparation, characterization and structure–property behavior of TPUUs for several decades. Through these studies we have demonstrated the critical roles played by; (i) chemical structure and the molecular weight of soft segments,[14–17] (ii) strength of hydrogen bonding,[15–18] and (iii) the symmetry of the diisocyanates[14,18] on the morphology and structure–property behavior of TPUUs. In this study we present a simple one-pot method on the use of water as an *in situ* chain extender for the preparation of a series of poly(urethaneurea)s based on aromatic diisocyanates and poly(tetramethylene oxide)glycol oligomers (PTMO). Structure–property behavior of these systems is also presented.

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Experimental Section

Materials. 4,4′-Diphenylmethane diisocyanate (MDI) and toluene diisocyanate (80/20 mixture of 2,4- and 2,6-isomers) (TDI) with purities of greater than 99.5% were kindly supplied by Bayer AG. Poly(tetramethylene oxide)glycol (PTMO) oligomers with number-average molecular weights (M_n) of 975 (PTMO-1000) and 2040 g/mol (PTMO-2000) were kindly supplied by Du Pont. Reagent grade dimethylformamide (DMF) (Aldrich) was used as received. Triple distilled water was prepared in our laboratories.

Polymerization Procedure. All reactions were conducted in 3-neck, round-bottom Pyrex flasks equipped with an overhead stirrer, addition funnel and thermometer. Prepolymers were prepared in DMF at a concentration of approximately 70% solids by mass. Prepolymer reactions based on aromatic diisocyanates MDI and TDI were conducted at room temperature and 50 °C respectively. Completion of the prepolymer formation reactions were determined by FTIR spectroscopy following the complete disappearance of strong and broad O−H absorption peak centered around 3400 cm^{-1} and formation of urethane and urea N−H at 3300 cm^{-1} and C═O peaks in 1725−1650 cm^{-1} range.

For chain extension, stoichiometric amount of water was dissolved in DMF and a fairly dilute solution (1/200 water/DMF by volume) was prepared. This solution was introduced into an addition funnel and added dropwise into the reaction mixture over a period of about 3−5 h. Chain extension reactions for TDI based copolymers were conducted at 70 °C, whereas for MDI based systems reactions were carried out at room temperature. Reaction mixture was diluted with DMF as the viscosity of the solution increased due to chain extension and formation of strongly hydrogen bonding urea groups. Depending on the structure of the diisocyanate used and the urea content of the copolymers formed the final concentration of the reaction mixtures varied between 10 and 20% by mass of solids.

Characterization Methods. FTIR spectra were recorded on a Nicolet Impact 400D spectrophotometer with a resolution of 2 cm^{-1}, using thin films cast on KBr disks. Solvent was completely removed by heating the KBr disk with a hot (100 °C) air gun for several minutes.

Intrinsic viscosities were determined using Ubbelohde viscometers at 25 ± 0.1 °C, in DMF.

Films used in AFM studies, DMA measurements and stress−strain tests were prepared by solution casting onto Teflon plates from DMF. Solvent was first evaporated in an air oven at 50 °C overnight and then in a vacuum oven at 75 °C until constant weight was reached. Typical film thickness obtained was about 0.5 mm. Films obtained were kept in sealed polyethylene bags in a desiccator for at least 3 days before any measurements.

Dynamic mechanical analysis (DMA) of the polymers was obtained on a TA DMA Q800 instrument. Measurements were made in tensile mode, between −100 and +250 °C, under nitrogen atmosphere, at a heating rate of 3 °C per minute and a frequency of 1 Hz.

Tapping mode atomic force microscopy (AFM) phase images of copolymer samples were captured under ambient conditions using a Veeco atomic force microscope equipped with a Nanoscope IVa controller. Nanosensors Point Probe Plus noncontact/tapping mode, high resonance frequency with a reflective aluminum coating (PPP-NCH-50) were used for imaging. These tips had a nominal force constant of 42 N/m, resonance frequency of ∼320 kHz and a radius of curvature < 10 nm. Images were captured at 1 Hz frequency and a set-point ratio of ∼0.6 (medium to hard tapping) under ambient conditions.

Stress−strain behaviors of the copolymers were determined using an Instron Model 4411 Universal Tester at room temperature. Dog-bone samples were tested with a crosshead speed of 25 mm/min. Dog-bone samples were cut from the films prepared using a standard (ASTM 1708) die.

Table 1. Chemical Compositions and Intrinsic Viscosities of Water Chain Extended TPUUs

polymer code	diisocyanate	PTMO $\langle M_n \rangle$ (g/mol)	[NCO]/[PTMO]/[H_2O]	HS (wt %)	$[\eta]^a$ (dL/g)
T-PT1−26	TDI	975	2:1:1	26.3	0.49
T-PT1−35	TDI	975	3:1:2	34.9	0.56
T-PT2−15	TDI	2040	2:1:1	14.6	0.48
T-PT2−20	TDI	2040	3:1:2	20.4	0.44
T-PT2−26	TDI	2040	4:1:3	25.5	
T-PT2−30	TDI	2040	5:1:4	29.9	0.66
M-PT1−34	MDI	975	2:1:1	33.9	0.54
M-PT1−44	MDI	975	3:1:2	43.5	
M-PT2−20	MDI	2040	2:1:1	19.7	0.72
M-PT2−27	MDI	2040	3:1:2	26.9	0.51
M-PT2−33	MDI	2040	4:1:3	32.9	

[a] Viscosity measurements were made in DMF at 23 °C.

Results and Discussion

Segmented poly(urethaneurea) elastomers (TPUU) are high strength materials which find many applications such as protective coatings, textile fibers, semipermeable membranes, shape-memory polymers, and biomaterials. TPUUs are usually prepared by the chain extension of a diisocyanate-terminated prepolymer with a low molecular weight diamine, such as ethylene diamine or hexamethylene diamine. Because of the formation of urea groups, which can form extremely strong, bidentate hydrogen bonding even in solution, physical gelation is a serious problem during diamine chain extension, even in very polar solvents such as DMF and DMAC. This limits the amount of urea hard segments that can be incorporated into these copolymers when aromatic diisocyanates are used. It is possible to use isopropyl alcohol as a cosolvent when aliphatic diisocyanates are employed,[19] which can prevent gelation during reactions. In this study we report a simple, novel route for the preparation of poly(urethaneurea)s with fairly high urea contents, where water is used as a chain extender. Although water is widely used as a reactant in PU foams, its use in thermoplastic PU systems has been very limited.[12,13] As already discussed, water reacts with an isocyanate group, converting it to an amine as shown in reaction 1, which immediately reacts with another isocyanate to form the urea linkage.

Table 1 gives the list of the copolymers synthesized, their molar compositions, hard segment contents and intrinsic viscosity values. The coding T-PT1−35 indicates a TPUU based on TDI, PTMO-1000 and water with 35% by weight urea hard segment content. Similarly M-PT2−27 denotes a TPUU made of MDI, PTMO-2000 and water with a hard segment content of 27% by weight. As shown in Table 1, by using water as an *in situ* chain extender it is possible to prepare aromatic poly(urethaneurea)s in DMF, with fairly high urea hard segment contents of 43.5%, which is very difficult, almost impossible to prepare by using conventional diamine chain extenders. As indicated by the intrinsic viscosity values provided in Table 1, the average molecular weights of the polymers formed are fairly high. They are all film forming with fairly high tensile strengths as discussed later on in the manuscript.

Figure 1 provides the 1800−1500 cm^{-1} region of the FTIR spectra for various stages during the synthesis of T-PT2−15 copolymer. Spectrum A is for the isocyanate terminated prepolymer, which displays a strong urethane C═O peak centered at 1725 cm^{-1}, and two well-defined peaks, one centered at 1603 cm^{-1} due to C═C stretching in the aromatic ring in TDI and the other centered at 1539 cm^{-1} due to amide-II (NH−C═O) bending absorption. In fact, the latter two absorption peaks are included as reference peaks since their position or magnitude do not change appreciably during the chain extension reaction. As the water is added as the chain extender, a small shoulder at 1673 cm^{-1} indicating urea formation, appears (spectrum B, at 20% water

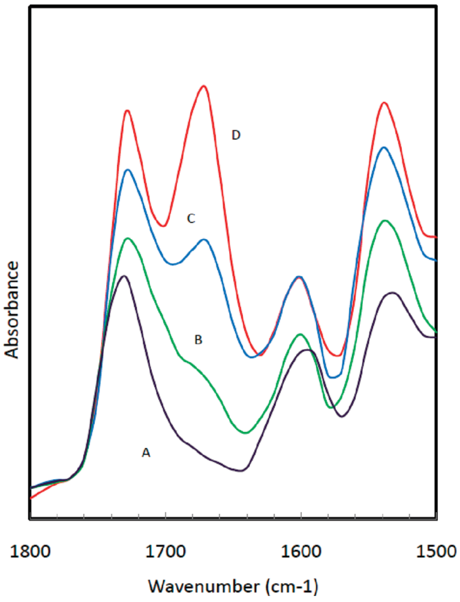

Figure 1. Carbonyl region of the FTIR spectrum at various stages during the synthesis of T-PT2–15 copolymer. (A) Isocyanate terminated prepolymer (B) after 20% water addition and (C) after 50% water addition and (D) final poly(urethaneurea) copolymer.

addition). At 50% water addition (spectrum C) 1673 cm^{-1} peak becomes well-defined. Upon completion of the chain extension process (spectrum D) two well-defined carbonyl peaks; one centered at 1725 cm^{-1} indicating the somewhat weakly hydrogen bonded urethane groups and the other at 1673 cm^{-1} showing strongly hydrogen bonded urea groups are present in the spectrum.

Tapping Mode AFM Studies. Tapping mode AFM is a very useful technique in studying the topology and near surface morphology of segmented polyurethane and polyurea copolymers,[16−18,20,21] which may be different than the bulk morphology. AFM phase images of various poly(urethaneurea)s prepared in this study are provided in Figures 2−4. The dark and the light regions in the phase images correspond to soft and hard domains respectively, which is also indicative of microphase separation in the system.

Parts a and b of Figure 2 provide the phase images of T-PT1−26 and T-PT1−35. In general it is difficult to obtain good microphase separation in TDI based polyurethanes prepared using PTMO-1000.[22,23] This is mainly due to the presence of fairly short PTMO oligomers in the system as a result of the normal molecular weight distribution in PTMO-1000, which leads to phase mixing. However, as shown in Figure 2a, when water is used as the chain extender, extremely rigid and polar aromatic urea groups obtained lead to a microphase separated morphology. Since urea content of the copolymer is not very high, the fibrillar hard segments formed are fairly short and randomly distributed. On the other hand, as the urea hard segment content increases to 35% as in T-PT1−35 sample (Figure 2b), fairly long urea hard segments form ribbons and lead to the formation of a percolated network through the soft matrix. As will be discussed later on in the manuscript such a change in the morphology leads to dramatic changes in the dynamic mechanical behavior and tensile properties of the copolymers.

For comparison AFM phase image of MDI and PTMO-1000 based copolymer (M-PT1−34) is provided on Figure 3. In fact this copolymer has the same molar composition as T-PT1−26, but since MDI has a much higher molecular weight than TDI, on percent weight basis it has higher hard segment content. This copolymer also displays microphase separation where hard segments seem to form both small randomly distributed domains and rather long ribbons.

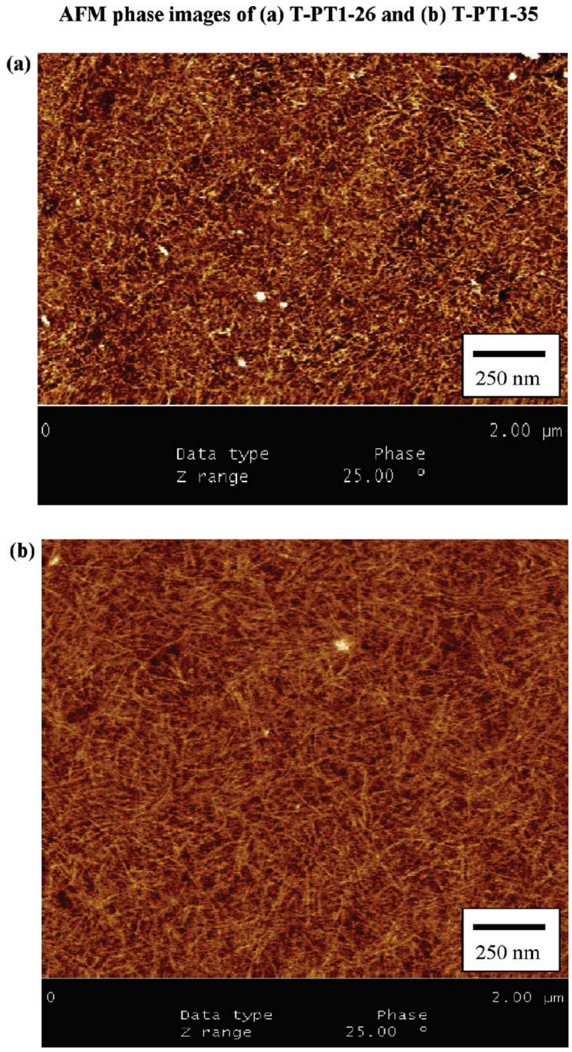

Figure 2. AFM phase images of (a) T-PT1−26 and (b) T-PT1−35.

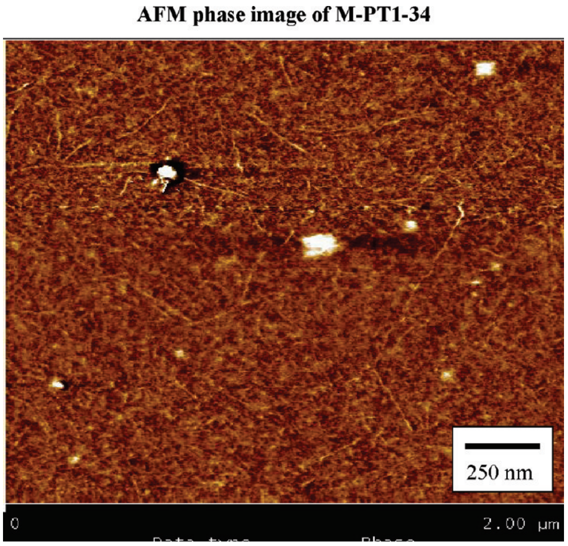

Figure 3. AFM phase image of M-PT1−34.

Unlike PTMO-1000 based systems, when PTMO-2000 is used as the soft segment (which is the main choice for most of

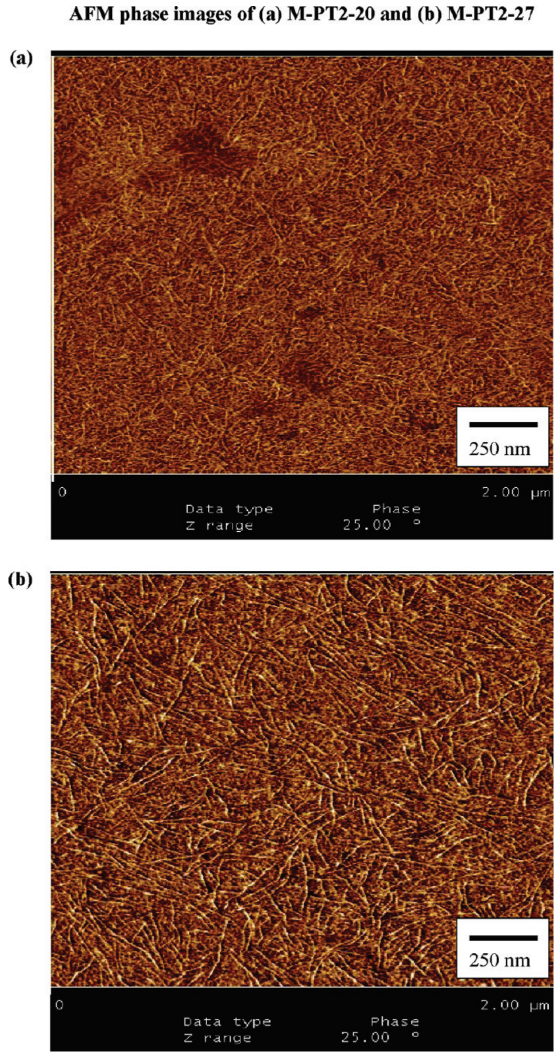

Figure 4. AFM phase images of (a) M-PT2−20 and (b) M-PT2−27.

the commercial polyether based polyurethane systems) better microphase separation is observed.[20−23] As shown on the AFM phase images provided in parts a and b of Figure 4, PTMO-2000 based poly(urethaneurea)s (M-PT2−20 and M-PT2−27) display excellent microphase separation. In both images, it is possible to see the formation of urea hard segment ribbons that percolate throughout the soft matrix. As the hard segment content increases (Figure 2b) the ribbons become thicker and much longer.[21] Average surface roughness of the films obtained may also be important for various applications, since roughness may affect properties such as friction coefficient, adhesion and surface hydrophobicity. From 2D AFM height images on 2.0 × 2.0 μm scans, average surface roughness values (R_q) of the samples were determined. These values, which are in 22−35 nm range are provided in Table 2. Lower surface roughness values on polyurethane films may be obtained if they are prepared by spin coating from dilute solutions.[24]

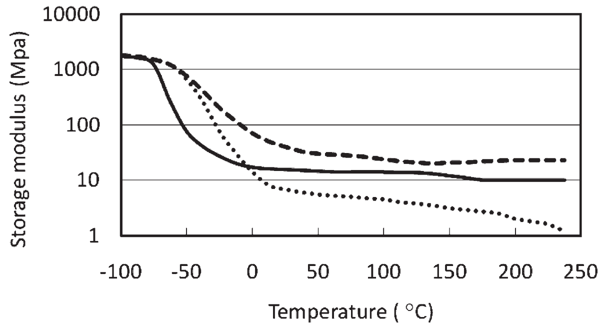

Figure 5. Storage modulus−temperature curves for T-PT1−26 (- - -), T-PT1−35 (•••) and T-PT2−20 (— —).

Table 2. Average Surface Roughness Values of Solution Cast Poly(urethaneurea) Films

polymer code	T-PT1−26	T-PT1−35	M-PT1−34	M-PT2−20	M-PT2−27
R_q (nm)	23.3	35.2	28.7	27.3	22.6

Dynamic Mechanical Analysis. Thermomechanical properties of segmented poly(urethaneurea)s are strongly dependent on their molecular structures, chemical compositions and resultant microphase separated morphologies. Comparative storage modulus−temperature curves for T-PT1−26, T-PT1−35, and T-PT2−20 are provided in Figure 5. As shown in Table 1, PT1-based copolymers have [TDI]/[PTMO]/[water] molar ratios of (2/1/1) and (3/1/2) and urea hard segment contents of 26.3 and 34.9% by weight, respectively. In DMA analysis (Figure 5), both polymers display a fairly broad soft segment glass transition that extends between −70 and 0 °C, typical for PTMO-1000 based TPUs.[25] As already explained in AFM discussions, this is due to the presence of significant amount of low molecular weight PTMO in the starting oligomer, which leads to phase mixing. Soft segment T_g values obtained from the inflection points of modulus−temperature curves are approximately −30 °C for both copolymers. Glass transition region is followed by a fairly long and temperature insensitive rubbery plateau extending beyond 200 °C. T-PT1−26 indicates rubbery flow above 200 °C, whereas no flow is observed in T-PT1−35 due to its very high and strongly hydrogen bonded urea hard segment content. At this point we would like to point out that urea groups typically start degrading around 225−250 °C.[26] That is why the DMA measurements were terminated at 250 °C. Furthermore, although all poly(urethaneurea) copolymers produced are thermoplastic in nature, due to degradation of urea groups they are difficult to process by thermal methods. As expected, the rubbery plateau modulus of T-PT1−35 is much higher than that of T-PT1−26 due to its higher urea content. Room temperature rubbery modulus values determined from Figure 5, for T-PT1−26 and T-PT1−35 are approximately 8 and 40 MPa, respectively. Very interestingly, these moduli values are very similar to Young's modulus values obtained from the tensile tests, which are given in Table 2, as 7.80 and 44.5 MPa for T-PT1−26 and T-PT1−35 respectively. As shown on Figure 5, unlike PTMO-1000 based copolymers poly(urethaneurea) based on PTMO-2000 (T-PT2−20) displays a very sharp soft segment glass transition around −65 °C, followed by a rubbery plateau that extends from −50 to well above 200 °C. Such a behavior also clearly indicates very good microphase separation in this copolymer with strongly hydrogen bonded urea hard segments. As can be seen in Figure 5, the rubbery plateau modulus of T-PT2−20 is around 10−12 MPa, which agrees very well with the Young's modulus (10.5 MPa) of this copolymer obtained from tensile tests and reported in Table 2.

Modulus−temperature curves for MDI based copolymers prepared by using PTMO-1000 (M-PT1−34) and PTMO-2000 (M-PT2−20) both with [MDI]/[PTMO]/[water] molar ratio of (2/1/1), are reproduced in Figure 6. As expected these copolymers also display two phase morphologies, with well-defined soft segment glass transitions followed by a rubbery plateau, extending well beyond 200 °C. M-PT2−20 also shows PTMO crystallization and melting clearly visible in

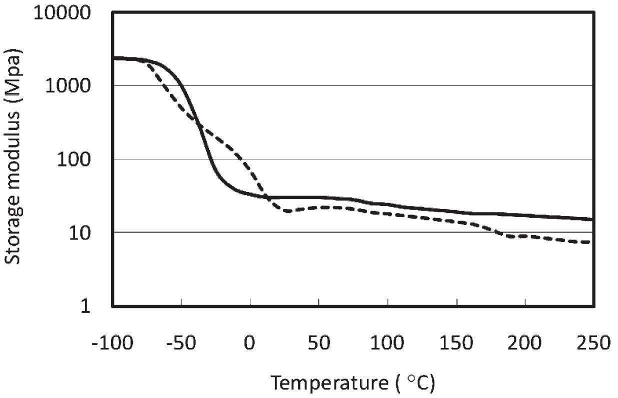

Figure 6. Storage modulus−temperature curves for M-PT1−34 (— —) and M-PT2−20 (- - -).

Table 3. Tensile Properties of Water Chain Extended TPUUs

polymer code	HS (wt %)	modulus (MPa)	tensile strength (MPa)	elongation (%)
T-PT1−26	26.3	7.80	20.0	1200
T-PT1−35	34.9	44.5	47.5	600
T-PT2−20	20.4	10.5	25.5	1000
T-PT2−26	25.5	24.0	32.5	800
T-PT2−30	29.9	41.0	40.0	650
M-PT2−20	19.7	19.5	24.5	900
M-PT2−27	26.9	33.0	32.1	720
M-PT2−33	32.9	65.0	48.8	500

the modulus−temperature curve just after T_g in the −50 to +25 °C range. From Figure 6, soft segment T_g values are determined as −65 and −40 °C for M-PT2−20 and M-PT1−34, respectively. As expected, these results indicate better microphase separation in MDI based copolymers when compared with those of TDI based systems. Rubbery plateau modulus for M-PT2−20 is estimated to be about 20−25 MPa from the DMA studies. Value of the Young's modulus for M-PT2−20, obtained from stress−strain measurements (Table 3) is 19.6 MPa.

Stress−Strain Behavior. Aromatic diisocyanate based water chain extended poly(urethaneurea)s display excellent elastomeric properties, such as; tensile strengths of up to almost 50 MPa and very high elongation at break values of up to 1200%. These materials also display excellent recovery or very low hysteresis and set, when released following 300% elongation. Representative stress−strain curves for TDI and MDI based copolymers with PTMO-1000 and PTMO-2000 soft segments and various urea hard segment contents are reproduced in Figure 7 and Figure 8. Results of stress−strain tests are summarized in Table 3 for all copolymers. As can clearly be seen from the stress−strain curves and also the data provided in Table 3, initial modulus and the ultimate tensile strengths of both TDI and MDI based copolymers increase with the hard segment content, whereas elongation at break values decrease, which is expected. All copolymers whether based on PTMO-1000 or PTMO-2000 also display strain induced crystallization, resulting in reasonable upturns in the stress−strain curves at high elongations. This is also an expected behavior for PTMO based segmented copolymers. These results clearly demonstrate that through the utilization of water as an *in situ* chain extender that forms urea linkages, it is possible to produce novel poly(urethaneurea) copolymers with a wide range of tensile properties.

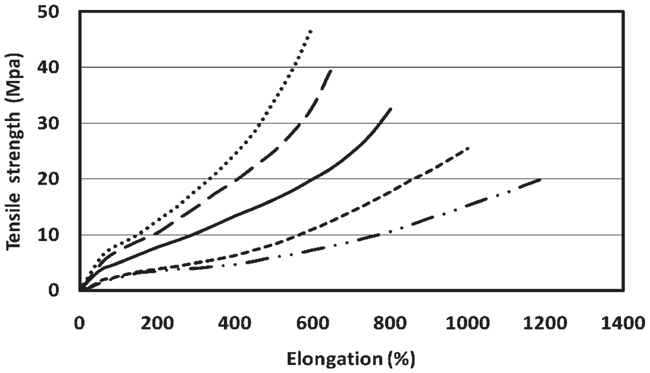

Figure 7. Stress−strain curves for TDI-based poly(urethaneurea)s T-PT1−26 (−••−), T-PT1−35 (•••), T-PT2−20 (- - -), T-PT2−26 (—), T-PT2−30 (− −).

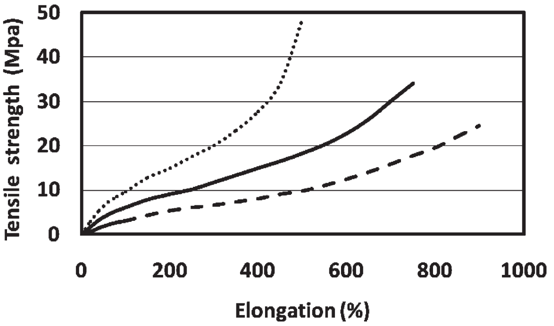

Figure 8. Stress−strain curves for MDI based polyurethanes M-PT2−20 (•••), M-PT2−27 (—) and M-PT2−33 (•••).

Conclusions

We demonstrated the use of water as an *in situ* chain extender leading to the formation of urea linkages, for the preparation of novel, high molecular weight, segmented poly(urethaneurea) elastomers, by following the conventional two-step prepolymer procedure. When aromatic diisocyanates, such as TDI and MDI, are used, reactions can be carried out in DMF solutions under very mild conditions (25−50 °C) without using any catalysts.

Poly(urethaneurea) copolymers obtained display structure and composition dependent microphase morphologies as determined by tapping mode AFM. Dynamic mechanical analysis of the copolymers also show microphase separation. Because of the presence of strongly hydrogen bonding urea groups all copolymers display fairly long rubbery plateau regions extending well over 200 °C. Copolymers also display excellent stress−strain properties as a function of polymer structure and composition, where ultimate tensile strengths in 20−50 MPa and elongations between 500−1200% are obtained.

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