Segmented Polythiourethane Elastomers through Sequential Thiol−Ene and Thiol−Isocyanate Reactions

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ABSTRACT: Highly elastic polythiourethanes were synthesized through sequential thiol reactions involving 1,6-hexanedithiol (HDT), 1,4-butanediol diacrylate (BDDA), and several diisocyanates (ISO). Thiol-terminated prepolymers prepared by the phosphine-catalyzed thiol Michael addition of HDT and BDDA form flexible thioether oligomers which were then incorporated as soft segments into polythiourethane main chains through a triethylamine-catalyzed thiol−isocyanate reaction with HDT and ISO to give polymers with both hard and soft segments. Real-time FTIR, used to investigate the kinetic conversion profiles of both reactions, and NMR showed that both the thiol Michael addition and the thiol−isocyanate reactions are very fast and efficient, having the chemical attributes generally associated with thiol−ene radical click reactions. The effects of the soft and hard segment length, soft/hard segment weight ratio, and chemical structure of the ISO on thermal and dynamic thermal mechanical properties was characterized in terms of microphase separation determined by DSC and DMA. Tensile properties of the polythiourethanes were measured and correlated with the degree of microphase mixing between the soft and hard segments.

Introduction

Sulfur-containing polymers such as polythiourethanes, polysulfides, polythioesters, polysulfones, and polythiocarbonates are beginning to attract increased attention due to many important attributes, not the least of which are excellent optical properties and biocompatibility.[1−10] Sulfur can lead to enhancement in refractive index, increased flexibility, and enhanced crystallinity when incorporated into polymer thermosets and thermoplastics.[1,9−16] However, in order for sulfur-containing polymers to be used in many applications, physical/mechanical properties such as extensibility and toughness must be tailored and optimized.

Multifunctional thiols (−SH) have been employed to form sulfur linkages in polymer backbones through reactions with unsaturated hydrocarbons (e.g., allyl ether, vinyl ether, (meth)-acrylate), epoxies, or isocyanates.[17−22] Such polymers have rather limited extensibility;[17−29] i.e., they are not good elastomers. However, the inclusion of difunctional and monofunctional thiols in thiol−ene network results in low-modulus, elastomeric materials.[30]

It is well-known that incorporation of urethane linkages into both linear polymers and cross-linked networks results in hydrogen-bonding capabilities that imparts exceptional elastic properties. Interestingly, in the case of thiol−acrylate/ene-based networks, incorporating urethane groups results into the network results in enhanced mechanical and thermal transitions with potential use in bio- and optical applications.[17,27,31] It can be projected that incorporation of a combination of sulfide linkages, which provide for the unique combination of flexibility and crystallizability,[9−16] and thiourethane groups in polymer systems would afford a distinct opportunity to control mechanical and thermal properties. This, combined with the well-known optical and mechanical (flexibility) advantages of thiourethane and sulfide groups in polymer chains, would result in significant potential for the synthesis of useful linear segmented polythiourethane elastomers. It has already been reported that the addition of difunctional thiols to difunctional isocyanates leads to the formation of simple nonsegmented polythiourethanes,[32,33] which are classified as members of the polyurethane family with the hydrogen-bonding features that typically accompany polyurethanes.[32,34,35] In addition to synthesizing polythiourethanes by thiol−isocyanate step growth polymerization processes, polythiourethanes made from cyclic dithiocarbonates by living cationic polymerization have been reported by Endo et al.[36−40] The use of these linear, nonsegmented polythiourethanes, characterized by controllable molecular weights and narrow molecular weight distributions resulting from the living cationic polymerization process, is limited to applications requiring glassy materials and/or highly dense cross-linked structures.[41,42] Since sulfide linkages incorporated into aliphatic polyesters have been reported to lead to the unique combination of flexible films with low glass transitions and high degrees of crystallization,[13] it is expected that the synthesis of segmented polythiourethanes with sulfide linkages in the soft segment would open up a new potential for elastomers with a unique combination of properties. While it is possible to use a combination of short chain dithiols and oligomeric polyols to make segmented elastomeric poly(thiourethane−urethane)s,[43] incorporation of sulfide linkages in the soft segment oligomer would certainly lead to a set of new polymers with high flexibility and enhanced crystallinity.

Herein, we report the efficient synthesis and characterization of segmented polythiourethanes with elastomeric properties induced by microphase separation between soft and hard segments. By making thiol-terminated oligomers with sulfide linkages in the oligomeric chain, followed by subsequent reaction with a combination of a diisocyanate and small molecule dithiol chain extender, the synthesis of a series of high molecular weight polythiourethanes with elevated sulfur content and excellent elastomeric properties has been accomplished. The first reaction involves the highly efficient phosphine catalyzed thiol−acrylate Michael addition reaction, which has been reported[44] as a quantitative, rapid click reaction that we project to proceed by an anionic chain process that is complete on the order of minutes or less upon mixing. This action was previously used to make star polymers in a dilute solution synthetic process.[44] While the triethylamine-catalyzed reaction of dithiols with diacrylates has been reported,[3,45] it is noted that the reaction is very slow and requires long reaction times. Herein, the

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phosphine-catalyzed reaction previously used for the synthesis of star polymers will be used for the first time for quantitative synthesis of thiol-terminated oligomers. The second reaction in the sequence will involve the reaction of the thiol-terminated oligomers and low molecular weight dithiols with diisocyanates using a triethylamine-catalyzed reaction. It has been reported that the tertiary amine-catalyzed thiol−isocyanate reaction is very rapid, proceeds to 100% conversion with no allphonates[33,46] or other side products typical of traditional alcohol−isocyanate reactions, and has many of the attributes of click reactions, including selectivity and no requirement for product cleanup. In the original article by Kolb, Finn, and Sharpless[47] that defined click chemistry, the amine−isocyanate reaction was noted to be quite efficient; the thiol−isocyanate reaction is very closely related to the amine−isocyanate reaction in that it is selective and rapid, resulting in high yields with no byproduct.[33,46] Thus, the sequential phosphine-catalyzed thiol−acrylate and tertiary amine-catalyzed thiol−isocyanate reactions are reported herein to be very effective for the general synthesis of high-performance materials. The segmented polythiourethanes are shown to be high-performance materials characterized by a flexible phase and a rigid hard phase with strong hydrogen bonding and crystallization, respectively. The degree of microphase separation between the soft and hard segments of the resulting series of polythiourethane has been systematically evaluated by thermal and dynamic mechanical analysis, and the results have been correlated with mechanical properties. The inclusion of sulfur in the form of sulfide linkages as well as thiourethane linkages provides a new methodology for the general synthesis of high-performance elastomers. The polythiourethane synthesis by the two sequential high yield reactions in this work presents a clear guide for designing the microstructure of high-performance elastic polythiourethanes with high sulfur content and tailoring the physical properties to meet a potential wide range of applications. It effectively moves sequential thiol chemistry to the realm of an industrially viable synthetic route for fabricating elastomeric polythiourethanes. Since there is a large availability of diacrylates and dithiols available commercially, the prospect for tailoring polythiourethane elastomers to meet a specific set of property requirements for a wide range of applications is significant.

Experimental Section

Materials. 1,6-Hexanedithiol (HDT, ≥97%) and 1,4-butanediol diacrylate (BDDA, 93.7% by GC), used to prepare the thiol-terminated prepolymers, diisocyanates (4,4′-methylenebis(phenyl isocyanate) (MDI, 98%), 4,4′-methylenebis(cyclohexyl isocyanate) (H_{12}MDI, ≥98%), tolylene-2,4-diisocyanate (2,4-TDI, ≥98%), isophorone diisocyanate (IPDI, 98%), and hexamethylene diisocyanate (HDI, ≥99%), dimethylphenylphosphine (DMPPh), and triethylamine (TEA), used as catalysts for the thiol Michael addition and thiol−isocyanate reaction, respectively, were purchased from Aldrich. Dimethylacetamide (DMAc, anhydrous grade), tetrahydrofuran (THF), and butyl acetate (BAc, urethane grade) were also obtained from Aldrich. All chemicals were used as received.

Synthesis of Thiol-Terminated Prepolymers. A 250 mL, round-bottom, three-necked flask with a magnetic stirrer equipped with an ice bath was used as a reactor. First, HDT was mixed with 0.1 wt % of DMPPh and diluted with DMAc to 50 wt % solution in the flask while nitrogen purging. BDDA was dripped into the mixture for 10 min, and the temperature was controlled below 30 °C with an ice bath in order to prevent BDDA from undergoing thermally initiated free-radical polymerization. After completion of adding BDDA, the mixture was further reacted for 10−20 min at room temperature until all the BDDA was consumed. Additional DMAc was added to make the solution 30% by weight of thiol-terminated prepolymer. The complete disappearance of carbon double bonds in BDDA was confirmed by peaks at 812 cm^{-1} for FTIR, 5.71 (q), 5.99 (q), and 6.23 (q) ppm for ^{1}H NMR, and 128.3 and 130.5 ppm for ^{13}C NMR. The molecular weights of thiol-terminated prepolymers (length of soft segment) were controlled by stoichiometry from 1000 to 3000 g/mol with excess thiol and dictated by theoretical calculation using the Carothers equation.[48] M_n was measured using titration and compared with the theoretical values (Table 1).

Table 1. Titration and DSC Results of Thiol-Terminated Prepolymers

SH:acrylate	$M_{n,theo}$ (g/mol)	$M_{n,titration}$ (g/mol)	T_g (°C)	T_m (°C)	ΔH_f (J/g)
1.515:1	1000	1017	−79	25	35.5
1.296:1	1500	1450	−74	29	41.5
1.207:1	2000	1858	−74	33	45.5
1.160:1	2500	2590	−73	44	59.0
1.130:1	3000	2811	−73	47	61.4

Table 2. Formulation of Segmented Polythiourethane Elastomers

run no.	$M_{n,theo}$[a] of hard segment	$M_{n,theo}$[a] of soft segment	wt % of hard segment	isocyanate
M0520	550	2000	21.6	MDI
M0720	750	2000	29.4	MDI
M1020	1000	2000	33.3	MDI
M1010	1000	1000	50.0	MDI
M1015	1000	1500	40.0	MDI
M1020	1000	2000	33.3	MDI
M1025	1000	2500	28.6	MDI
M1030	1000	3000	25.0	MDI
M1020	1000	2000	33.3	MDI
H1020	1000	2000	33.3	HDI
HM1020	1000	2000	33.3	H_{12}MDI
IP1020	1000	2000	33.3	IPDI
T1020	1000	2000	33.3	2,4-TDI

[a] Theoretical molecular weight (length) of segment.

Synthesis of Polythiourethane Elastomers. HDT and thiol-terminated prepolymers were mixed with 0.1 wt % of TEA and DMAc to give a 30% solution, followed by feeding the requisite isocyanate for 10 min at room temperature. Temperature was maintained at less than 30 °C with an ice bath during feeding. The mixtures were further reacted at 60 °C for 1 h. The complete consumption of NCO was confirmed by the disappearance of the FTIR isocyanate peak at 2250 cm^{-1}. The length of the hard segment varied from 550 to 1000 g/mol by stoichiometry. The formulations for the polythiourethane elastomer synthesized are shown in Table 2.

Kinetics. Kinetic profiles of the thiol Michael addition reaction of HDT and BDDA and the subsequent polythiourethane reaction were obtained using real-time infrared (RTIR) spectroscopy. A modified Bruker IFS 88 FTIR spectrometer was equipped with a horizontal sample accessory. Samples for thiol-terminated prepolymer were prepared by adding BDDA into the 40 wt % HDT solution in BAc with 0.006 wt % of DMPPh based on the total solution weight. For polythiourethane formation, the requisite diisocyanate was dissolved in THF and added into the premixed THF solution of HDT, thiol-terminated prepolymer, and 0.03 wt % of TEA based on the total solution weight. The solid content of the final mixture was 20 wt %. Thin samples (25 μm) between two salt plates sealed with silicon were placed immediately in the RTIR after mixing the samples; note that there is some delay in initiating the kinetic measurement which introduces some error into the measurement. The conversion of BDDA and HDT as a function of time was measured by monitoring the peaks of the carbon double bond and thiol at 812 and 2570 cm^{-1}, respectively, while the peak at 2250 cm^{-1} was used to measure the isocyanate conversion.

Characterization. Molecular weights (MW) of the thiol-terminated prepolymer prepared via thiol Michael addition of HDT to BDDA were determined using a thiol titration strategy.[49] In a 250 mL flask, prepolymers were dissolved in 15 mL of pyridine (99%, Aldrich) followed by the addition of 0.4 M silver nitrate aqueous solution (5 mL). This mixture was magnetically stirred for 5 min, and 100 mL of di-H_2O was added with 6 drops of phenolphthalein indicator solution. This mixture was titrated with 0.1 M sodium hydroxide aqueous solution until a light pink color formed. The method was standardized by titration of a known amount of 6-mercapto-1-hexanol; 98.99% reliability was obtained. For the polythiourethane elastomers, molecular weights and PDI were determined using a Viscotek-TDA size exclusion chromatography (GPC) unit comprised of a 302 nm RI (633 nm), 7 mW 90° and 7° true low-angle light scattering detectors, and Viscotek I-Series Mixed Bed low-MW and mid-MW columns. A 20 mM LiBr DMF eluent at 60 °C was used at a flow rate of 1.0 mL/min controlled by an Agilent 1100 series pump. M_n, M_w, and PDI were determined using the Viscotek refractometer and OmniSec software.

^{1}H and ^{13}C NMR spectra of thiol-terminated prepolymers were obtained on a Varian 500 MHz NMR in $CDCl_3$ with tetramethysilane (TMS) as the internal reference.

Thiol-terminated prepolymers and films of polythiourethanes for thermal and mechanical property measurements were prepared by casting the polythiourethane solution on a Teflon mold. After evaporation of DMAc at 80 °C for 24 h and 100 °C for 48 h, the films were further dried and kept at 25 °C under vacuum.

Thermal properties of the thiol-terminated prepolymers and polythiourethane elastomers were characterized by differential scanning calorimetry (DSC, TA Instruments Q 1000) equipped with RCS 90 (Refrigerated Cooling System). Three calibration steps (T_{zero}, enthalpy constant, and temperature calibration) were performed before the measurements. All experiments were carried out under nitrogen with a flow rate of 50 mL/min. Sample weights were 8.0 ± 1.0 mg to ensure sufficient sensitivity for heat capacity measurements. For thiol-terminated prepolymers, DSC scans were conducted over a temperature range from −90 to 100 °C using 10 °C/min heating and cooling rates. On the first heating scan, samples were equilibrated at 60 °C (higher than the T_m of the thiol-terminated prepolymer) for 10 min to erase thermal history and hysteresis of the samples, followed by cooling to −90 °C and a subsequent second heating to 100 °C. The temperature range for scanning the polythiourethane elastomers was −90 to 280 °C to ensure all thermal transitions of the soft and hard segments were observed. All samples were equilibrated at 150 °C (higher than the T_g hard segment) for 10 min before cooling to −90 °C and reheating to 280 °C. Heating and cooling rates were 10 °C/min. The second heating scans were recorded for all thiol-terminated prepolymers and polythiourethane elastomer films.

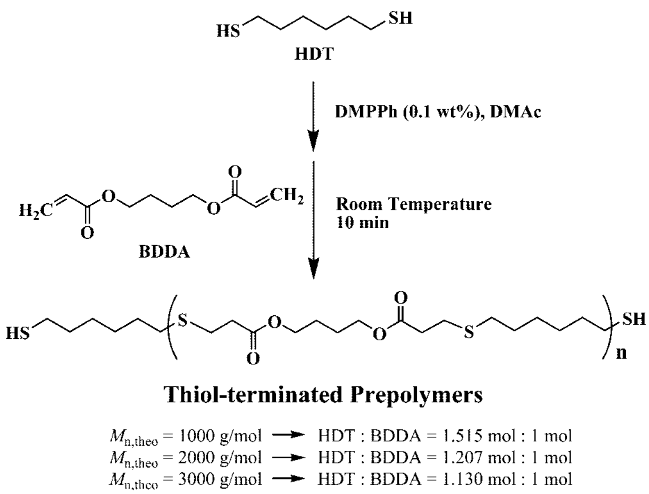
Dynamic thermal mechanical properties of thin cast films were measured using a DMTA (MK VI, Rheometrics). Measurements were conducted in the vertical tension mode with dimensions of $10 \times 5.0 \times 0.5$ mm ($L \times W \times T$) from −110 to 250 °C at a 5 °C/min heating rate and 1 Hz frequency with 0.05% strain.

Tensile property measurements were made with a mechanical testing machine (MTS, Alliance RT/10) according to ASTM D882 using a 100 N load cell with a specimen gauge length of 20 mm at a crosshead speed of 500 mm/min.

Results and Discussion

The highly elastomeric and tough mechanical properties of polyurethanes result from a segmented molecular structure consisting of at least two dissimilar phases along the backbone. Polythiourethanes, as a member of the polyurethane family, are characterized by high refractive index values and biocompatibility as well as strong hydrogen bonding with accompanying outstanding mechanical properties.[41−43] However, polythiourethanes as elastomers have not been reported because of the absence in availability of flexible long-chain polythiols. In this study, thiol−acrylate and thiol−isocyanate reactions which have many of the attributes of click chemistry including high efficiency, little side products, benign catalysts, and high reaction rates were used to synthesize segmented polythiourethanes; we note that in this work we used an organic solvent in which the oligomers and polymers were soluble. In order to incorporate soft segments into polythiourethanes, difunctional thiol (HDT) reacted with difunctional acrylate (BDDA) to form flexible thioether linkages by a very rapid phosphine-catalyzed Michael addition reaction with no byproducts. Hard segments were formed by the reaction of the isocyanates with difunctional thiol (HDT) using triethylamine (TEA) as the catalyst resulting in thiourethane linkages with strong hydrogen bonds. Microphase separation was systematically introduced by the difference in the polarity and chemical structures between soft and hard segments, resulting in structures with highly elastic mechanical properties.

Scheme 1. Synthetic Procedure for the Thiol-Terminated Prepolymers



Thiol-Terminated Prepolymers. The procedure for the preparation of thiol-terminated prepolymers as soft segments in the polythiourethane is shown in Scheme 1. The target theoretical number-average molecular weight values ($M_{n,theo}$) for the thiol oligomers selected to range from 1000 to 3000 g/mol were based upon the use of similar molecular weight diol oligomers for synthesis of high-performance polyurethanes.[50−55] The phosphine-catalyzed thiol (HDT)−acrylate (BDDA) reaction was performed in 50 wt % DMAc solution with only 0.1 wt % of dimethylphenylphosphine (DMPPh); the temperature was carefully controlled to prevent any extraneous free-radical acrylate homopolymerization. In Figure 1, the complete loss of the carbon double bonds in BDDA is shown 20 min after mixing. ^{1}H and ^{13}C NMR for an uncatalyzed mixture of HDT and BDDA and the thiol-terminated prepolymer are given in Figure 2, clearly showing that all of the carbon double bonds completely reacted. No side product formation was detected, indicating that the reaction was quantitative, requiring absolutely no cleanup. Additionally, careful analysis of neat small molecule thiol−acrylate reactions using the nucleophilic DMPPh catalyst also shows that these coupling reactions are quantitative. We have already reported that DMPPh catalyzed thiol−acrylate coupling reactions in dilute solution proceeded rapidly to 100% conversion

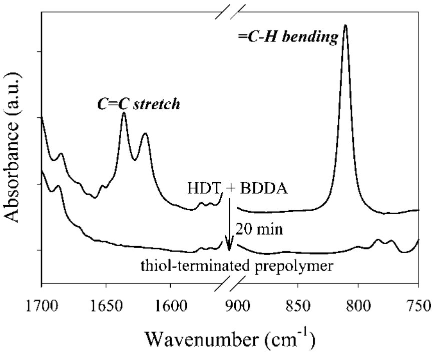


Figure 1. FTIR spectrum of the HDT and BDDA mixture and thiol-terminated prepolymer after the completion of thiol Michael addition reaction.

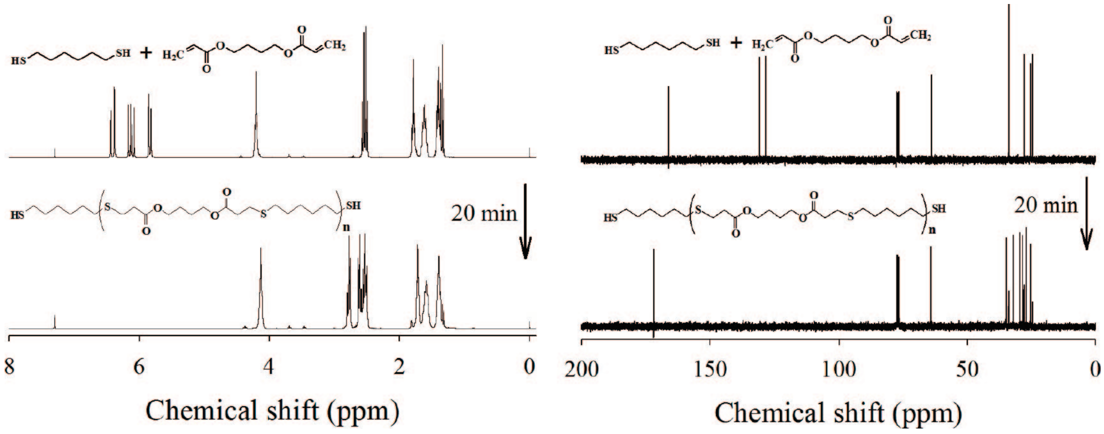


Figure 2. ^{1}H and ^{13}C NMR spectrum of the HDT + BDDA mixture and thiol-terminated prepolymer after the completion of thiol Michael addition reaction.

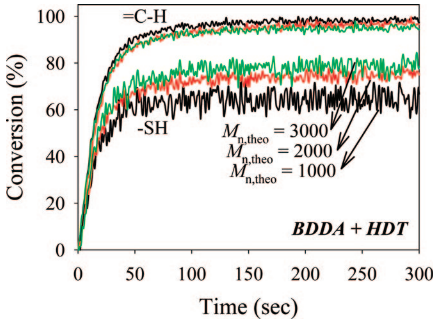


Figure 3. Kinetic profiles of thiol Michael addition reaction with HDT and BDDA as a function of time.

Table 3. Conversion of 1,6-HDT and 1,4-BDDA by RTIR

$M_{n,theo}$ (g/mol)	conversion$_{C=C}$ (%)	conversion$_{thiol}$ (%)
1000	98	65 (65)[a]
2000	96	77 (80)
3000	94	80 (82)

[a] Parentheses is the theoretical conversion of thiols at the actual conversion of acrylate.

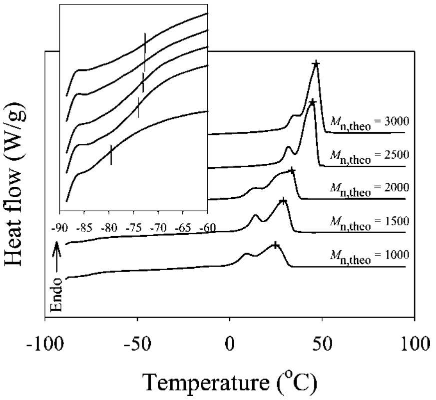


Figure 4. DSC heating scans of thiol-terminated prepolymers.

using a combination of NMR and MALDI to confirm the product identity with no side product formation.[44] The thiol−acrylate coupling reaction mediated by nucleophilic phosphine catalysts is a very powerful click reaction with short reaction times. The kinetic profiles of three samples obtained by RTIR with low concentration of DMPPh (0.006 wt %) in Figure 3 show that the phosphine-catalyzed Michael addition reaction is indeed exceptionally fast and efficient with acrylate conversions of 98%, 96%, and 94%. The corresponding percent thiol conversions in 5 min were 65%, 77%, and 80%, well within experimental error to the values of 65%, 80%, and 82% that are calculated via the corresponding acrylate conversions after adjusting for the SH:acrylate ratios in Table 3. The conversion of thiol varies based on stoichiometry. The acrylate conversion reaches higher than 90% within 200 s regardless of initial component concentration, eventually attaining 100% conversion. The kinetic profiles in Figure 3 show the reaction in real time for the first 5 min. The NMR results in Figure 2 confirm that 100% reaction has occurred by the time samples could be evaluated by NMR, i.e., a few minutes. In order to extend the NMR and IR results and provide an assessment of the molecular weight of the thiol-terminated prepolymers, a method based on end-group analysis by silver nitrate titration was used to assess the number-average molecular weight of all of the samples. In Table 1, titration results for the five thiol-terminated prepolymers prepared using the thiol Michael addition reaction of HDT with BDDA are given. The M_n values obtained by titration are in good agreement with the theoretical molecular weights calculated by the Carothers equation. It is apparent that the molecular weight of the thiol-terminated prepolymers was effectively controlled by the component stoichiometry and the efficient thiol Michael addition reaction. DSC was used to characterize the thermal properties of the thiol-terminated oligomers as a function of molecular weight. As shown in Figure 4 and Table 1, T_g, T_m, and the heat of fusion (ΔH_f) increase with increasing molecular weight, typical of the effect of molecular weight on the thermal transitions of linear crystalline polymers.

Polythiourethane Elastomers. Segmented polythiourethane elastomers were next synthesized by using a triethylamine (TEA)-catalyzed thiol−isocyanate reaction in DMAc, as shown in Scheme 2. It is well-known that segment length, overall composition (soft/hard segment ratio), and the chemical structure of each segment affects the microphase separation process that leads to the highly elastic and tough mechanical properties of polyurethanes. In addition to the variation of soft segment length, i.e., the molecular weight of dithiol oligomers described above, the length of the hard segments was also controlled from 550 to 1000 g/mol by varying the molar ratio of HDT to MDI at a fixed soft segment molecular weight (2000 g/mol). The effect of isocyanate chemical structure was also investigated for a fixed length of the soft (2000 g/mol) and hard (1000 g/mol) segments, as shown in Table 2. The ratios of thiol:isocyanate and dithiol:thiol oligomer were selected based upon the use of similar molecular weight diols and polyol oligomers for synthesis of high-performance polyurethanes.[50−55] GPC results in Table 4 show that $M_{n,GPC}$ of the polythiourethanes is 21 000−56 000 g/mol with reasonably low PDI values, indicating that the thiol-terminated prepolymers were successfully incorporated into

Scheme 2. Synthetic Procedure for Segmented Polythiourethane Elastomers and the Structure of Diisocyanates

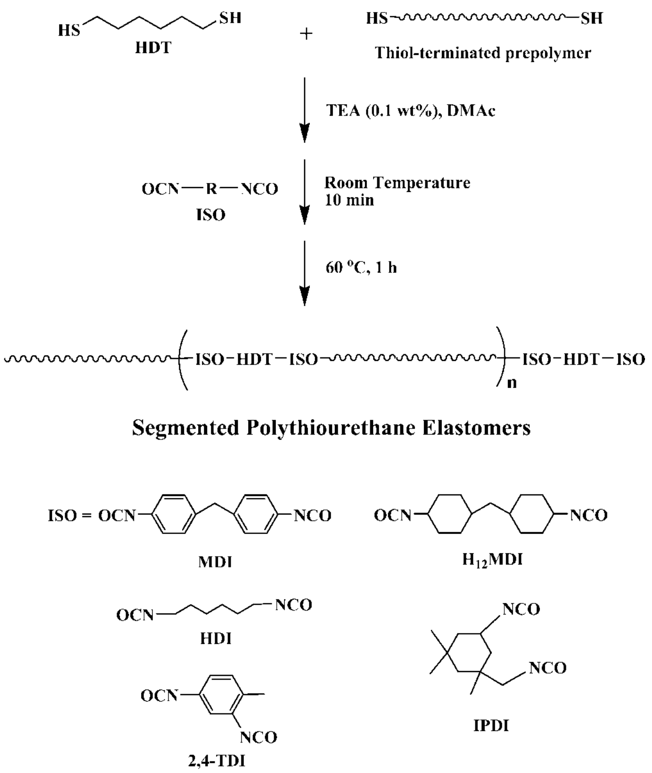


Table 4. GPC and DSC Results of Segmented Polythiourethane Elastomers

			hard segment		soft segment	
run no.	$M_{n,GPC}$ (g/mol)	PDI	T_g	T_m	T_g	T_m
M0520	40 624	2.1	131	236	−52	23
M0720	39 646	2.6	130	220	−51	n/d
M1020	56 071	1.9	131	221	−45	n/d
M1010	36 271	2.4	132	223	−23	n/d
M1015	44 978	2.1	132	220	−41	n/d
M1020	56 071	1.9	131	221	−45	n/d
M1025	34 944	2.3	131	222	−50	18
M1030	50 523	1.5	133	219	−57	28
M1020	56 071	1.9	131	221	−45	n/d
H1020	insoluble[a]	insoluble[a]	n/d	186	−57	n/d
HM1020	38 720	2.2	n/d	131	−44	n/d
IP1020	25 440	2.6	n/d	n/d	−26	n/d
T1020	21 004	1.5	n/d	n/d	−40	n/d

[a] Insoluble in DMF at room temperature.

polythiourethane backbones and that hard segments consisting of HDT and diisocyanates were formed based on the stoichiometry.

The rate of the reaction in THF was evaluated using real-time IR spectroscopy. In order to obtain real-time kinetic plots as a demonstration of the efficiency of the segmented polyurethane formation, low concentrations of the base catalyst TEA (0.03 wt %) were used since the reaction was completed in very short times with the concentrations actually employed for the synthesis in DMAC such that real-time analysis could not be performed; i.e., it was not possible to begin the real-time IR analysis before significant conversion had taken place. It is well-known that the thiol−isocyanate reaction is much slower than the corresponding alcohol−isocyanate reaction in the absence of a catalyst. However, base catalysts readily abstract protons from the more acidic thiols, resulting in the formation of thiolate anions which are strong nucleophiles.[46] In Figure 5a, kinetic profiles of the TEA catalyzed MDI-based polythiourethane reactions (Scheme 2) obtained by monitoring the NCO peak as a function of time show that conversion of the isocyanate reaches 95% within 10 min. This kinetic plot is representative of the reaction between the thiol-terminated oligomers, dithiol extender (HDT), and diisocyanate (MDI). As already stated, for the preparation of the materials used for physical and mechanical analysis, a higher concentration of TEA (0.1 wt %) was used to ensure higher conversions. For comparison, kinetic profiles of the reactions between HDT and MDI using a 0.03 wt % TEA catalyst are shown in Figure 5b. The reaction comprising MDI, HDT, and thiol-terminated oligomers (soft segment) is a little slower than the reaction of HDT and MDI due to the lower concentration of functional groups and viscosity restricted chain mobility of the higher molecular weight polythiourethanes. Nevertheless, it is clear that the TEA-catalyzed thiol−isocyanate reaction is exceptionally fast and efficient even when high molecular weight thiol-terminated prepolymers are used. Focusing attention again on the results in Figure 5, we note that the reaction attains 100% conversion (no detectable side products) using the 0.03% TEA catalyst without the necessity of using highly anhydrous conditions; i.e., the catalyzed thiol−isocyanate reaction exhibits most of the aspects of a click reaction, provided that one begins with pure thiols and isocyanates. It has been previously reported that tertiary amine-catalyzed thiol−isocyanate reactions give a single thiocarbamate product with no side products.[32,33]

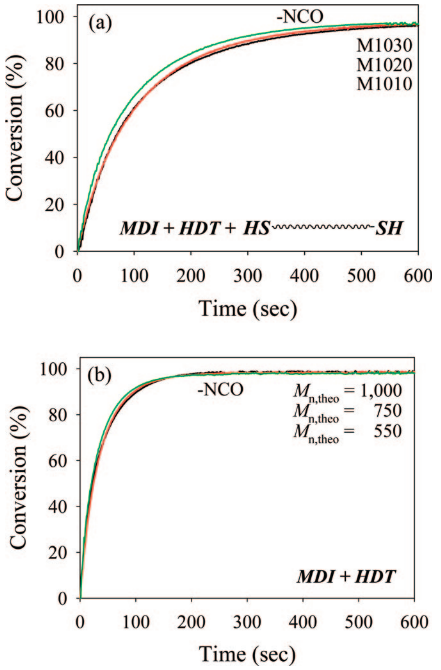


Figure 5. Kinetic profiles of polythiourethane (a) and hard segment formation (b) as a function of time using TEA catalyst concentrations of 0.03 wt %.

Microphase Separation Behavior. As already mentioned, the highly elastic properties of polyurethane-type materials result from the microphase separation between the soft and hard segments. The microphase behavior of segmented polythiourethane prepared by sequential thiol reactions was investigated in terms of the length of each segment, the segment weight ratio, and the structure of the hard segments. The thermal properties of the polythiourethanes obtained by DSC are shown in Figure 6 and Table 4. The glass transitions were observed at two distinctively separated temperatures for all of the MDI-based polythiourethanes (Figure 6a,b). The lower T_g was observed from −57 to −23 °C while the higher T_g appeared at about 130 °C, clearly confirming that this set of polythiourethanes consists of two distinctive separate phases with concomitant T_gs that are correspondent to the glass transition temperature of the soft (HDT + BDDA) and hard

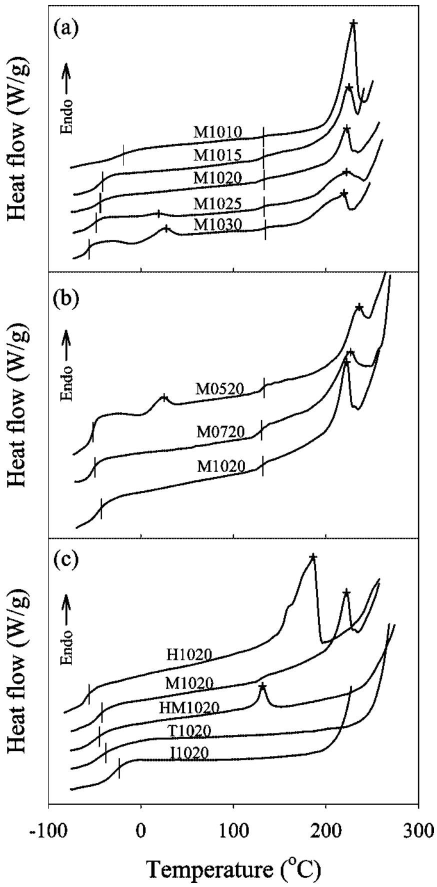


Figure 6. DSC heating scans of segmented polythiourethane elastomers.

segments (HDT + MDI), respectively. In Figure 6a, it is seen that the T_g of the soft segment increases as the length of the soft segment decreases from 3000 (M1030) to 1000 g/mol (M1010), with the hard segment T_g in each case around 130 °C. The higher hard segment content and consequential decreased segmental mobility of the soft segments result in increased physical cross-linking density and higher T_g of the soft segment. The soft segment melting points (T_m) are observed only for M1025 (18.3 °C) and M1030 (27.5 °C) since these two samples have longer flexible chains and reduced hard segment content, which is conducive to crystallization of the soft segment. The T_ms of the hard segments are observed at about 220 °C regardless of the soft segment length because the length of the hard segment is fixed at 1000 g/mol. However, the area of the endothermic melting peak (Figure 6a) increases from M1030 to M1010 due to an increase of the hard segment content, as shown in Table 2. Figure 6b shows the effect of the hard segment length with fixed soft segment length on the thermal properties. As the length and content of the hard segment decreases from 1000 (M1020) to 550 g/mol (M0520), the T_g of the soft segment decreases and the T_m of the hard segment increases. The endothermic melting peak of the soft segment for M0520 reflects the higher degree of phase separation between the soft and hard segments, resulting in more mobile and flexible soft segments capable of crystallizing. Apparently, the soft segments of samples M0720 and M1020 which have larger hard segment content cannot crystallize due to restricted chain mobility prohibiting more extensive phase separation. The effect of hard segment structure on thermal properties of segmented polythiourethane elastomers with fixed soft and hard segment lengths of 2000 and 1000 g/mol, respectively, is shown in Figure 6c. The T_g of the soft segment depends on the degree of phase separation (or mixing) between the soft and hard segments. IPDI (IP1020) and 2,4-TDI (T1020) based polythiourethanes have a higher single T_g than HDI (H1020), MDI (M1020), or H_{12}MDI (HM1020) based polythiourethanes, indicating the higher degree of phase mixing between soft and hard segments due to the asymmetric structure of IPDI and 2,4-TDI. This prevents hard segment domain formation and crystallization of soft segments resulting in pronounced phase mixed microstructure. In other words, it can be concluded that coarsely formed hard segments are dissolved into soft segment matrix rather than forming rigid hard phase separated domains. The lowest soft segment T_g at −57 °C and the largest endothermic melting peak are observed for H1020. It seems that the similarity in chemical structure between HDT and HDI with the same number of hydrocarbon (6) causes the formation of the larger crystalline hard segment domain, resulting in more pronounced phase separation. However, the lower melting point observed at 185.8 °C for H1020 compared to 221.2 °C for M1020 is due to the lesser stiffness effect thiourethane linkages formed from an aliphatic diisocyanate vs an aromatic diisocyanate.[56] The hydrogenated MDI (H_{12}MDI) based polythiourethane (HM1020) also has a lower T_m and smaller endothermic peak at 130.8 °C than M1020.

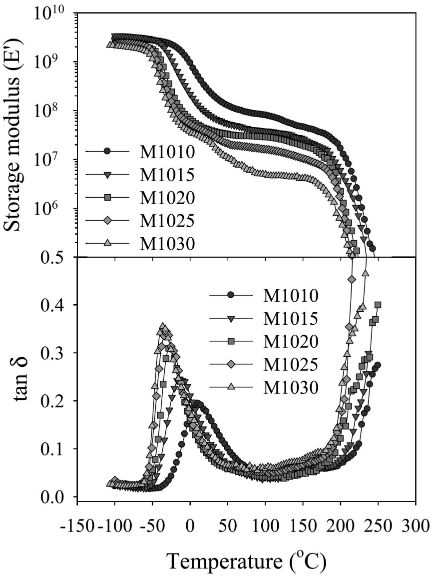


Figure 7. Dynamic mechanical properties of segmented polythiourethane elastomers with variation of soft segment length.

The microphase behavior of segmented polythiourethane elastomers would be expected to have a significant influence on dynamic mechanical properties (Figures 7−9). For the series with different soft segment length (Figure 7), the T_g of the soft segment, defined by the tan δ peak maximum or E' inflection point, increases along with the rubbery modulus with decreasing soft segment length from $M_{n,\text{theo}} = 3000$ (M1030) to $M_{n,\text{theo}} =$ 1000 g/mol (M1030). The increase in hard segment content with the decrease in soft segment length results in a material with higher physical cross-link density. This leads to an increase in the rubbery modulus (G_N°) commensurate with the ideal rubber theory according to eq 1[57]

$$G_N^\circ = \frac{\rho RT}{M_C} \qquad (1)$$

where ρ, R, and T are the density, ideal gas constant, and absolute temperature, and M_c represents the molecular weight between cross-links. In Figure 8, the effect of hard segment length on the microphase behavior of polythiourethanes results in obvious differences in the DMTA scans. The T_g of the soft segment increases with increasing hard segment length at a constant soft

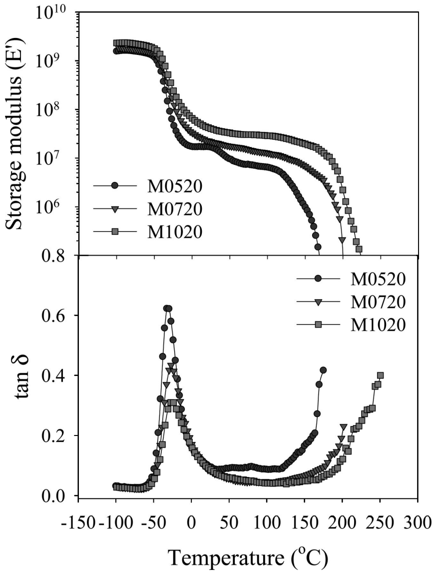


Figure 8. Dynamic mechanical properties of segmented polythiourethane elastomers with variation of hard segment length.

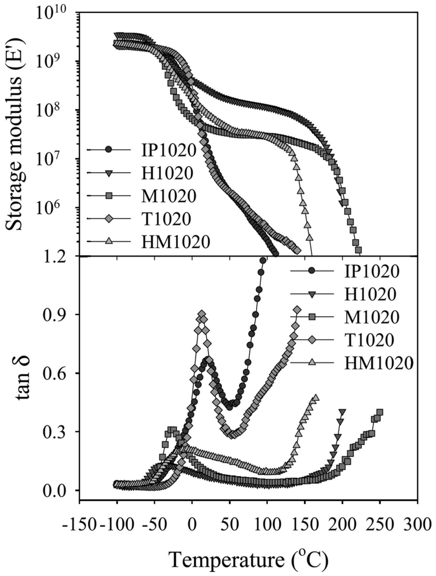


Figure 9. Dynamic mechanical properties of segmented polythiourethane elastomers with different diisocyanate structures.

segment length (2000 g/mol), i.e., from M0520 to M1020, owing to phase mixing, which is consistent with the DSC results. In addition, increasing the hard segment content from M0520 to M1020 gives rise to a notable increase in the rubbery modulus which is, as discussed above in the context of eq 1, due to an increase in physical cross-link density. Also, a significant increase of the melt flow temperature occurs with increased hard segment content; i.e., melt flow for M1020 occurs at the highest temperature. Finally, the E' vs temperature plot in Figure 8 shows a distinct drop in modulus for the M0520 sample corresponding to melting of the soft segment noted by the DSC scan in Figure 6b for the M0520 sample only. Figure 9 shows the effect of hard segment structure on the tan δ and E' of each of the different types of the segmented polythiourethane elastomers. IP1020 and T1020 prepared with the asymmetric diisocyanates IPDI and 2,4-TDI have much lower rubbery modulus values than any of the other samples with melt flow starting at very low temperatures around 100 °C. As discussed already, the asymmetric structures of IPDI and 2,4-TDI hinder hard segment crystallization and formation of rigid domains that induce phase mixing between the soft and hard segments resulting in only a single low T_g. The lowest soft segment T_g at −40 °C for H1020 (Figure 9) and melt flow temperatures corresponding to T_m of hard segments at 130, 180, and 210 °C for HM1020, H1020, and M1020, respectively, are all consistent with the DSC results. Finally, it can be concluded from the DSC results in Figure 6 and Table 4 and the DMTA results in Figures 7−9 that the length of the soft and hard segment has a significant impact on the degree of phase separation. In addition, the structure of the diisocyanate also plays a crucial role in influencing microphase behavior as well as thermal and mechanical transitions.

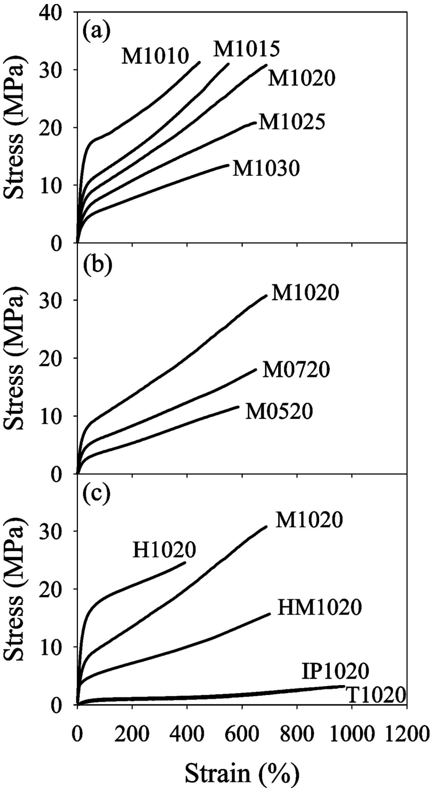


Figure 10. Tensile properties of segmented polythiourethane elastomers.

Mechanical Properties. The tensile properties of the segmented polythiourethane elastomers are shown in Figure 10. It is well-known that Young's modulus, in accordance with the results for the rubbery modulus obtained by E' of DMA at room temperature (measurement temperature of tensile property), should be directly related to the amount of hard segment content in an elastomer. In Figure 10a,b it is observed that Young's modulus and the tensile stress at break increase as a function of increasing hard segment content from M1030 to M1010 and from M0520 to M1020. On the other hand, the elongation at break decreases from M1020 to M1010 as well as from M1020 to M1030 in Figure 10a, implying that an optimum hard segment content or degree of phase separation exists for optimum elongation. Figure 10b shows that the elongation at break increases with increasing hard segment length from 550 to 1000 g/mol. The essential difference in tensile properties for segmented polythiourethane elastomers synthesized with the structurally different diisocyanates shown in Figure 10c is dictated by the different degrees of microphase separation. The symmetric structure of the diisocyanates and stronger hydrogen bonding of the corresponding thiourethane linkages derived from MDI and HDT units produce more pronounced hard segment domains which act as physical cross-links or reinforcing fillers, resulting in superior mechanical properties. H1020, which has the biggest hard segment endotherm melting peak by DSC (Figure 6), has the highest Young's modulus. However, the tensile behavior of the microphase mixed systems, i.e., IP1020 and T1020, exhibit very low modulus and tensile strength but very large elongations at break (~1000%), typically observed for un-cross-linked rubbery materials. HM1020 prepared from the hydrogenated MDI (cyclo-aliphatic diisocyanate) shows almost the same elongation at break as MDI (aromatic diisocyanate) based M1020, but Young's modulus and yield stress are less than half due to the less rigid hard segment. Summarizing, the mechanical properties of segmented polythiourethane elastomers can be systematically controlled by the length of soft or hard segment, ratio of soft–hard segment, and chemical structure of the hard segment governing microphase separation.

Conclusions

This study represents a new and highly efficient procedure for the rapid synthesis of highly elastic segmented polythiourethanes and provides a clear rationale for designing and controlling microphase separation and thermal/mechanical properties. The sequential phosphine catalyzed thiol–acrylate and tertiary amine-catalyzed thiol–isocyanate reactions used to synthesize the segmented polythiourethanes under the conditions described herein bear the salient attributes of click-type reactions as identified by kinetics and product analysis; we do note that the reactions were conducted in an organic solvent to ensure that all components were molecularly dissolved. Thermal and dynamic thermal mechanical property measurements showed that the soft and hard phases could be separated and the degree of phase mixing controlled by varying the length of each segment, the ratio of two phases, and the chemical structure of the hard segment. The tensile property results represented materials with a very wide spectrum of Young's modulus, tensile strength, and elongation at break governed by microphase separation behavior. The efficient synthesis of segmented polythiourethanes reported herein opens up a totally new materials platform since the thiol oligomers can be readily synthesized in high yields with no side products in a matter of seconds. Since there is an extensive range of commercially available acrylates and thiols, there is significant opportunity to literally tune the polythiourethane elastomer over a wide range of physical and mechanical properties. Finally, it is expected that the sequential reaction process demonstrated herein, due to the extremely efficient and rapid nature of the reactions with essentially no appreciable byproducts, can be extended to efficient bulk reactions that can be used for the production of segmented thermoplastic polythiourethanes by in situ formation of hard and soft segments using melt processing. The ability of thiol–isocyanate reactions to proceed in more rigorous environments where other reactive components are present is currently being conducted to define any competitive reaction pathways that might limit the utility of the chemistry.

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