

Investigation on novel thermoplastic poly(urethane-thiourea-imide)s with enhanced chemical and heat resistance

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ABSTRACT

A new generation of segmented thermoplastic poly(urethane-thiourea-imide)s (PUTIs) was synthesized via reaction of polyethylene glycol and thiourea-based prepolymer with dianhydride as chain extenders. NCO-terminated prepolymer was synthesized from a new diisocyanate, 3-(3-((4-isocyanatophenyl)carbamoyl)thioureido)phenyl-4-isocyanatophenylcarbamate (IPCT), as a hard segment and PEG forming soft segment. The starting materials and polymers were characterized by conventional methods and physical properties such as solubility, solution viscosity, molecular weight, thermal stability and thermal behavior were studied. PUTIs showed partially crystalline structures. Weight average molecular weights of PUTIs (GPC measurements) were in the range of 1,68,694–1,97,035. Moreover, thermogravimetric analysis indicated that poly(urethane-thiourea-imide)s were fairly stable above 500 °C having T_{10} of 521–543 °C. Investigation of the results authenticated the approach of introducing thiourea (using IPCT) and imide structure in polyurethanes for the improvement of thermal stability. In comparison to typical polyurethanes, these polymers exhibited better heat resistance, chemical resistance as well as processability.

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1. Introduction

Polyurethane, a versatile polymer, is becoming increasingly important as engineering materials because it has properties of both elastomer and plastics. The tailor-made properties from super soft foam to tough elastomers and long-wearing coatings have resulted in many applications [1]. Thermoplastic polyurethane with a segmented structure can be easily synthesized by a simple polyaddition reaction of polyol having different molecular weights, isocyanate and a chain extender. The properties of these polymers are due to the combination of chain segment flexibility, rigidity of aromatic units, chain entanglement and orientation of segments, hydrogen bonding and other intermolecular interactions [2]. Unfortunately, the conventional polyurethane are known to exhibit poor resistance to heat, e.g. the acceptable mechanical properties (strength, moduli, etc.) disappear above 80–90 °C and thermal degradation takes place beyond 200 °C [3–5]. Low heat resistance is the main reason for limitation in technical application of polyurethanes. Attempts to improve thermal stability of polyurethane have been made over a long period. An established course to the improved thermal stability of polyurethanes is the chemical

modification of its structure by blending or copolymerization with thermally stable polymers [6]. Presently, more attention has been paid to modification via heterocyclic groups such as incorporation of imide, oxazolidone, triazine and phosphazene units into polyurethane spine [7–10]. Polyimides are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical, electrical and durable properties [11–14]. Various attempts have been made to incorporate polyimide units into polyurethanes. Well-adapted methods to obtain poly(urethane-imide)s (PUIs) were the reaction of isocyanate terminated polyurethane prepolymer with aromatic acid anhydride, diamines, dianhydride, diols, diacids and polyols containing build-in imide groups [15–24]. Intermolecular Diels–Alder reaction of molecules containing bis(2-furyl-carbamate) units with bismaleimides [25] has also been utilized. Furthermore, the reaction of epoxy resins containing imide structure with polyurethane prepolymers [26] and the reaction of poly(amic-acid) with blocked polyurethane prepolymers [27,28] were successful approaches for polyurethane fabrication. Hence, subsequent improvements in thermo-mechanical properties of poly(urethane-imide)s have been reported [29,30]. Although structures and properties of PUIs have attained extensive consideration, most of the studies focused only on thermal properties of copolymers having various kinds and contents of hard and soft segments, in which the compatibility between hard and soft segments plays an important role [31,32].

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Generally, thermal analysis is an effective method to evaluate the microphase separation between hard and soft segments in PUIs.

Here, we have reported the preparation of novel poly(urethane-thiourea-imide)s (PUTIs) using isocyanate terminated prepolymer having built-in thiourea functionalities and dianhydrides as chain extenders. The key objective of this research was to study the effect of new aromatic diisocyanate and dianhydrides chain extenders on the structure and thermal properties of segmented PUTIs. New isocyanate terminated prepolymer was obtained from the diisocyanate compound 3-(3-((4-isocyanatophenyl)carbamoyl)thioureido)phenyl-4-isocyanatophenyl carbamate (IPCT). In this way, thiourea-derivative diisocyanate and dianhydrides chain extenders were introduced as hard segments while polyethylene glycol (PEG) with molecular weight of 2000 g/mol formed soft segments in PUTIs. Many studies on the influence of diisocyanate type on various properties of segmented polyurethanes with a polyether or polyester soft segment have been reported earlier [33–37]. The presence of an aromatic diisocyanate in the hard segments of polyurethanes generally produces stiffer polymer chains with higher melting points because of strong cohesion forces between the hard segments resulting in poor solubility. Interesting point of the introduction of thiourea moieties in poly(urethane-thiourea-imide)s is that thiocarbonyl (C=S) moieties slightly undermined the packing efficiency of polymer hard segments by forming flexible intermolecular hydrogen-bonding networks as compared to urethane carbonyl (C=O), thus enhancing their solvent miscibility. Moreover, combine effect of the introduction of C=S plus carbonyl units together with high temperature resistant anhydride-entities in hard segments can be seen as high thermal stability of these polyurethanes. Thus diisocyanate, IPCT, can result in high performance polyurethane by careful selection of chain extenders and polyol backbone. Synthesis and characterization of the prepared monomer, prepolymer, polymers and also the physical and thermal properties of the polymers are discussed. Exploration of results obtained from this work validated the approach of introducing thiourea and imide structure in polyurethanes for improvement of thermal stability.

2. Experimental

2.1. Materials

Ammonium thiocyanate (98%), dimethylformamide (DMF) (99%) and tetrahydrofuran (THF) (99.5%) were supplied by Fluka.

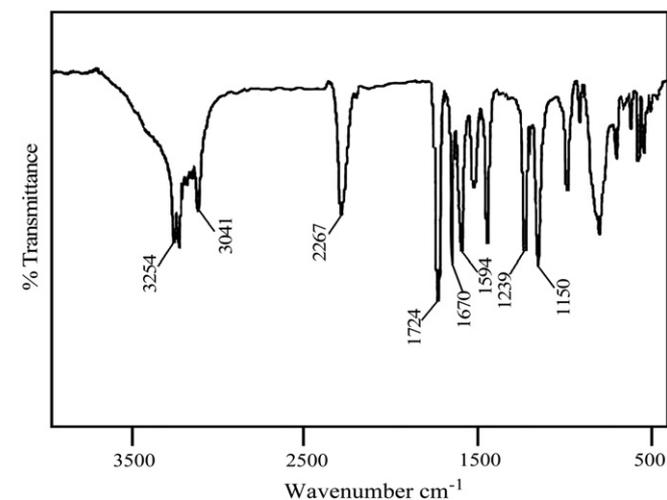


Fig. 1. FTIR spectrum of IPCT.

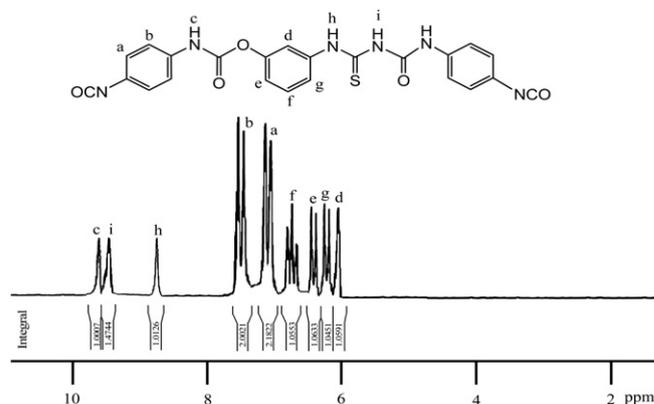


Fig. 2. ^1H NMR spectrum of IPCT.

Polyethylene glycol (PEG-2000) (molecular weight of 2000 g/mol), N-methylpyrrolidone (NMP) (99%) and dimethyl sulfoxide (DMSO) (99%) were procured from Merck. 1,4-Phenylene diisocyanate (PDI) (99%), pyromellitic dianhydride (PMDA) (97%), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (96%), 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride (6FDA) (99%) and N,N-dimethylacetamide (DMAc) (99%) were purchased from Aldrich.

2.2. Measurements

Perkin–Elmer 2400 CHN elemental analyzer was utilized for elemental analysis. FTIR Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD (4 cm^{-1} resolution) was used for recording IR spectra. NMR spectra were recorded at room temperature using BRUKER Spectrometer operating at 300.13 MHz for ^1H and at 75.47 MHz for ^{13}C NMR. Solvent used for analysis was deuterated dimethyl sulfoxide (DMSO- d_6). Inherent viscosity (η_{inh}) was measured in DMF with an Ubbelohde viscometer on 0.5 g/dL polymer solutions. The number average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity were evaluated through GPC using DMF as an eluent and refractive index (RI) detector. Thermal stability of the polymers was determined by METTLER TOLEDO TGA/SDTA 851^e thermogravimetric analyzer.



Fig. 3. ^{13}C NMR spectrum of IPCT.

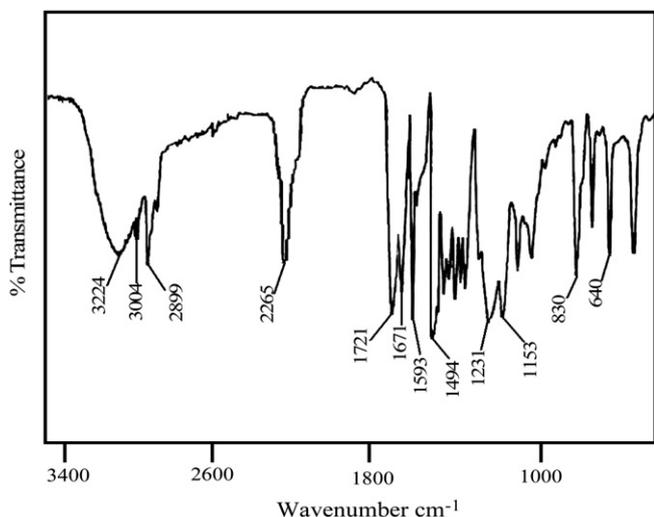


Fig. 4. FTIR spectrum of prepolymer.

using 1–5 mg of the sample in Al_2O_3 crucible at a heating rate of $10^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) was performed by METTLER TOLEDO DSC 822^e differential scanning calorimeter taking 5–10 mg of samples in aluminum pans and heated at a rate of $10^\circ\text{C}/\text{min}$. The dynamic mechanical analysis was performed on the polymeric materials in the temperature range of $0\text{--}300^\circ\text{C}$ with DMA Q800 (frequency of 5 Hz, heated at $10^\circ\text{C}/\text{min}$). X-ray diffractometer (3040/60 X'pert PRO) with Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) was used to obtain X-ray diffractograms of polymers at room temperature. In order to study the chemical resistance of polyurethanes, various chemicals were used. Teflon petri dishes coated with films of the polyurethanes ($65 \pm 5 \mu\text{m}$ thickness) were kept in 250 mL beakers containing 150 mL of various chemical media at ambient temperature ($30 \pm 2^\circ\text{C}$) for 7 days.

2.3. Synthesis of 1-(3-hydroxyphenyl)thiourea

At first, 3-amino phenol (0.1 mol), 9 mL of conc. HCl, ammonium thiocyanate (0.1 mol) and 120 mL of deaerated water were

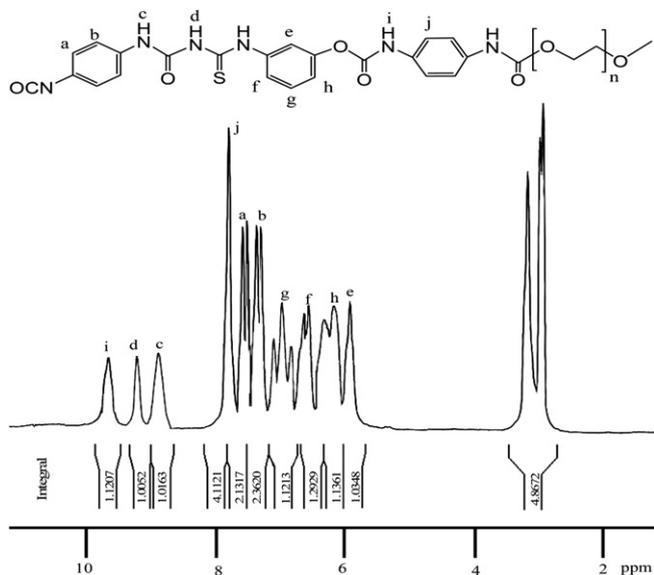


Fig. 5. ^1H NMR spectrum of prepolymer.

exhaustively mixed and heated (steam bath) in a porcelain dish for 2 h and allowed to cool to room temperature. Subsequently, the above mixture was again evaporated gradually to dryness for 6–7 h. Later, the product obtained was boiled with small quantity of charcoal in ethanol, filtered and cooled. Ultimately, 1-(3-hydroxyphenyl)thiourea obtained was recrystallized from ethanol and dried under reduced pressure at 85°C for 36 h [38].

2.4. Synthesis of 3-(3-((4-isocyanatophenyl)carbamoyl)thioureido)phenyl-4-isocyanatophenyl carbamate (IPCT)

1-(3-hydroxyphenyl)thiourea (0.01 mol) was charged into a three-necked round bottom flask (250 mL) equipped with gas inlet tube, magnetic stirrer and thermometer, followed by addition of 50 mL of DMF with vigorous stirring. Afterward, 1,4-phenylene diisocyanate (0.02 mol) was added with continuous stirring under N_2 atmosphere. The temperature was then increased to 60°C for 2 h. After cooling, the mixture was precipitated in petroleum ether and dried in vacuum at 80°C for 12 h yielding the solid product, 3-(3-((4-isocyanatophenyl)carbamoyl)thioureido)phenyl-4-isocyanatophenyl carbamate, with 95% yield. Elemental analysis for $\text{C}_{22}\text{H}_{16}\text{N}_6\text{O}_5\text{S}$ (IPCT): Calculated = % C 56.55, % H 3.30, % N 17.20; Found = % C 56.12, % H 3.25, % N 17.17. FTIR (KBr) of IPCT (Fig. 1): 3254 cm^{-1} (N–H stretch), 1594 cm^{-1} (N–H bend), 3041 cm^{-1} (aromatic C–H stretch), 2267 cm^{-1} (–N=C=O stretch), 1724 cm^{-1} (urethane C=O stretch), 1670 cm^{-1} (amide C=O stretch), 1239 cm^{-1} (C–O stretch), 1150 cm^{-1} (C=S stretch). ^1H NMR (300.13 MHz, DMSO-d_6 , δ ppm) presented in Fig. 2: 7.22 (d, 2H, H_a), 7.63 (d, 2H, H_b), 9.70 (s, 1H, H_c), 6.21 (s, 1H, H_d), 6.49 (d, 1H, H_e), 6.89 (t, 1H, H_f), 6.30 (d, 1H, H_g), 8.90 (s, 1H, H_h), 9.64 (s, 1H, H_i). ^{13}C NMR (75.47 MHz, DMSO-d_6 , δ ppm) specified in Fig. 3: 126.1 (C_1), 129.2 (C_2), 125.0 (C_3), 127.7 (C_4), 133.1 (C_5), urethane C=O 160.1 (C_6), 117.1 (C_7), 151.7 (C_8), 118.2 (C_9), 129.7 (C_{10}), 123.3 (C_{11}), 137.5 (C_{12}), thio-carbonyl 177.6 (C_{13}), C=O 169.1 (C_{14}).

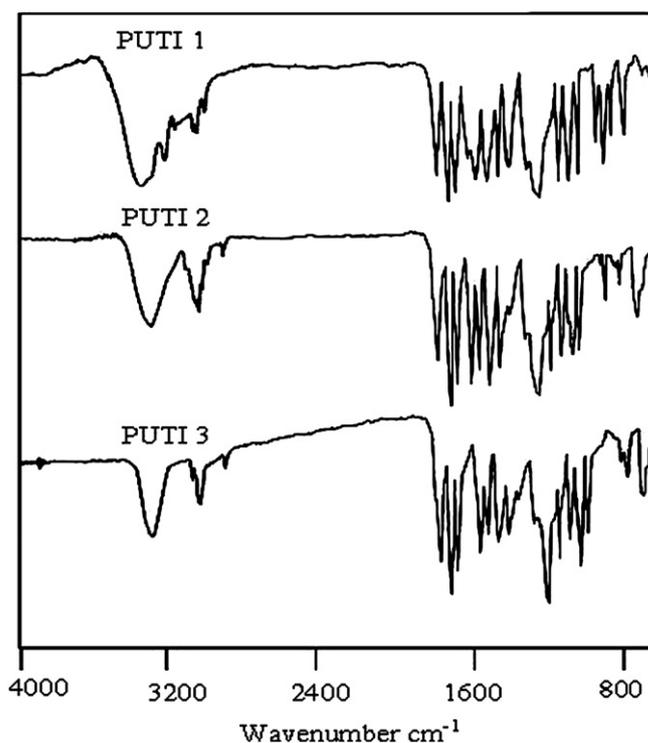


Fig. 6. FTIR spectra of PUTIs.

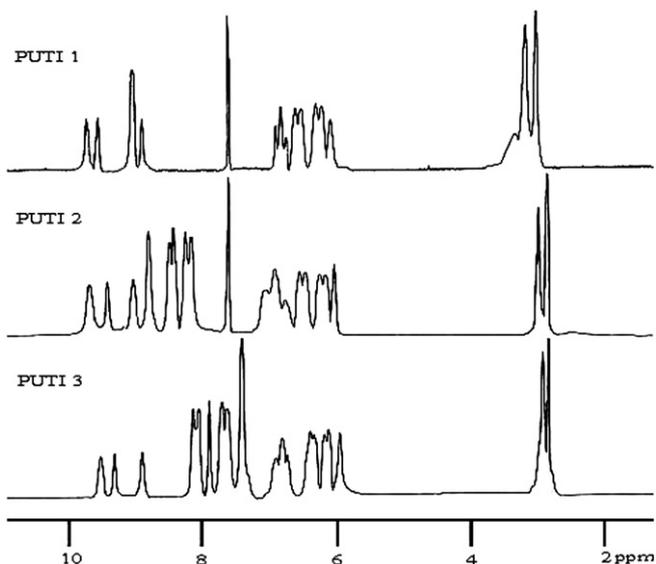
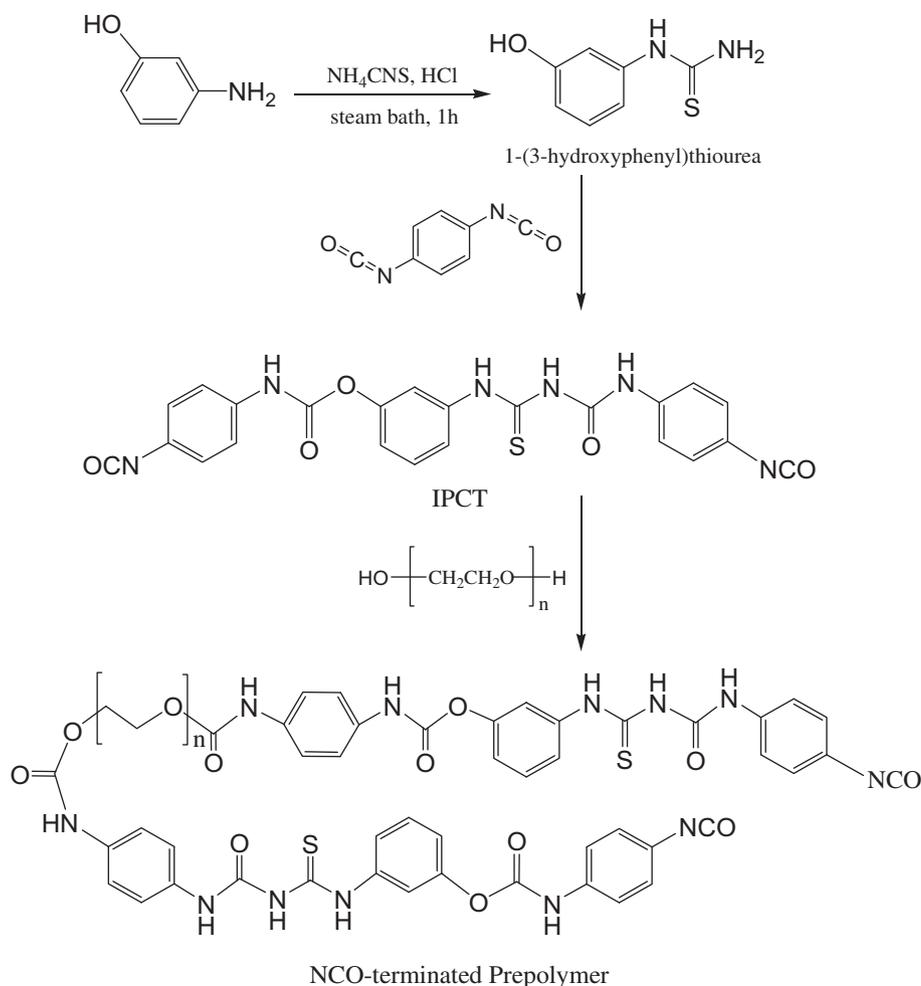


Fig. 7. ^1H NMR spectra of PUTIs.

2.5. Synthesis of isocyanate terminated prepolymer

HO-terminated soft segment (PEG) (0.006 mol) was degassed and dried in a 500 mL four necked reaction kettle equipped with magnetic stirrer, reflux condenser, dropping funnel, thermometer



Scheme 1. Scheme for the synthesis of monomer and prepolymer.

and N_2 inlet under high vacuum (20 Pa) at 100°C for 1 h. After the temperature was cooled to 40°C , a solution of IPCT (0.012 mol) in DMF was charged into the flask in a molar ratio of 2/1 (NCO/OH) [39]. The mixture in the flask was kept at 70°C for 4 h under stirring, resulting in a solution of NCO-terminated prepolymer. The resulting solution was concentrated, dissolved in toluene, precipitated in petroleum ether and vacuum dried ($70\text{--}80^\circ\text{C}$) for 12 h. The yield was around 95%. The product was stored as such under N_2 until further use. FTIR (KBr) of prepolymer (Fig. 4): 3224 cm^{-1} (N–H stretch), 1593 cm^{-1} (N–H bend), 3004 cm^{-1} (aromatic C–H stretch), 2899 cm^{-1} (aliphatic C–H stretch), 2265 cm^{-1} (--N=C=O stretch), 1721 cm^{-1} (urethane C=O stretch), 1671 cm^{-1} (amide C=O stretch), 1231 cm^{-1} (C–O stretch), 1153 cm^{-1} (C=S stretch). ^1H NMR (300.13 MHz, DMSO-d_6 , δ ppm) (Fig. 5): 7.52 (d, H_a), 7.24 (d, H_b), 8.90 (s, H_c), 9.64 (s, H_d), 6.01 (s, H_e), 6.53 (d, H_f), 6.98 (t, H_g), 6.27 (d, H_h), 9.71 (s, H_i), 7.87 (s, H_j), 2.99–3.36 (aliphatic protons of polyol units).

2.6. Synthesis of segmented poly(urethane-thiourea-imide)s

NCO-terminated prepolymer was dissolved in DMF in a 250 mL four necked reaction kettle equipped with magnetic stirrer, reflux condenser, dropping funnel, thermometer and N_2 inlet. Then the flask was cooled to 0°C , where the low temperature was controlled by cooling the flask in an ice-water bath. Later on, appropriate amount of dianhydride chain extender dissolved in DMF was added into the above flask through dropping funnel over a period of

3. Results and discussion

3.1. Synthesis of monomers and polymers

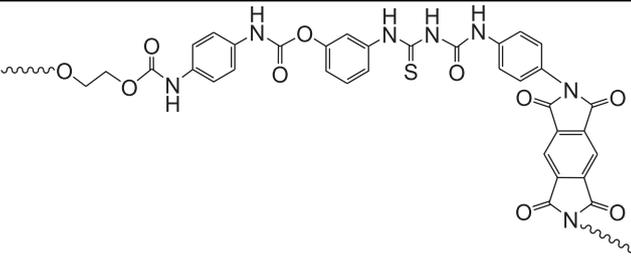
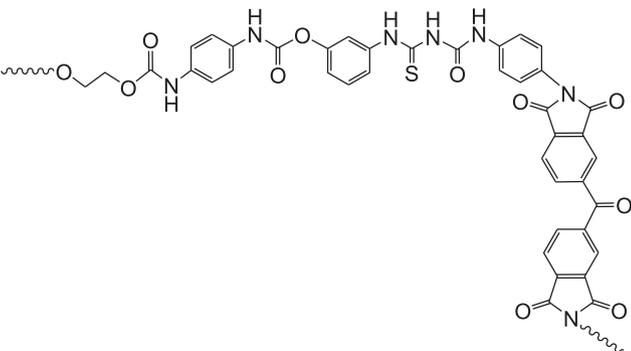
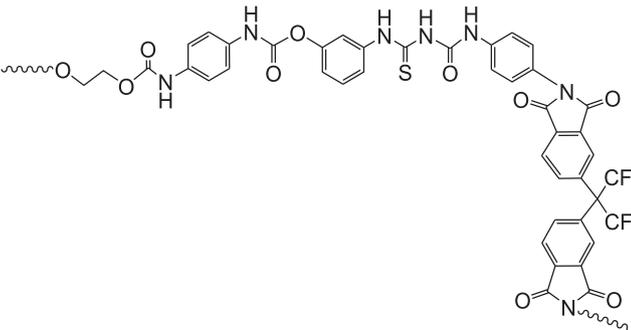
There are numerous methods for the incorporation of thermally stable imide structures into polyurethane backbone. Among them introduction of imide groups *via* chain extender has the benefit of enhancing the phase separation due to strong dipole–dipole interactions between imide groups present in hard segment. Though, an imide structure is highly rigid, so introduction of these groups cause decrease in flexibility and extensibility of polyurethanes. In the present work, two simultaneous strategies were applied, initially keeping the backbone flexibility *via* new thiourea-based diisocyanate forming hard segment and secondly the introduction of imide structures by using dianhydride monomers with build-in imide groups as chain extender. The synthesis of diisocyanate (IPCT) was accomplished using 1-(3-hydroxyphenyl)thiourea (Scheme 1). IPCT, along with PEG, was further utilized in the preparation of thiourea-based NCO-terminated prepolymer

($M_n = 13,324$, $M_w = 25,277$). Fabrication of novel thermoplastic segmented poly(urethane-thiourea-imide)s was achieved (Scheme 2) using the prepolymer and dianhydrides (chain extenders), in which IPCT and imide units formed hard segments while PEG behaved as a soft segment. The structures of IPCT, prepolymer and PUTIs were established by elemental analysis, FTIR, ^1H and ^{13}C NMR spectral data. The synthesized PUTIs were further characterized by solubility tests, viscometry, TGA, DSC, DMA, GPC and X-ray diffraction techniques.

3.2. Organosolubility

Solubility of poly(urethane-thiourea-imide)s in different solvents was studied and data are collected in Table 1. All the polymers showed good solubility in polar aprotic solvents DMF and DMSO. The rate of dissolution depends on the introduced imide structures in hard segments. The introduction of bulky hexafluoroisopropylidene substituents caused increase in the rate of dissolving of polyurethane. It takes up to 1 h for complete

Table 2
 η_{inh} , M_w , polydispersity and % yield of PUTIs.

Chemical structure	η_{inh} dL/g	M_w	M_w/M_n	Yield%
 <p>PUTI 1</p>	1.56	1,97,035	2.08	93
 <p>PUTI 2</p>	1.54	1,79,291	2.15	94
 <p>PUTI 3</p>	1.49	1,68,694	2.01	93

dissolution of PUTI 2 sample in DMF, while 6FDA-derived PUTI 3 was quickly soluble. Moreover, PUTI 1 having –IPCT–PMDA– units in hard segments was insoluble in chloroform and THF, whereas PUTI 3 was soluble on heating. Such an improvement in solubility can be attributed to the bulky substituent introduced, which appears to force two polymer chains far apart thus initiating inter-chain spacing. The solubility study confirmed that co-presence of thiourea units in the hard segments could preserve good solubility of poly(urethane-thiourea-imide)s in common organic solvents. Therefore, it is possible to introduce imide along with C=S structures content in hard segments to enhance heat resistance without sacrificing the solubility properties of polyurethanes.

3.3. Viscometry and molecular weight analysis

The η_{inh} of poly(urethane-thiourea-imide)s were evaluated in DMF at 30 °C and the results fell within the range of 1.49–1.56 dL/g (Table 2). It was observed that PUTI 1 having rigid PMDA units displayed highest η_{inh} affording higher chain symmetry and packing efficiency. In contrast, η_{inh} decreased with the incorporation of bulky benzophenone and hexafluoroisopropylidene groups in PUTI 2 and 3 respectively. Correspondingly, PUTI 3 has lowest η_{inh} (1.49 dL/g) among PUTIs attributed to the presence of C(CF₃)₂ groups along the polymer backbone. In fact, bulky –C(CF₃)₂ groups impede the polymer chain stuffing, so, enhance molecular spacing between these chain. In addition, molecular weights of PUTIs were determined by gel permeation chromatography. The values of weight-average molecular weight (M_w) were in the range of 1,68,694–1,97,035 and polydispersity index (M_w/M_n) around 2.01–2.15 (Table 2). Predictably, PMDA-derived PUTI 1 displayed highest value of M_w about 1,97,035. Thus, reasonably high η_{inh} and M_w were divulged by PUTIs bearing C=S and imide units in hard segments. In relation to previously synthesized poly(urethane-imide)s, PUTIs offered much higher η_{inh} and molecular weights [16].

3.4. Thermal stability of polyurethanes

Thermal stability of PUTIs was evaluated by TGA and DSC. Temperatures due to various transitions concerning thermal stability and thermal behavior of the prepared PUTIs are presented in Table 3. Thermograms of the polymers (Fig. 8) were almost similar with each other and showed no significant weight loss below 500 °C in N₂ atmosphere. Accordingly, poly(urethane-thiourea-imide)s exhibited T_0 of about 518–525 °C, T_{10} in the range of 521–543 °C, T_{max} around 575–589 °C and char yields of 57–65% at 600 °C. Compared to the conventional polyurethanes [16,22,40], the decomposition temperatures of PUTIs improved showing that employed approach was really effective. According to the acquired results, PMDA-derived polyurethane (PUTI 1) offered highest thermal stability that could be ascribed to the incorporation of rigid PMDA units in hard segments. On the other hand, introduction of benzophenone and hexafluoroisopropylidene units appear to diminish the packing density as well as intermolecular interactions of molecular chains in –IPCT–BTDA– and –IPCT–6FDA– hard

Table 3
Thermal analyses data of different PUTIs.

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Y_c at 600 °C (%)
PUTI 1	224	525	543	589	65
PUTI 2	222	522	531	582	60
PUTI 3	208	518	521	575	57

T_g : Glass transition temperature; T_0 : Initial decomposition temperature; T_{10} : Temperature for 10% weight loss; T_{max} : Maximum decomposition temperature; Y_c : Char yield; weight of polymer remained.

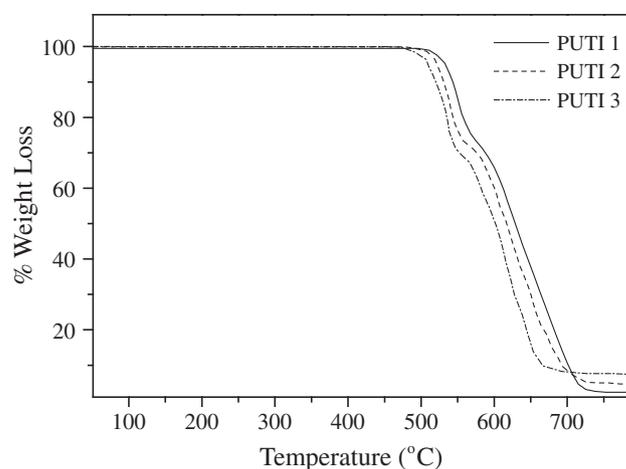


Fig. 8. TGA curves of PUTIs at a heating rate of 10 °C/min in N₂.

segments respectively. Some endothermic thermal transitions in DSC analysis of polyurethanes (Fig. 9) can be observed due to physical changes in polymeric segments. It has been shown that endothermic behavior is melting, resulting from long-range ordering and disordering of the hard segment domains in segmented polyurethanes. Thus, destruction of inter-chain hydrogen bonding causes a DSC endotherm [40]. Consequently, presence of IPCT and imide units in the chemical structure (hard segments) of PUTIs resulted in a shift of the observed thermal transition to higher temperature. As, PUTI 1 exhibited an endothermic peak at 288 °C, owing to rigid pyromellitimide unit in hard segments, –IPCT–PMDA–, which clearly correlates with the presence of crystalline structure whose diffraction peak is located at a smaller diffraction angle ($2\theta = 20$). Whilst, low temp endothermic peaks typically associated with the soft segments [41] were absent in DSC scans of new segmented polyurethanes. Eventually, it is rather difficult to find out T_g 's from this type of DSC scans. So, glass transition temperatures of PUTIs were investigated using a more sensitive technique to find out T_g 's i.e., dynamic mechanical analysis (DMA) and results are given in Table 3 (Fig. 10). Correspondingly, PUTI 1 and 2 based on PMDA and BTDA chain extenders showed higher glass transition temperatures of 224 °C and 222 °C respectively. Seeing that, presence of more rigid hard segment contents in PUTI 1 and 2, –IPCT–PMDA– and –IPCT–BTDA– in that order, enhanced the polyurethane chain stiffness thus confined their

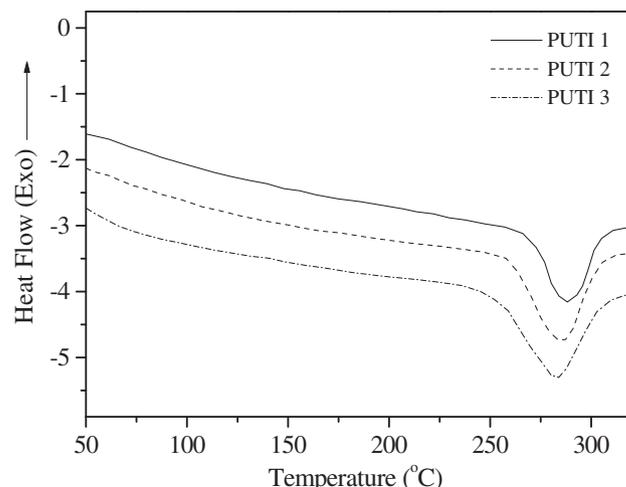


Fig. 9. DSC thermograms of PUTIs at a heating rate of 10 °C/min in N₂.

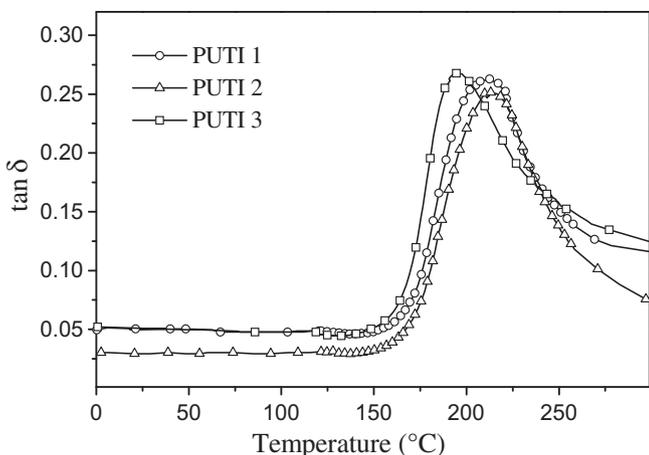


Fig. 10. Variation of loss tangent ($\tan\delta$) with temperature for PUTIs.

segmental motion. On the other hand, PUTI 3 with –IPCT–6FDA– hard segments possessed relatively lower T_g of 208 °C. However, generally PUTIs own fine heat stability according to DMA upshot. Outstanding thermal stability of poly(urethane-thiourea-imide)s as compared to several reported poly(urethane-imide)s should be attributed to their structural modification. TGA results of these novels multifunctional polyurethanes undoubtedly demonstrated that co-occurrence of urethane carbonyl and thiocarbonyl moieties along with highly rigid heat resistant imide-ring component in hard segments are supposed to be responsible for their exceptionally high thermal stability. Thus, inclusion of C=S moieties in polyurethane hard segments is significant to retain the solubility of polyurethanes together with increased heat resistance.

3.5. Crystallinity

XRD patterns obtained for poly(urethane-thiourea-imide)s (Fig. 11) indicated partially crystalline structures of polymers. The most distinct diffraction peaks were observed for all the samples around $2\theta = 19$ – 20 , on account of better polymer chain packing due to –IPCT–imide– hard segments. Furthermore, some correlations between XRD and DSC results were observed. Consequently, this small amount of crystallinity in PUTIs can be associated with high temperature endothermic peaks in DSC curves. Thus, endotherms of this series of polymers (at room temperature) should be connected with the melting of hard segments.

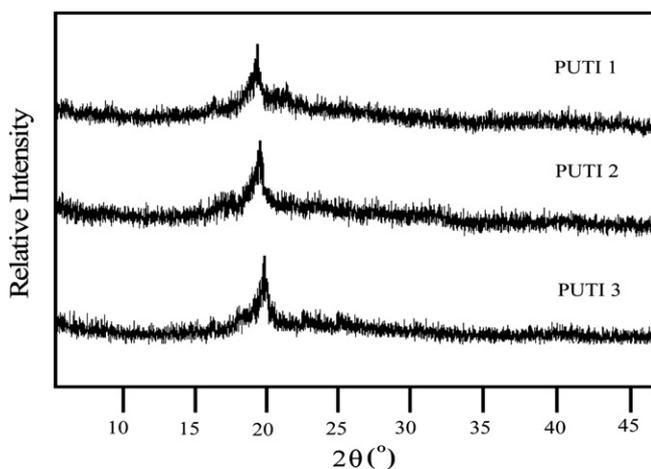


Fig. 11. X-ray diffraction patterns of PUTIs.

Table 4
Chemical resistance behavior of PUTIs.^a

Sample	20 wt% aqueous H ₂ SO ₄	37 wt% aqueous HCl	40 wt% aqueous NaOH	23 wt% aqueous NaCl	Distilled water
PUTI 1	++	++	++	++	++
PUTI 2	++	++	++	++	++
PUTI 3	–	–	+	++	++

^a ++ very resistant; + resistant; – non-resistant.

3.6. Chemical resistance of poly(urethane-thiourea-imide)s

Investigation of chemical resistance of PUTIs by visual change in the appearance or loss of film integrity in different media confirmed that samples showed excellent chemical resistance in acidic, basic as well as water media. As shown in Table 4, the polyurethanes are resistant in acidic media (20 wt% aqueous H₂SO₄ and 37 wt% aqueous HCl), basic media (40 wt% aqueous NaOH), in 23 wt% aqueous NaCl and also in distilled water. All the samples, except PUTI 3, were chemical resistant and there was no effect on their surface (PUTI 1 and 2) after finishing the test period. PUTI 3 (which contains –IPCT–6FDA– hard segments) degraded completely in aqueous H₂SO₄ and HCl media. It seems that presence of PMDA and BTDA in hard segments of PUTI 1 and 2 respectively led to enhanced inter-chain interactions which increased their resistance to acidic media. Moreover, PUTI 3 sample underwent some degree of swelling in basic medium. Reason for the overall good solvent resistance of polyurethane films, relative to reported polymers [42], is considered to be brought about by the formation of uniformly arranged imide and urethane structure in PUTIs.

4. Conclusions

An aromatic diisocyanate (IPCT) containing thiourea moieties was synthesized and successfully used for the preparation of NCO-terminated polyurethane prepolymers. Novel segmented poly(urethane-thiourea-imide)s (PUTIs) were obtained from NCO-terminated prepolymer and dianhydride chain extenders. Investigation of physical and thermal properties showed that in comparison to conventional polyurethanes, thermal stability of PUTIs was enhanced considerably and simultaneously processability preserved. In this manner, thermal stability of PUTIs was found to increase by the introduction of aromatic diisocyanate and dianhydride chain extenders in hard segments of polyurethanes. The resulting thermally stable segmented PUTIs were high molecular weight solids with good chemical resistance. Considering these physical and chemical properties, PUTIs have several merits over competitive polyurethane materials. Thus, the simplicity of synthesis combined with the possibility of choosing readily available cost-effective raw material as a monomer source for the prepolymer, makes PUTIs materials substantially attractive for a number of commercial applications. Nonetheless, because of various advantages such as storage stability, non-sensitivity to moisture and different solubility behavior, PUTIs have found potential applications in coating industry (powder, automotive, insulating, plastic coatings, and so on) where chemical as well as heat resistance are intensely demanded.

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