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Poly(urethane-imide-imide), a new generation of thermoplastic polyurethane elastomers with enhanced thermal stability

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Abstract

A new generation of polyurethane thermoplastic elastomers were synthesized via the reaction of NCO-terminated polyurethane with 2,2′-pyromellitdiimidodisuccinic anhydride chain extender. The starting materials and polymers were characterized by conventional methods and physical, mechanical and thermal properties were studied. In comparison to typical polyurethanes, these polymers exhibited improved thermal stability as well as good processability and flexibility.

Keywords: Polyurethane; Polyimide; Poly(urethane-imide-imide)

1. Introduction

The reaction between diisocyanates and a mixture of diols of different molecular weights provides thermoplastic polyurethane elastomers with a block segment structure. The preparation of thermoplastic polyurethane elastomers with a wide range of properties can be carried out by changing the combining ratios of reactive intermediates with variations in molecular structure. The properties of these polymers appear to result from a combination of chain segment flexibility, the rigidity of aromatic units, chain entanglement, orientation of segments, hydrogen bonding, and other intermolecular interactions [1–3].

Typical polyurethanes are known to exhibit small resistance to heat. This low heat resistance is the main reason for limitation in technical application of polyurethanes. One accepted approach for the improvement of thermal stability of polyurethanes is the chemical modification of its structure by blending or copolymerization with more thermally stable polymers [4,5]. More attention has been paid to chemical modification by hetereocyclic groups like imide, isocyanate, oxazolidone, triazine, and phosphazene [6–11]. Polyimides have received wide spread attention due to their unique properties, including an extremely high thermal stability, high mechanical strength, and good dielectric properties [12–17]. The incorporation of imide group as hard segments in polyurethanes has been successfully accomplished and their bulk properties have been reported in the literature. Various attempts to incorporate polyimide units into polyurethanes can be classified as (a) reaction of isocyanate or blocked isocyanate terminated polyurethane prepolymers with acid anhydrides [18–23], (b) reaction of amine terminated polyurethane prepolymers with acid anhydride [24,25], (c) reaction of isocyanate terminated polyurethane prepolymers with diols or diacids containing build-in imide groups [26–29], (d) intermolecular Diels–Alder reaction of molecules containing bis(2-furyl-carbamate) units with bismaleimides [30–32], (e) thermal crosslinking of polyurethane prepolymers containing maleimide functions [33–36], (f) reaction of diisocyanates containing build-in imide groups with different polyols [37–41], (g) reaction of epoxy resins containing imide structure with blocked polyurethane prepolymers [42], (h) reaction of hydroxyl containing polyimides with blocked polyurethane prepolymers [43,44], (i) reaction of polyimide precursor, poly(amic acid), with blocked polyurethane prepolymers [45,46], and (j) blending of thermoplastic polyurethanes with poly(ether imide)s [47].

The investigation of results obtained from these researches have validated the approach of introducing imide structure in polyurethanes for improvement of

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thermal stability, and work reported in this article was designed to extend heuristic options through the synthesis of 2,2′-pyromellitdiimidodisuccinic anhydride and its uses as chain extender for reaction with NCO-terminated polyurethane prepolymers. Best condition of polymerization was obtained via synthesis of model compound. Monomer, model compound and polymers were characterized and their physical and mechanical properties including inherent viscosity, solubility behavior, thermal property, thermal stability, modulus, tensile strength and elongation at break are also studied.

2. Experimental

Polyester polyol, CAPA 225, molecular weight 2000, from Interox Chemicals was dried at 70 °C in vacuum for 24 h before use. 4,4′-methylenebis(phenyl isocyanate) (MDI Aldrich) was vacuum distilled before use. *N*-methyl pyrrolidone (NMP) was vacuum distilled from CaH_2 and stored over 4 Å molecular sieves. Pyromellitic anhydride (Fluka) was purified by recrystallization from acetic anhydride. Other chemicals and solvents were used as received.

FTIR spectra were performed on a Bruker-IFS 48 instrument. ^1H NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) or chroroform ($CDCl_3$) using a Bruker Avance DPX 250 MHz instrument. The mass spectra were recorded on a Shimadzo GC-MS-QP 1000EX instrument. Thermal gravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) were performed on a Stanton STA-780 with heating rate of 10 °C/min in air. Melting points were determined in open capillaries with a Buchi 535 instrument. Inherent viscosities of polymers were determined for solution of 0.5 g/dl in DMF at 30 °C using an Ubbelohde viscometer. Tensile properties were determined from stress–strain curves with a MTS tensile tester Model 10/M at a strain rate of 5 cm/min. Measurement were performed at 25 °C with a film thickness of about 1 mm and stamped out with a ASTM D412 die. Dynamic mechanical testing was carried out on a UK Polymer Lab dynamic mechanical thermal analyzer, Model MK-II, over a temperature range of -100–200 °C at heating rate of 10 °C/min and a frequency of 1 Hz. The dimension of samples were $30 \times 10 \times 1\ mm^3$. The value of tan δ and the storage modulus verses temperature were recorded for each sample.

2.1. Preparation of monomer

2.1.1. Synthesis of N,N′-(2,5-dicarboxyterephthaloyl)diaspartic acid (TA)

In a round-bottomed flask equipped with magnetic stirrer and reflux condenser was placed PMDA (4.36 g, 0.020 mol) and 150 ml of a mixture of pyridine with acetic acid solvents (volume ratio 2:3). L-aspartic acid (5.32 g, 0.040 mol) was added with stirring. The stirring was continued at room temperature overnight and then the reaction mixture was refluxed for 5 h. The excess of acetic acid/pyridine mixture was removed under reduced pressure. After addition of about 10 ml concentrated hydrochloric acid and stirring, a white precipitate was formed which was filtered and washed with plenty of hot water and finally dried under vacuum at 70 °C overnight (8.24 g, 92% yield).

2.1.2. Synthesis of 2,2′-pyromellitdiimidodisuccinic anhydride (DA)

A round-bottomed flask was charged with TA (8.1 g, 0.018 mol), freshly distilled thionyl chloride (15 ml) and chloroform (10 ml).The reaction mixture was refluxed for 5 h. The excess thionyl chloride and chloroform were removed under reduced pressure. The crystals of DA were filtered and washed two times with 10 ml of dry benzene. Finally white solid was dried under vacuum at 100 °C for 5 h (7.12 g, 96% yield).

2.2. Preparation of model compound (MII)

In a 100 ml three-necked round-bottomed flask equipped with a thermometer, nitrogen gas inlet tube, reflux condenser and magnetic stirrer were placed phenyl isocyanate (0.476 g, 0.004 mol) and dry NMP (5 ml). While stirring at 0 °C, DA (0.824 g, 0.002 mol) was added portion wise over a period of 15–20 min. The stirring of the solution was continued for further 30 min and then allowed to attain to room temperature and maintained for 20 min. The flask was slowly heated to 40 °C and kept at this temperature for 2.5 h. It was then heated to 90 °C and maintained for 2 h. Carbon dioxide gas evolution was observed at this temperature. The reaction temperature was raised to 130 °C and kept for 20 h. After cooling, the solution was poured into water and the precipitated compound was filtered and washed several times with hot water and then dried under vacuum at 100 °C for 5 h.

2.3. Synthesis of NCO-terminated polyurethane prepolymers

Into a 250 ml four necked reaction kettle equipped with mechanical stirrer, reflux condenser, dropping funnel and N_2 inlet and outlet was placed MDI and the temperature was increased to 60 °C and maintained for 30 min. Then appropriate amount of heated dry polyol (hot enough to maintain the melted stage of MDI now in the reactor) was added drop wise to the reactor at a rate, where the reaction temperature will not surpass 70 °C. The temperature was then increased to 85 °C and the reaction was continued till the NCO content reached to the theoretical value as determined by dibutylamine titration. The product was stored as such under N_2 until further use.

Table 1
Different formulations of PUIIs

Polymer	CAPA225, g (mmol)	MDI, g (mmol)	DA, g (mmol)	Hard segment content (%)
PUII-1	50 (25)	12.5 (50)	10.3 (25)	31
PUII-2	50 (25)	18.75 (75)	20.6 (50)	44
PUII-3	50 (25)	25 (100)	30.9 (75)	53

2.4. Synthesis of poly(urethane-imide-imide) (PUII)

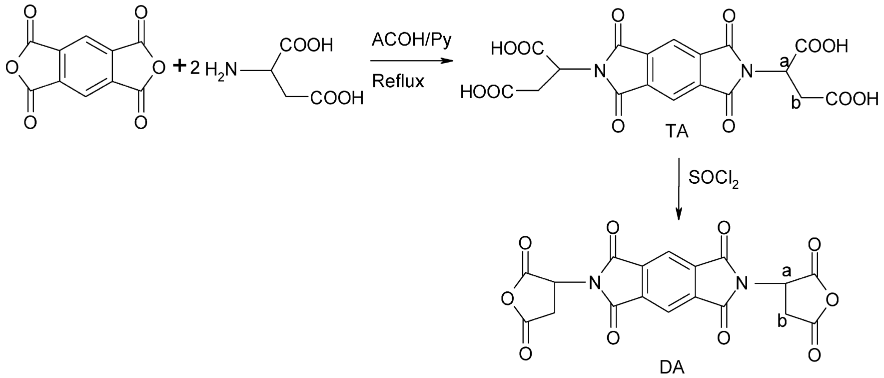
In a 250 ml four necked polymerization kettle equipped with mechanical stirrer, condenser, dropping funnel and N_2 inlet and outlet were placed NCO-terminated polyurethane prepolymer and NMP solvent. Then the kettle was cooled to 0 °C and appropriate amount of DA dissolved in NMP was dropped into the kettle through dropping funnel over a period of 15–20 min. The total solid content of reaction mixture was fixed at 40 w/w%. The stirring of reaction mixture at this temperature was continued for further 30 min and increased to room temperature during 20 min. Then the reaction temperature was fixed at 40 °C for 2.5 h. It was then heated to 90 °C and maintained for 2 h. Finally the reaction was completed at 130 °C for 20 h. The product was poured into a Teflon mold and placed in a vacuum oven under reduced pressure at 60 °C until the most of solvent was removed. Then the temperature was raised to 120 °C and maintained for 3 h until trace of solvent was removed. The freestanding film was used for further study. Different formulations of PUIIs are collected at Table 1.

3. Results and discussion

There are several methods for incorporation of thermally stable imide structures into the polyurethane backbone. Among them introduction of imide groups via chain extender has some benefits such as possibility of using commercially available NCO-terminated polyurethane prepolymers and enhancing the phase separation due to strong dipole–dipole interaction of imide groups present in hard segment. However, the imide structures have high rigidity, so increasing the concentration of these groups cause decrease in flexibility and extensibility of polyurethanes. In the present work two simultaneous strategies were tried (a) increasing the amount of imide structures by using an dianhydride monomer with build-in imide groups as chain extender, (b) keeping the flexibility via introduction of aliphatic imide groups, i.e. succinimide structures.

The synthetic route for preparation of DA is outlined in Scheme 1. The reaction of one equivalent of PMDA with two equivalents of L-aspartic acid in pyridine/acetic acid solvents mixture leads to TA, which was subsequently transformed to DA. FTIR spectrum of TA showed acidic bands at 3420–2520 cm^{-1} (O–H stretching) and 1707 cm^{-1} (C=O stretching). Also the characteristic bands of imide groups were appeared at 1772 and 1730 cm^{-1} due to asymmetric and symmetric stretching of carbonyl groups, 1386, 1186, 731 cm^{-1} as a results of axial, transverse and out of plane vibrations of cyclic imide structure, respectively. ^{1}H NMR spectrum of TA showed a doublet of doublets for CH (a) proton at 5.21 ppm and two distinct doublets of doublets at 2.94 and 3.16 ppm for two protons of CH_2 (b), respectively. The aromatic C–H protons were appeared at 8.27 ppm and peak at ~11 ppm was assigned to COOH protons.

The TA was converted to DA using excess amount of thionyl chloride in chloroform solvent under reflux condition. FTIR spectrum of DA showed absorption of anhydride C=O at 1870 and 1725 cm^{-1} (asymmetric and symmetric stretching) and imide C=O at 1790 and 1720 cm^{-1} (asymmetric and symmetric stretching), also peaks at 1390, 1111 and 727 cm^{-1} were due to axial, transverse and out of plane vibration of cyclic imide structure, respectively. In ^{1}H NMR spectrum of DA a doublet of doublets was observed at 5.6 ppm for CH (a) proton which shift to downfield due to higher electron withdrawing effect of anhydride group in comparison to acid groups of TA. Also two distinct doublets of doublets were observed at 3.03 and 3.23 ppm for two different protons of CH_2 (b) group. The peak at ~11 ppm due to COOH protons was totally disappeared, which confirmed the complete conversion of TA to DA. Also in mass spectra



Scheme 1. Synthesis of 2,2′-pyromellitdiimidodisuccinic anhydride.

Table 2
Physical and spectral data of monomer and model compounds

Compound	Yield (%)	Mp (°C)	IR (cm^{-1})	^1H NMR (ppm)[a]
TA	92	>270	3420–2520, 1772, 1730, 1707, 2383, 1286, 1248, 1186, 731	11.6(s, 4H), 8.27(s, 2H), 5.21(dd, 2H), 3.16(dd, 2H), 2.94(dd, 2H)
DA	96	>270	2953, 1870, 1790, 1725, 1390, 1265, 1232, 1111, 1072, 1009, 727	8.27(s, 2H), 5.60(dd, 2H), 3.23(dd, 2H), 3.03(dd, 2H)
MII	72	>270	2963, 1780, 1730, 1634, 1383, 1234, 1100, 725	8.48(s, 2H), 7.47–6.94(m, 10H), 5.42(dd, 2H), 3.19(dd, 2H), 2.97(dd, 2H)

[a] Solvent DMSO-d_6.

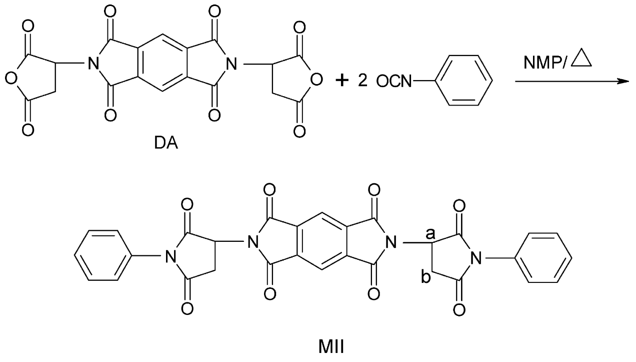
Table 3
Physical and spectral data of PUIIs

Polymer	Yield (%)	η_{inh} (dl/g)	IR (cm^{-1})	^1H NMR (ppm)[a]
PUII-1	90	0.51	3344, 2943, 2866, 1780, 1732, 1599, 1230, 1165, 727	9.61(s), 9.43(s), 8.92(s), 8.48(s), 7.50–6.90(m), 5.51(dd), 4.12(t), 3.90(t), 3.8(s), 3.10(dd), 2.90(dd), 2.33(t), 1.70–1.10(m)
PUII-2	92	0.50	3342, 2945, 2865, 1779, 1728, 1599, 1230, 1165, 727	9.61(s), 9.43(s), 8.92(s), 8.48(s), 7.51–6.91(m), 5.51(dd), 4.12(t), 3.90(t), 3.8(s), 3.11(dd), 2.91(dd), 2.33(t), 1.72–1.11(m)
PUII-3	91	0.52	3340, 2943, 2866, 1778, 1726, 1599, 1230, 1165, 727	9.61(s), 9.43(s), 8.92(s), 8.48(s), 7.52–6.91(m), 5.51(dd), 4.12(t), 3.92(t), 3.8(s), 3.10(dd), 2.93(dd), 2.33(t), 1.71–1.12(m)

[a] Solvent $CDCl_3$.

of DA, molecular ion peaks at 412 was observed, respectively. The elemental analysis of DA, C 52.03 (52.43, calculated), H 1.87 (1.94), N 6.34 (6.80) showed good correlation of calculated and found data, which confirmed the proposed structure of DA monomer. Spectroscopic data of DA and TA were collected in Table 2.

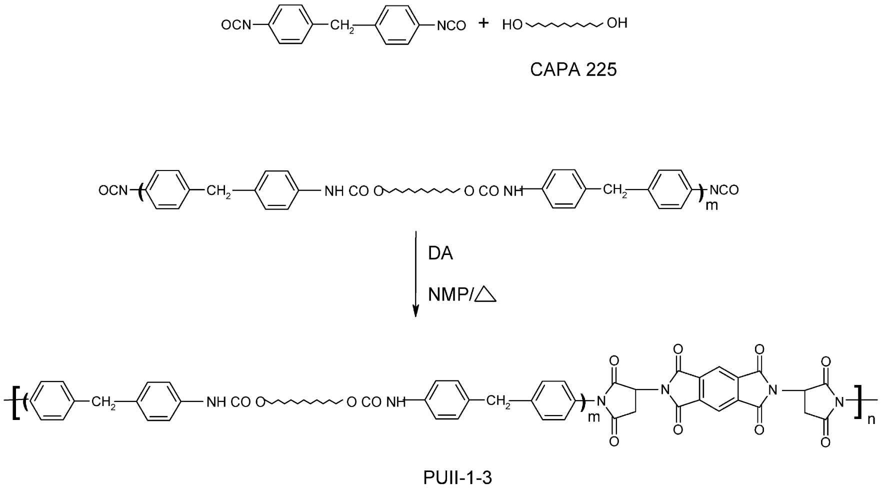
For obtaining optimum conditions of polymerization and confirming the structure analysis of the resulting polymers, the model reactions were carried out, using phenyl isocyanate as a monofunctional isocyanate (Scheme 2). The model reaction were performed in several steps which their duration and temperature were altered in order to find conditions of maximum yields and purity for MII. FTIR spectrum of model compound showed characteristic peaks of imide structure at 1780, 1730, 1383, 1100 and 725 cm^{-1}. There were no sign of anhydride carbonyl band at 1870 cm^{-1}, which indicate the complete reaction of anhydride groups with isocyanate functional groups and formation of imide structures. In ^1H NMR spectrum of model compound proton of C (a) showed a doublet of doublets at 5.42 ppm. Two doublets of doublets were observed at 2.97 and 3.19 ppm for each protons of CH (b) group. Aromatic C–H protons of phenyl succinimide part of molecules were observed at 6.90–7.47 ppm. The elemental analysis of MII, C 61.17 (61.06, calculated), H 3.28 (3.20), N 9.82 (9.96) showed good correlation of calculated and found data. Spectroscopic data of MII were collected in Table 2.



Scheme 2. Synthesis of model imide-imide compound.

According to the optimized conditions obtained from the study of model compounds, three different PUII were prepared from reaction of DA with three different NCO-terminated polyurethane prepolymers, which themselves obtained via reaction of excess amount of MDI with CAPA 225 polyol. The outline of reaction was depicted in Scheme 3, and different formulations of PUII were collected in Table 1.

The FTIR spectra of all PUII showed prominent characteristic bands of the imide and urethane groups. The bands around 1780 and 1730–1710 cm^{-1} were due to the imide and ester/urethane carbonyl linkages. N–H stretching band of urethane groups was observed around 3340 cm^{-1}. The ^1H NMR spectra of PUII showed the phenylene rings protons in the region 6.90–7.50 ppm, pyromellitimide rings protons at 8.48 ppm, succinimde rings protons at 5.51 and 3.10–2.90 ppm. The resonance signals for methylene protons of the polymer appeared in the region 1.10–1.70 ppm depending on the position of methylene protons from neighboring ester and urethane groups. Also characteristic bands of urethane N–H protons appeared at 9.61–8.92 ppm. The spectral data of all polymers are collected in Table 3.



Scheme 3. Synthesis of poly(urethane-imide-imide)s.

Table 4
Solubility behavior of PUIIs in different solvents

Polymer	NMP	DMF	DMAC	DMSO	$CHCl_3$	CH_2Cl_2	THF	Toluene
PUII-1	+	+	+	+	+	+	+	−
PUII-2	+	+	+	+	±	±	±	−
PUII-3	+	+	+	+	±	±	±	−

+ , Soluble; − , insoluble; ±, soluble after 1 h stirring.

The solubility of PUIIs at different solvents was studied and data are collected at Table 4. All the polymers show excellent solubility in polar aprotic solvents as well as chlorinated and polar solvents such as chloroform and tetrahydrofuran. The rate of dissolving depends on the concentration of imide structures. The decrease of imide content causes increase in the rate of dissolving. It takes up to 1 h for complete dissolving of PUII-3 sample in less effective solvents such as THF. The result of solubility study confirmed that the co-presence of succinimide units in the hard segment could preserve good solubility of polyurethanes in common organic solvents. So it is possible to increase the imide structures content in hard segment without sacrificing the solubility properties of polyurethanes. All polymers produced flexible and tough films, which could be cast from the solution of polymers in DMF solvent. The inherent viscosity of the PUIIs were measured at DMF solvent at 25 °C and the result are presented in Table 3. The result revealed that the PUIIs were of high molecular weight. So the optimum condition of polymerization obtained via study of model compound was adequate for synthesis of polymers with acceptable molecular weight.

Mechanical properties data as determined by stress–strain analysis were summarized in Table 5. The good mechanical properties of PUIIs may be due to the cumulative effect of the formation of more hydrogen bonds since two carbonyl groups per imide groups are available and also dipole–dipole interaction of imide rings present in hard segments. The imide content of PUIIs were increased with increase of the amount of free isocyanate groups present in the prepolymer as well as using DA as chain extender, which contain preformed imide structures. It is found that the elongation decreased with increasing the contents of imide structures (hard segment), while the tensile strength was increased inversely proportional to the contents of imide portion.

Table 5
Mechanical properties data of PUIIs

Polymer	Tensile strength (Mpa)	Elongation at break (%)	Modulus (Mpa)
PUII-1	2.7	287	3
PUII-2	6.2	220	5.5
PUII-3	7.9	189	12

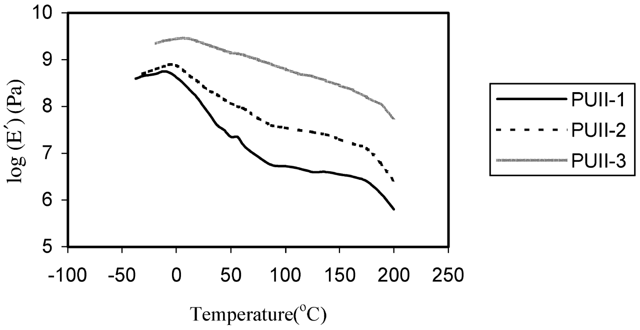


Fig. 1. Tensile storage modulus of samples PUII-1, PUII-2 and PUII-3.

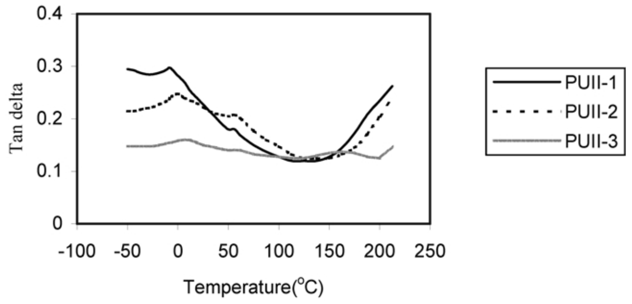


Fig. 2. Tan δ for samples PUII-1, PUII-2 and PUII-3.

For polyurethane elastomers, better phase separation and a more developed reinforcing hard domain structure will increase the stiffness of the material and improve the tensile strength [48]. Ng et al. [49] used DMTA method to characterize several linear segmented polyurethanes of well-defined hard and soft segment molecular weights and molecular weight distributions. Chen et al. [50] showed that increasing the hard and soft segment length for a fixed hard/soft segment composition ratio provides more complete phase separation an increase in modulus, and a decrease in soft domain T_g (due to purer soft phase).

The investigation of DMTA curves of PUIIs (Fig. 1), showed that the modulus of the almost plateau region increased and extended to higher temperature as the hard segment content increased. Also investigation of loss tangent curves showed that tan δ curves of the samples (Fig. 2) increased with temperature. As the hard segment content increased, the α-type transition peak shifted to higher temperature and the β-type transition peak corresponding to the glass transition of CAPA 225 soft segment phase also increased and broadened. These phenomena indicate partially phase-mixed morphology with increasing hard segment content.

The thermal stability of PUIIs was evaluated by TGA. Ten percent weight loss of the polymers, as a criterion of thermal stability of polymers was in the range of 358–370 °C. Compared to the conventional polyurethanes, the decomposition temperature of PUIIs improved showing that this approach was effective.

DSC thermograms of polymers showed $T_g h$ around 170 °C, which is much higher than typical polyurethanes. Also, the exotherm due to the thermal decomposition of PUIIs which indicates the upper limit for use of these polymers, began at around 350 °C which were in accordance of TGA data.

The temperature of various transitions concerning the thermal stability and thermal behavior of the prepared PUIIs are presented in Table 6.

Table 6
Thermal properties of PUIIs

Polymer	$T_{10\%}$[a]	T_{max}[b]	Ch.Y%[c]	$T_g s$[d]	$T_g h$[e]
PUII-1	358	422	12	−6	170
PUII-2	362	432	15	−1	178
PUII-3	370	441	17	+8	182
BPU[f]	250	315	0	−20	75

[a] 10 wt% loss temperature.
[b] Maximum decomposition temperature.
[c] Weight of remained polymer at 600 °C.
[d] Soft segment glass transition temperature.
[e] Hard segment glass transition temperature.
[f] Prepared from CAPA225/2TDI/1,4-butanediol.

4. Conclusions

An imide containing disuccinic anhydride was synthesized and successfully used as chain extender for NCO-terminated polyurethane prepolymers. Using this method, four imide structures (two rigid aromatic and two flexible aliphatic ones) per repeating unit of final polymers were introduced in hard segment.

Investigation of physical and thermal properties showed that in comparison to conventional polyurethanes, thermal stability of PUIIs were enhanced considerably and simultaneously good mechanical properties and processability preserved.

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