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Synthesis and properties of novel thermoplastic poly(urethane-imide)s

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Abstract

A new class of poly(urethane-imide)s (PUI) thermoplastic elastomers were synthesized via the reaction of NCO terminated polyurethane with imide containing chain extender diols. The prepared chain extenders and polymers were characterized by conventional methods, and physical properties such as solution viscosity, solubility property, thermal stability and thermal behavior were studied. Compared to typical polyurethanes, these polymers exhibited better thermal stabilities due to the presence of the imide groups. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(urethane-imide); Thermoplastic polymer; Thermal stability; Diol

1. Introduction

Polyurethane (PU) is a versatile polymer and can be easily prepared by a simple polyaddition reaction of polyol, isocyanate and a chain extender. The tailor-made properties from super soft flexible foam to tough elastomers and to long-wearing coatings have resulted in many end applications [1–4]. Unfortunately, the conventional PU is known to exhibit poor thermal stability which limits its applications. For example, the acceptable mechanical properties disappear above 80–90°C and thermal degradation takes place at temperatures above 200°C [5]. Attempts to improve the thermal stability of polyurethane have been made over a long period. 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. Recently, more attention has been paid to modifications by heterocyclic groups. Polyimides are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical, electrical, and durable properties [6,7].

Various attempts to incorporate polyimide units into PU have been made. Reaction of isocyanate terminated PU prepolymer with acid anhydride was the method most often utilized to introduce the imide function into the PU backbone [8–10]. A modified method was the reaction of isocyanate terminated PU prepolymer with aromatic diamines and dianhydride to prepare PU with imide groups in the backbone [11]. Reaction of isocyanate terminated PU with diols or diacids containing imide groups was also utilized [12,13]. Intermolecular Diels–Alder (DA) reaction of 4-methyl-1,3-phenylene bis(2-furanyl-carbamate) with various bismaleimides was reported to give a series of poly(urethane-imide)s [14–16]. Also, in order to improve the solvent resistance to ordinary organic solvents, a network structure was prepared via the reaction of PU prepolymer with polyimide precursor (polyamic acid) [17,18].

In our previous work, we reported the preparation of novel PUI using diisocyanates containing built-in imide structure [19], and we have now explored the possibility of introducing the imide function in the polyurethane backbone through the reaction of imide containing diol chain extenders with the isocyanate terminated PU prepolymer. Synthesis and characterization of the prepared monomers and polymers and also the physical and thermal properties of the polymers are discussed.

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2. Experimental

2.1. Materials

Polyester polyol, CAPA 225, molecular weight 2000, obtained from Interox Chemicals was dried at 70°C in vacuum for 24 h before use. Toluene diisocyanate (TDI, mixture of 80% 2,4 and 20% 2,6 isomers, Merck) was vacuum distilled before use. *N,N′*-dimethyl-formamide (DMF) and *N*-methyl pyrrolidone (NMP) were vacuum distilled from CaH_2 and stored over 4A° molecular sieves. Trimellitic anhydride (Fluka) was purified by recrystallization from acetic anhydride. 4,4′-Diaminodiphenyl ether (Fluka) was purified by vacuum drying at 50–60°C. Ethylene glycol (EG), diethylene glycol (DEG), and 1,3-propylene glycol (1,3-PG) (Merck) were dried under vacuum at 90°C. Other chemicals and solvents were used as received.

2.2. Instruments

FTIR spectra were recorded on a Bruker-IFS 48 instrument. ^{1}H-NMR spectra were obtained using a Jeol-Japan GNM-EX instrument at 90 MHz. TGA and DSC analyses were performed on a Stanton STA-615 with heating rate of 20°C/min in air. Melting points were determined in open capillaries with a Buchi 535 instrument. Inherent viscosities of polymers were determined for solutions of 0.5 g/dl in DMF at 30°C using ubbelohde viscometer.

2.3. Synthesis of N,N′-(4,4′-diphenyl ether) bis trimellitimide (**I**):

Trimellitic anhydride (15.3 g, 0.08 mol) was dissolved in NMP (50 ml) at 50°C in a 250 ml round-bottom flask equipped with a condenser, magnetic stirrer, nitrogen inlet and a thermometer. After cooling the solution to room temperature, 4,4′-diaminodiphenyl ether (8.17 g, 0.04 mol) was added to the flask and left for 5 h at room temperature under stirring. The temperature was then slowly raised to 180°C and maintained there for 4 h to complete the reaction. The product was isolated by pouring the reaction mixture into 500 ml of distilled water, filtered, and repeatedly washed with distilled water. The product was dried under vacuum at 60°C. This monomer was purified by recrystallization from boiling acetic anhydride.

2.4. Synthesis of imide containing chain extenders (**II**–**IV**)

Diacid (**I**) (6 g, 0.011 mol) was made to react with either EG,DEG or 1,3 PG (0.44 mol) in a 250 ml flask equipped with a condenser, magnetic stirrer and a thermometer at reflux condition. After the reaction mixture became clear (about 4 h), it was allowed to react further for 1 h. The product was cooled and poured in excess methanol. The precipitate was filtered and washed again with methanol to remove excess diol and then finally recrystallized in 1,1,2,2-tetrachloroethane.

2.5. Synthesis of isocyanate terminated prepolymer

In a 250 ml three necked reaction kettle equipped with magnetic stirrer, reflux condenser, dropping funnel and N_2 inlet was placed polyol (12 g, 0.006 mol), and TDI (2.09 g, 0.012 mol) was added dropwise while maintaining the temperature at 60°C under N_2 atmosphere. The temperature was then increased to 90°C and the reaction was continued till the NCO content reached half the value as determined by dibutylamine titration. The product was stored as such under N_2 until further use.

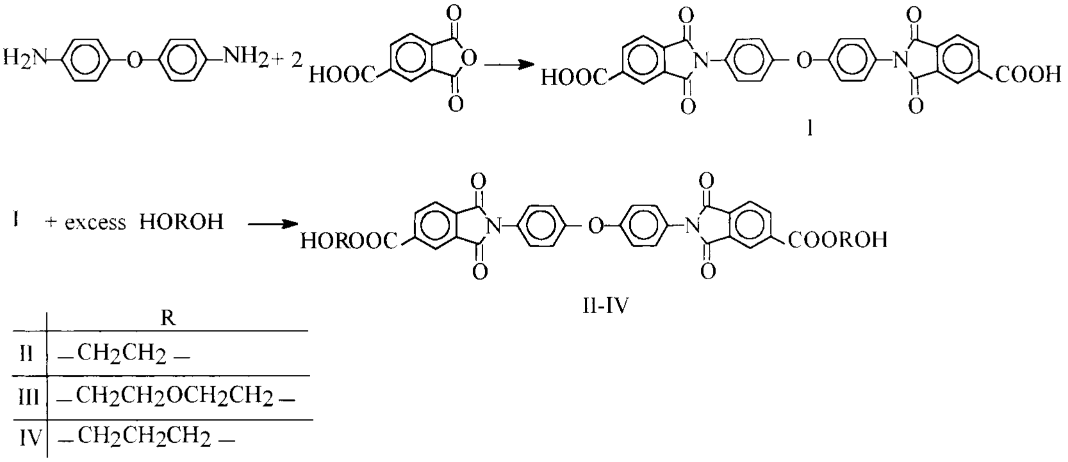
2.6. Synthesis of poly(urethane-imide)s

The NCO-terminated PU was dissolved in DMF to form 20 wt.% solution at 50°C. To the solution formed under stirring and N_2 bubbling was added one equivalent of chain extender dissolved in DMF. The reaction mixture was stirred for 0.5 h and then 0.1 wt.% of stannous octoate catalyst was added to it. The temperature of the reaction was raised to 90°C and it was allowed to get completed, as evidenced from the disappearance of the peak at 2250 cm^{-1} in the IR spectrum.

3. Results and discussion

As mentioned previously, there are several methods for introducing the imide group into the polyurethane backbone. In the present work, introduction of the imide group via the chain extender was tried. By using this approach, two benefits could be derived: (a) possibility to use commercially available NCO-terminated polyurethane, (b) enhancing phase separation of the hard and soft segments of the thermoplastic elastomer because of very strong intermolecular attraction of the imide group which is present in the hard segment. Scheme 1 outlines the synthetic route for the preparation of chain extender diols (**II**–**IV**).

Diacid **I** was conveniently prepared by the condensation of two equivalents of trimellitic anhydride with 4,4′-diaminodiphenyl ether in NMP. Diacid **I** was subjected to a reaction with an excess amount of diols (EG,DEG,1,3PG), and the resulting chain extender diols (**II**–**IV**) were prepared with excellent yields. Mass spectrum of diacid **I** showed that $m/z = 548$, corresponding to the molecular ion peak. IR spectrum of diacid **I** showed characteristic imide group absorption peaks at



Scheme 1.

1780, 1720, 719 cm^{-1}, acid carbonyl group absorption peak at 1693 cm^{-1} and aromatic ether group absorption peak at 1225 cm^{-1}. ^{1}H-NMR spectrum of diacid **I** showed characteristic bands of aromatic protons at 8.5–7.3 ppm. IR spectra of diols (**II**–**IV**) showed characteristic peaks of imide groups and the combination of imide and ester carbonyl absorption peak at 1720 cm^{-1}. Also peaks due to the hydroxyl groups and aliphatic CH_2 group were observed at 3450 and 2950 cm^{-1}, respectively. The ^{1}H-NMR spectra of the diols were in accordance with the proposed structures. All spectral data of compounds **I**–**IV** are indicated in Table 1.

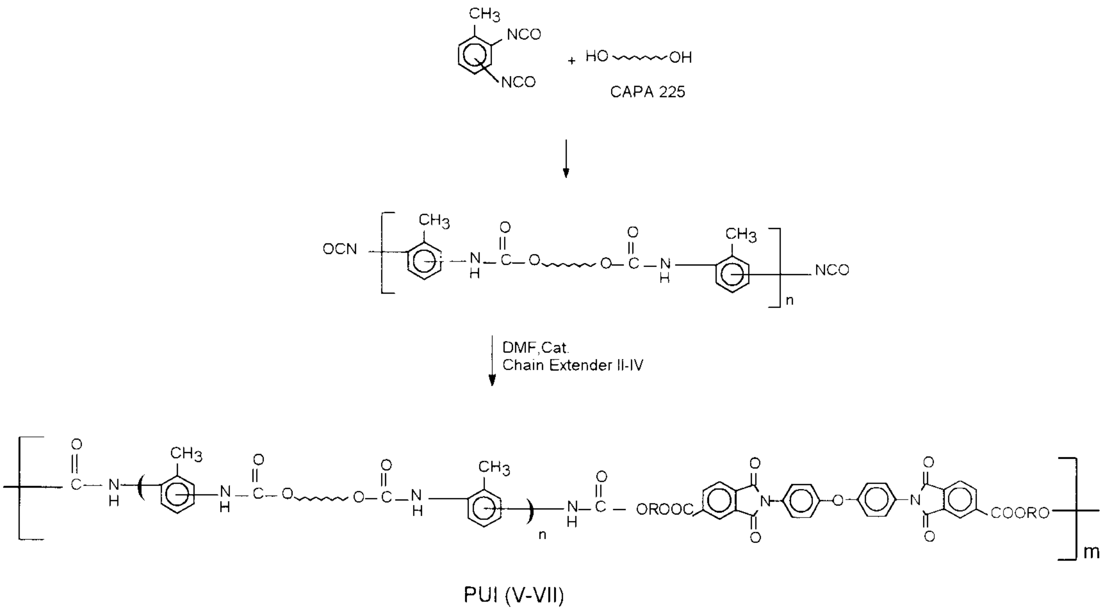
Poly(urethane-imide)s were prepared easily through transformation of the polyol to the isocyanate terminated prepolymers and subsequent reaction with equimolar quantity of imide containing diol chain extenders (Scheme 2).

The IR spectra of all the poly(urethane-imide)s contained prominent characteristic bands of the imide and urethane groups. The bands around 1780–1770 and 1740–1710 cm^{-1} were due to the imide and ester/urethane carbonyl linkages and N–H stretching band of urethane group was observed around 3400–3350 cm^{-1}. The ^{1}H-NMR spectra of polymers showed the aromatic ring protons in the region 7.31–7.56 ppm and aromatic protons of trimellitimide rings at 8.08–8.53 ppm. The resonance signals for methylene proton of the polymers appeared in the region 1.68–4.48 ppm depending on the position of the methylene protons from the neighboring ester and urethane groups. Also characteristic bands of urethane N–H proton appeared at 9.60, 9.43, 8.90, 8.72, 8.55 ppm. The spectral data of all the polymers are collected in Table 2. The solubility properties of PUIs were studied using several solvents. As shown in Table 3, all the polymers show excellent solubility in polar aprotic solvents and chlorinated solvent such as tetrachloroethane, but less efficient solvents such as toluene and xylene could not solve the polymers.

Table 1
Spectral and physical data of compounds **I**–**IV**

Compound	Yield%	mp C	IR (cm^{-1})	NMR (ppm)[a]
I	80	380	1780, 1720, 1390, 1110, 1693, 3600, 3100, 1600, 1580, 1225, 719	8.53(s,2H), 8.37(d,2H), 8.08(d,2H), 7.56(d,4H), 7.31(d,4H)
II	82	128	1780, 1720, 1380, 1160, 729, 3450, 2950	8.53(s,2H), 8.37(d,2H), 8.08(d,2H), 7.56(d,4H), 7.31(d,4H), 4.85(t,4H), 4.65(t,4H), 4.32(s,2H)
III	83	111	1778, 1720, 1385, 1115, 725, 3450, 1924	8.53(s,2H), 8.37(d,2H), 8.08(d,2H), 7.56(d,4H), 7.31(d,4H), 4.85(t,4H), 4.65(t,4H), 4.32(s,2H), 3.65(t,8H)
IV	82	119	1780, 1720, 1385, 1119, 725, 3422, 2874	8.53(s,2H), 8.37(d,2H), 8.08(d,2H), 7.56(d,4H), 7.31(d,4H), 4.85(t,4H), 4.65(t,4H), 4.32(s,2H), 1.68(m,4H)

[a] Solvent: DMSO-d6.



Scheme 2.

The inherent viscosities of the polymers were measured in DMF solvent at 30°C and the results are presented in Table 2. The results revealed that the polymers were of moderately high molecular weight. All these polymers produced clear, flexible and tough films which could be cast from solution of the polymers in the DMF solvent. This showed good mechanical strength of the films.

The thermal stability of PUIs was evaluated by thermal gravimetric analysis. Ten percent weight loss of the polymers, as a criterion of thermal stability of polymers, was in the range of 310–320°C. Compared to the conventional polyurethanes, the decomposition temperatures of PUIs prepared by our method were improved showing that this approach was effective. It seems that increased phase separation and domain cohesion because of strong dipole–dipole interaction of imide groups, present in the hard segment are responsible for the improvement of thermal properties. Thermal behavior of PUIs was studied by DSC. The glass transition temperature of the hard segment was observed around 100–110°C, which is higher than the typical polyurethanes. This behavior can be attributed to the incorporation of imide rings in PUIs. Also, the exotherm due to the thermal decomposition of PUIs which indicates the upper limit for use of these polymers began at around 300°C. The temperature of various transitions concerning the thermal stability and thermal behavior of the prepared PUIs, are presented in Table 4.

Table 2
Spectral data, yield, and inherent viscosity of polymers

Polymer	Yield%	inh	IR (cm^{-1})	NMR (ppm)[a]
V	90	0.42	3348, 2947, 2888, 1780, 1728, 1380, 1234, 1149, 730	9.61(s), 9.43(s), 8.92(s), 8.72(s), 8.55(s), 8.37(d), 8.08(d), 7.56(d), 7.31(d), 4.85(t), 4.65(t), 4.04(t), 2.35(t), 2.13(s), 1.80(m)
VI	91	0.41	3348, 2947, 2866, 1780, 1728, 1385, 1234, 1169, 729	9.61(s), 9.43(s), 8.92(s), 8.72(s), 8.55(s), 8.37(d), 8.08(d), 7.56(d), 7.31(d), 4.85(t), 4.65(t), 4.04(t), 3.62(t), 2.35(t), 2.13(s), 1.80(m)
VII	90	0.41	3345, 2947, 2870, 1780, 780, 1728, 1375, 1230, 1170, 732	9.61(s), 9.43(s), 8.92(s), 8.72(s), 8.55(s), 8.37(d), 8.08(d), 7.56(d), 7.31(d), 4.85(t), 4.65(t), 4.04(t), 3.62(t), 2.35(t), 2.13(s), 1.80(m), 1.68(m)

[a] Solvent: DMSO-d6.

Table 3
Solubility of PUIs

Polym.	DMF	DMAc	NMP	THF	$CHCl_3$	$C_2H_2Cl_4$	Xylene	Toluene
V	++	++	++	+	+	++	–	–
VI	++	++	++	++	+	+	–	–
VII	++	++	++	+	+	++	–	–

++: soluble at room temperature, +: soluble after warming, −: insoluble.

Table 4
Thermal properties of PUIs

Polymer	T_g[a]	$T_{10\%}$[b]	T_{max}[c]	Ch. Y.%[d]
V	110	320	355	14
VI	100	315	335	11
VII	105	310	345	10
VIII[e]	75	250	315	0

[a] Glass transition temperature.
[b] 10% weight loss.
[c] Maximum decomposition temperature.
[d] Weight of remained polymer at 600°C.
[e] Prepared from CAPA225/2TDI/1,4-buthanediol.

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