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Preparation and properties of polyamide from amine terminated poly(urethane-urea) oligomers

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Summary

A new class of segmented poly(urethane-urea-amide) (PUUA) block copolymers contained poly(oxytetramethylene) (POTM) were prepared by direct condensation of diacid chloride with amine-terminated poly(urethane-urea) (ATPUU) oligomers. The ATPUUs were prepared from the reaction of NCO-terminated polyurethane prepolymer with different diamines. The PUUAs having reduced viscosities ranged from 0.87 to 1.82 dL/g. These polymers were soluble in various polar solvents and gave transparent, tough, and flexible films by casting from m-cresol The copolymers were studied by utilizing differential scanning calorimetry (DSC), thermogravimetry (TG), and tensile testing.

Introduction

The unique and novel characteristics of thermoplastic polymers have recently led to an extensive study of their synthesis, morphology, and mechanical properties (1-9). These materials are a broad class of polymers composed of chemically dissimilar units commonly denoted as hard and soft segments. The unique properties of these copolymers are related directly to their two-phase microstructure, with the hard domains acting as a reinforcing filler and as a thermally reversible cross-link.

The incorporation of urea linkages in the polyurethane hard segments has profound effect on the phase separation (2,10,11). The driving force for this phase separation is primarily due to the formation of intermolecular hydrogen bonding networks. Segmented poly(urethane-urea) is commercially available as Biomer and has been widely used for cardiovascular prostheses such as blood pumps for artificial heart systems mainly due to its antithrombogenecity and excellent mechanical properties (12-14). In this paper, the properties of a newly synthesized class of segmented polyether poly(urethane-urea-amide) block copolymers were studied.

Experimental

Materials

Poly(oxytetramethylene) (POTM) of molecular weight 1000 (DuPont) was vacuum dehydrated at 70°C. 4,4'-Oxydianiline (ODA, Merck), 4,4'-methylenedianiline (MDA, Merck), and terephthaloyl chloride (TC, Fluka) were vacuum sublimed to yield off white solid. 1,6-Hexanediamine (HDA,Prolabo), 1,12-dodecanediamine (DDA, Merck), and dimethylacetamide (DMAc, Fluka) were fractionally vacuum distilled. Reagent grade lithium chloride was dried at 150°C under vacuum. before use. Tolylenediisocyanate (TDI, Merck) utilized a mixture of the 2,4- and 2,6- isomer of 80 and 20%, respectively, and adipoyl chloride (AC, Fluka) were used as received.

Synthesis

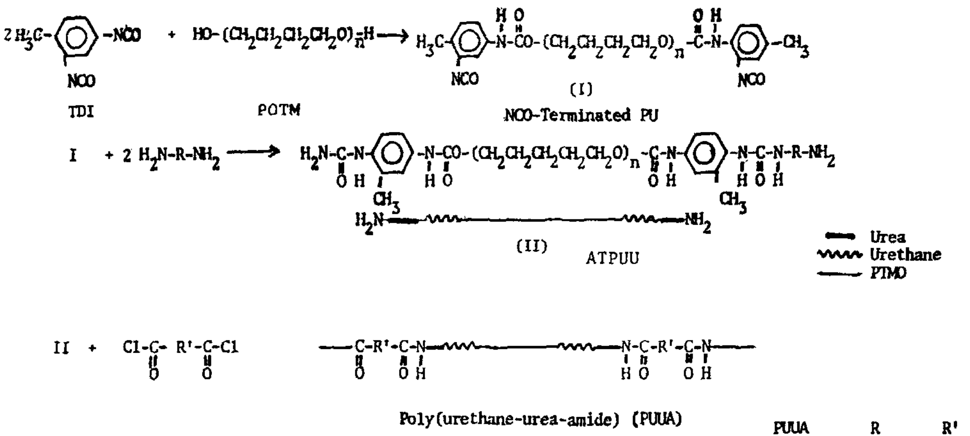
Syntheis of amine-terminated poly(urethane-urea) oligomers (ATPUU)

NCO-terminated polyurethane (PU) prepolymer at 6.4% NCO determined by di-n-butylamine titration method was prepared by reacting two equivalents of TDI with one equivalent of POTM. One equivalent of NCO-terminated PU prepolymer was dissolved in dry DMAc, produced 40-45% solids by weight was added to two equivalents of a diamine solution at 0°C. The reaction was continued for 1 h at 0°C and at room temperature until the theoretical amine content (determined by nonaqueous titrimetry) was reached. The reactions were performed under a continuous purge of dry nitrogen. The detailed procedure has been published elsewhere (15).

Synthesis of poly(urethane-urea-amide) block copolymers (PUUA)

The PUUAs used in this study were synthesized by the reaction of ATPUU with diacid chloride as shown in Fig. 1. All polymerizations were carried out by following the similar procedures as described below: ATPUU solution at a concentration of 10-15% solids (w/w) was placed in a 500 mL reaction kettle equipped with a nitrogen inlet, stirrer, a condenser, and a drying tube. The solution was cooled to 0°C and a 15 weight percent of diacid chloride solution in 5% LiCl-DMAc was added in four additions over 40 min. The stirring was continued for 3 h at 0°C and for 3 h at room temperature. The vicous solution was added to stirred methanol. The precipitated fibrous polymer was collected by filtration, followed by through washing with water, methanol, and methylene chloride. The resulting fibrous polymers were dried at 80°C *in vacuo*. The yield was 97% and the reduced viscosity of the copolymers in *m*-cresol listed in Tab. 1 ranged from 0.87 to 1.82 dL/g, measured at a concentration of 0.1 g/dL at 30°C. The IR spectra (KBr) showed absorptions at 3270 cm^{-1} for hydrogen bonded NH groups, 1725 cm^{-1} for urethane carbonyl 1640 cm^{-1} for hydrogen the hydrogen bonded urea or amide carbonyl, and 1540 cm^{-1} for the hydrogen bonded NH group, which indicated the formation of urethane, urea, and amide linkages.

The sample films used for characterization were made by solution casting of 6 wt% copolymer solution in *m*-cresol on an aluminum molds coated with teflon and the solvent



PUUA	R	R'
A	MDA	AC
B	ODA	AC
C	HDA	TC
D	DDA	TC

Fig. 1. Synthesis of PUUA block copolymers

evaporated in circulated air oven at 80°C and further dried *in vacuo* at 80°C for 96 h, giving transparent, tough plastic films. The composition of the sample materials is tabulated in Tab. 1.

Tab. 1. Composition and reduced viscosity (η_{red}) of PUUA materials

	Mole ratios of reactants					η_{red}
sample	TDI	POTM	Diamine	AC	TC	dL/g
A	2	1	2 (MDA)	1	-	0.87
B	2	1	2 (ODA)	1	-	0.85
C	2	1	2 (HDA)	-	1	1.82
D	2	1	2 (DDA)	-	1	1.79

Characterization

The reduced viscosity of PUUAs were measured with 0.1% solution in m-cresol at 30°C using Ubbelholde viscometer. Infrared (IR) spectra were recorded on a Pye-Unicam IR spectrophotometer with KBr plates. Differential scanning calorimetry (DSC), thermogravimetry (TG, DTG) were performed on a DuPont Thermal Analyzed 2000 system in a combination with a standard DSC cell and TG-951. Measurements were carried out at a heating rate of 20°C/min. The stress-strain measurements were made at room temperature on an Instron tensile testing machine, Model 1026. ASTM D-638 procedure was followed, employing a crosshead speed of 5 cm/min.

Results and Discussion

The solubility behavior of the PUUAs obtained was studied qualitatively, and the reults are summarized in Tab. 2. All the block copolymers were soluble in m-cresol, DMA, and most of them dissolved in N,N-dimethylformamide, and dimethylsulfoxide at high temperature.

Tab. 2. Solubility of PUUA materials

	Solvent*						
sample	$CHCl_3$	CH_2Cl_2	NMP	DMAc	DMF	DMSO	m-cresol
A	-	-	+	++	+	++	++
B	-	-	+	++	+	++	++
C	-	-	+	+	+	+	++
D	-	-	+	+	+	+	++

* (+) Partially soluble; (++) Readily soluble;
(-) Insoluble NMP = 1-Methyl-2-pyrrolidone;
DMF = N,N-Dimethylformamide; DMSO = Dimethylsulfoxide;
DMAc = N,N-Dimethylacetamide

The results of the DSC of PUUAs are shown in Fig. 2 and the data are summarized in Tab. 3. The glass transition temperature of the PUUAs was found to be about 25-37°C higher than the Tg of the pure soft segment (POTM) which was found -78°C. The mixture of 2,4- and 2,6- isomers have been shown to provide a degree of a morphous character to urethane and amide hard segments as contrasted to more symmetrical, such as 4,4'-diphenylmethane diisocyanate (16). The analysis of Tgs for these copolymers suggests that the development of a microphase separation within these block copolymers has occured to high degree comparing to PU prepared from TDI, POTM, and 1,4-butanediol or PUU. The phase separation was observed by the presence of POTM melting point at about 16°C, suggests that soft segment crystallize. The crystallization of POTM arises from the high polarity of urea and amide groups compared to ether groups. The degree of phase separation in these polymers based on TDI is still less than the polymers prepared from more symmetrical diisocyanates due to the unsymmetrical nature of the isomeric TDI.

Typical TG and DTG curves of PUUAs show more or less similar pattern and are given in Fig. 3. Loss in weight of

Tab.3. DSC data of PUUA materials

	Glass transition, °C				
PUUA	onset	midpoint	endpoint	Tc, °C [1]	Tmc, °C [2]
A	-38	-32	-29	8	45
B	-31	-23	-20	10	43
C	-37	-28	-24	-6	37
D	-38	-34	-28	-3	42

1 = Crystallization peak; 2 = Crystalline melting peak

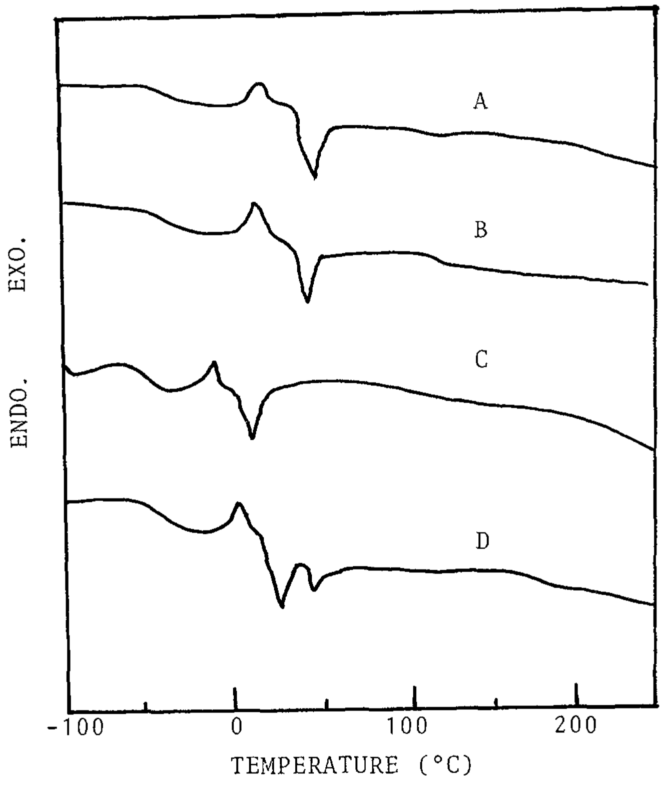


Fig. 2. DSC thermograms of PUUA block copolymers

Tab. 3. Thermal properties of PUUA materials

	Temp. in °C at various percentage of decomposition				
PUUA	10	20	30	40	50
A	325	355	385	415	430
B	325	352	385	417	435
C	330	360	390	425	440
D	330	360	395	430	445

the polymers at different temperatures were determined from the respective TG and DTG and is presented in Tab. 3. The PUUAs decompose in the region of 300-350°C. The TG curves show a gradual weight loss up to 450°C. Above this temperature the weight loss is rapid.

The stress-strain data of PUUAs are shown in Fig. 4 and are summarized in Tab. 5. The films had tensile strength of 25 MPa, and elongation at break of 300%. Among them, PUUAs prepared from aromatic diamines afforded the highest tensile strength and Young's modulus.

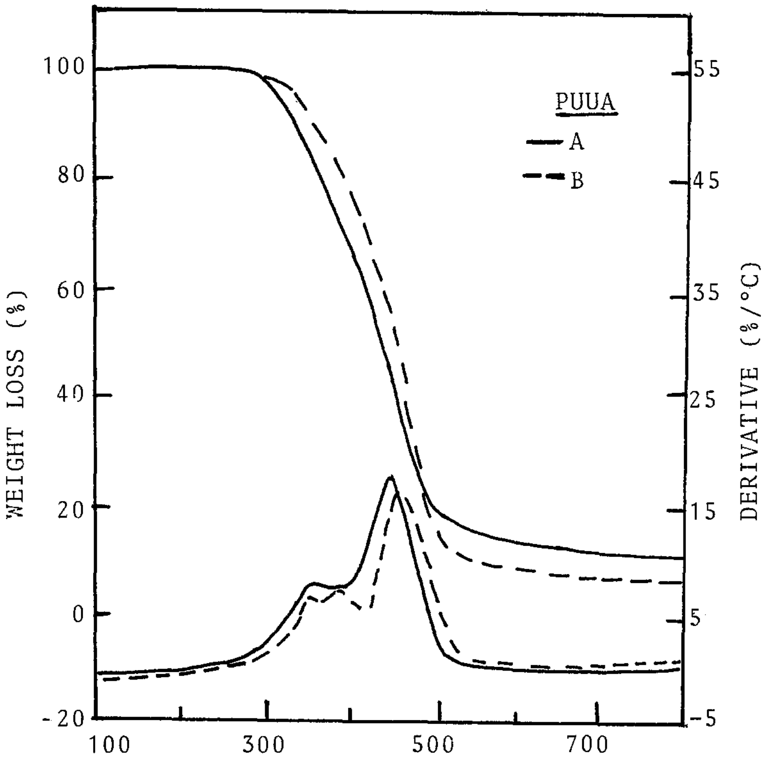


Fig. 3. Typical TG and DTG thermograms of PUUA materials

Tab. 5. Tensile properties of PUUA materials

PUUA	E (%)	Ts (MPa)	M_{100} (MPa)	M_{200} (MPa)	M_{300} (MPa)	Eσ (MPa)
A	260	26	16	20	-	43
B	310	24	15	19	21	41
C	398	18	8	11	13	28
D	554	14	6	8	9	22

Keywords: E = Elongation at failur; Eσ = Young's modulus;
M_{100}; M_{200};M_{300} = Secant modulus at 100, 200,and
300% elongation; Ts = Ultimate tensile strength

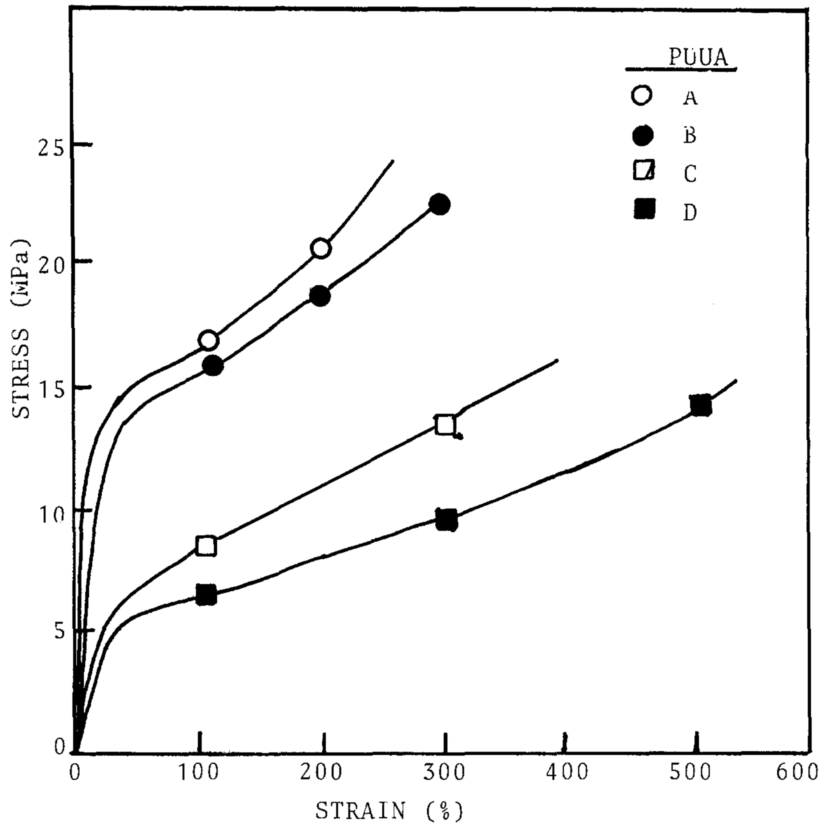


Fig. 4. Stress-strain plots of PUUA materials

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