

# Synthesis and Characterization of Excellent Transparency Poly(urethane-methacrylate)

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**ABSTRACT:** A series of novel crosslinked poly(urethane-methacrylate) (PUA) was synthesized. PUA was polymerized in a three-step process: The low number average molecular weight unsaturated polyester (UPE) containing hydroxyl groups was synthesized by 1,2-propanediol (PG), 2-butyl-2-ethyl-1,3-propanediol (BEPD) and maleic anhydride (MA). A series of prepolymers, which had double bonds at the end of the chain, was prepared from isophorone diisocyanate (IPDI), UPE, and  $\beta$ -hydroxyethyl methacrylate (HEMA) in the presence of dibutyltin dilaurate (DBTL) as catalyst. The novel functional prepolymer was initiated by 2,2-azobis-isobutyronitrile (AIBN) to form

thermosetting materials. The structure of the thermosetting materials was characterized by Fourier Transform Infrared (FTIR). Mechanical, thermal, and optical properties were tested. The results showed that the advanced PUA had good thermal and mechanical properties and high transparency. The throughput of PUA was above 90%, thus the PUA was possible to be used as excellent optical material. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 724–729, 2009

**Key words:** prepolymer; polyurethane-methacrylate; thermoset; transparency

## INTRODUCTION

Macromonomer is a kind of monomer with a reactivity site consisting of vinyl group at the end of the chain.<sup>1–4</sup> A lot of materials are obtained by changing the arrangement of acrylic structural units on the macromonomer chain.<sup>5–12</sup> Therefore, macromonomer has been widely applied in coating, inks, dry toners, instrument calibration, chromatography, and biomedical treatment etc.<sup>13–21</sup>

Polyurethane is an important material in optics,<sup>22</sup> automotive parts,<sup>23</sup> and optoelectronics<sup>24,25</sup> for its outstanding properties, such as transparency in a wide wavelength range, strong damage resistance for laser irradiation, good physical properties, high heat-proof thermal properties, chemical stability, good dimensional stability, etc. PUA elastomers represent a new class of polyurethanes which contain “soft” segments formed from polyester or aliphatic polyether chains, and “hard” segments formed from urethane groups and acrylic structural units. Normally, they are synthesized by a two-step process.<sup>26</sup> An excess molar concentration of a diisocyanate reacted with a polyether or a polyester diol<sup>27</sup> to prepare an isocyanate-terminated prepolymer in bulk or in solvent. Urethane-methacrylate macromonomer is

synthesized by the prepolymer and an aliphatic acrylate with hydroxy. The bulk polymerization reaction without any solvents becomes a practical, convenient and economical route.

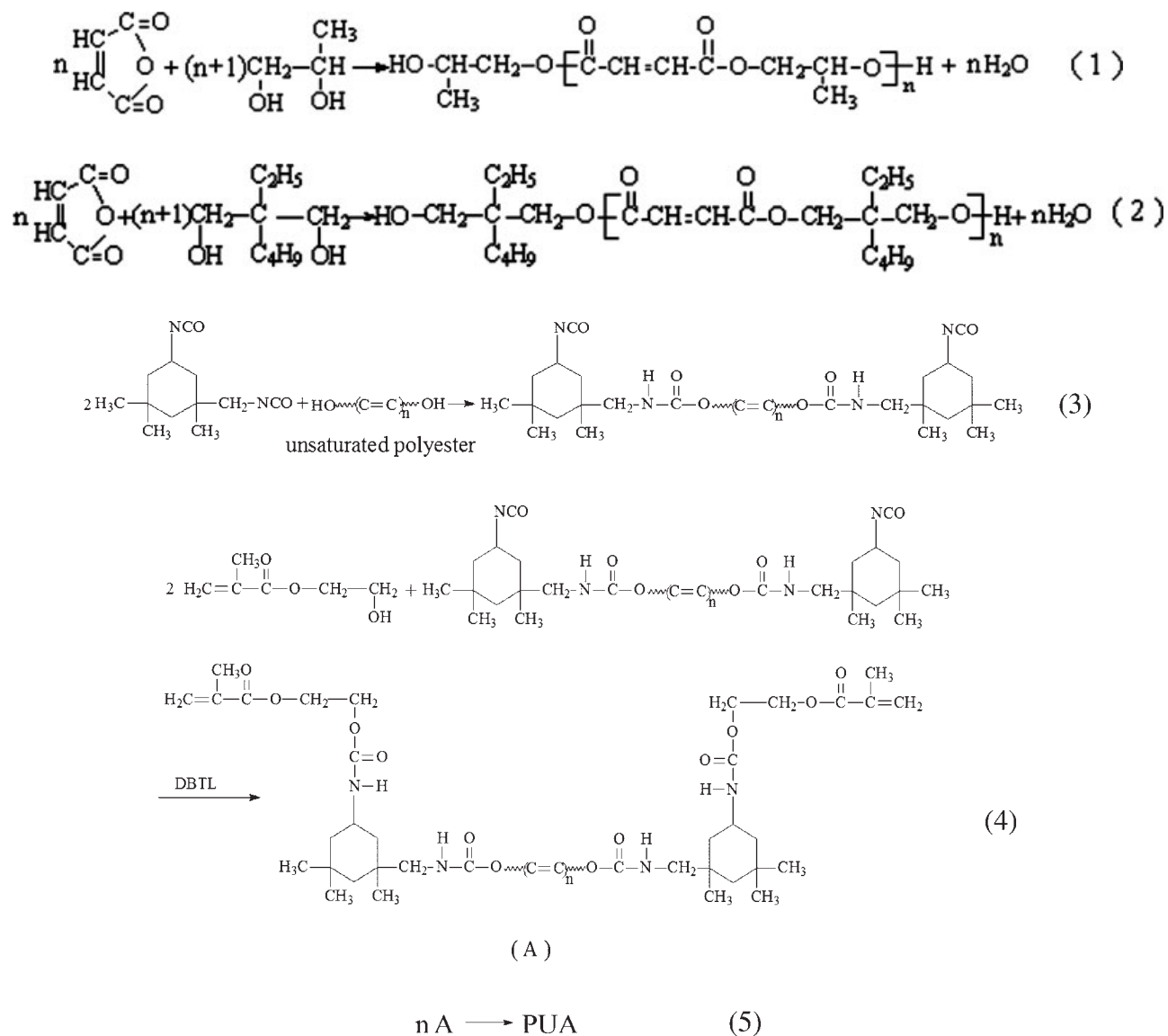
In this article, PUAs based on a series of polyester (soft segments), IPDI and HEMA (hard segments) were studied, which made it possible to synthesize polyurethane containing acrylic groups. The different soft segments brought significant effects on the ultimate physical properties of these materials, such as tensile and impact strength. These results would be helpful for theoretical and practical application of PUA.

## EXPERIMENTAL

### Materials

MA and PG were purchased from Tianjin Kermel Chemical. MA:  $\rho = 1.32$ ; mp = 52°C; bp = 200°C. PG:  $\rho = 1.03$ ; bp = 187°C. BEPD was purchased from Shanghai Bofeng Trading. BEPD:  $\rho = 0.93$ ; mp = 40–44°C; bp = 178°C/50 Torr. IPDI was provided by Degussa. IPDI:  $\rho = 1.058$ ; mp = –60°C; bp = 50°C/0.90 Pa. HEMA was provided by Tianjin Chemical Reagent Research Institute. HEMA: mp = –12°C,  $\rho = 1.074$ , bp = 95°C/1.33 Pa. AIBN was purchased from Tianjin Fuchen Chemical Reagents Factory. AIBN: mp = 99–103°C, which was recrystallized from alcohol and dried by vacuum distillation.

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Scheme 1 Synthesis of UPE-1 (1), UPE-2 (2), and PUA-1 (3)–(5).

DBTL was provided by Shanghai Far Navigation Chemical Reagent Factory. DBTL:  $\rho = 1.05$ ; mp = 22–24°C; fp = 226.67°C.

### Preparation of UPE

UPE was synthesized in a one-step reaction as shown in reactions (1) and (2), Scheme 1.

The UPEs were synthesized by a melting process. The mole ratios between acid anhydrides and glycols were 1 : 1.5 for UPE-1 and 1 : 2 for UPE-2, respectively. The reactions took place under 200°C until the acid content reached about 46 mg (KOH)/g for UPE-1 and 17 mg (KOH)/g for UPE-2. The acid content was determined by titrating the solutions of unsaturated polyester in toluene/ethanol ( $v/v$  : 2/1), with 0.1 mol/L KOH in toluene/ethanol (2/1) solution using phenolphthalein as indicator. Number-average

molecular weights of UPE-1 and UPE-2 were 362 and 371 (Table I), respectively.

### Preparation of PUA

PUA-1 was synthesized in a multi-step reaction as shown in reactions (3)–(5), Scheme 1.

3.62 g (0.010 mol) UPE-1, 50.01 g (0.225 mol) IPDI were introduced in a 500 mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet valve and the temperature was held at 80°C for 30 min. And 55.96 g (0.430 mol) HEMA was added and stirred for 30 min. Then 5.00 g (0.030 mol) AIBN was added and stirred for 5 min. Finally, the system was poured into the glass grinding apparatus at room temperature, warming up to 60°C for 5 h, and increasing to 80°C for 5 h to cure. During this process, the double bond polymerized, and the obtained

**TABLE I**  
**Characterization of Unsaturated Polyester (UPE)**

Samples	UPE-1	UPE-2
Molar coefficient ( <i>r</i> )	0.6667	0.5000
Measured acid value (mg KOH/g)	46	17
Measured alcohol value (mg KOH/g)	120	170
Reaction degree ( <i>P</i> )	0.9130	0.9366
Average molecular weight of structural unit ( <i>M</i> <sub>0</sub> )	84.9	139.4
Polymer degree ( $\bar{X}$ )	4	3
Number-average molecular weight (g/mol)	362	371
Appearance	Transparent liquid	Transparent liquid
Unsaturated degree (mol/kg)	5.15	2.50
Yield (%)	74.81	93.70

polyurethane materials were used for subsequent testing.

The synthesis of PUA-0, PUA-2, PUA-3, PUA-4, PUA-5, PUA-6, PUA-7, and PUA-8 was the same as PUA-1 (Table II).

### Characterization

#### FTIR spectroscopy

Room temperature infrared spectra of these samples were taken using a 5DXB Nicolet FTIR spectrometer with a detector at a resolution of 4 cm<sup>-1</sup> in the range of 400–4000 cm<sup>-1</sup>. A total of 32 scans were used for signal averaging. The samples, in the form of power, were sandwiched in the KBr pellets.

#### Thermogravimetric analyses (TGA)

Thermogravimetric analyses (sample weight: 10 mg) were carried out using a NETZSCH TG 204 apparatus. The thermograms were run at a heating rate of 10°C/min from room temperature to 600°C under a nitrogen atmosphere (45.0 mL/min).

#### Mechanical-properties measurement

Stress–strain measurements were performed in uniaxial tensile with a constant speed (50 mm/min) using a CMT 6104 apparatus. Samples for tensile tests were applied dumb-bell geometry with dimension of 150 mm × 10 mm × 4 mm. Tensile properties were performed according to GB/T 1040-92. Six samples were tested for each group, and the data were reported as the mean of the data.

Unnotched freely supported beam impact strength of each sample was tested conforming to ISO 179-1982. All samples tested were unnotched so they would be more sensitive to the transition between

ductility and brittleness. As mentioned by Nielsen,<sup>28</sup> a notch tended to decrease the apparent ductility of material and usually had a greater effect on ductile materials than that on brittle ones. Specimens with dimension of 80 mm × 10 mm × 4 mm were tested at ambient temperature. At least 10 specimens were tested for each of the samples to ensure the accuracy of the results.

#### Hardness measurement

Rockwell hardness was tested with XHR-150 apparatus. Rockwell hardness was performed according to ISO 2039/2-1981. Specimen thickness is 4 mm. At least 8 specimens were tested for each of the samples to ensure the accuracy of the results.

#### Optical properties measurement

The transmittances were recorded on a WGT-S Ubest-35 spectrometer according to GB 2410-80.

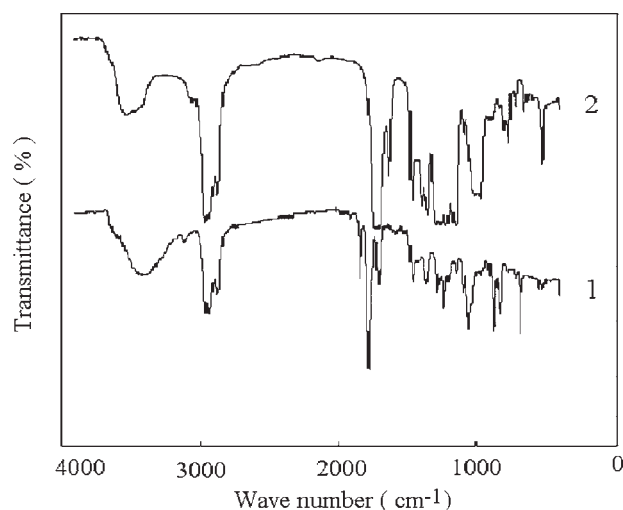
## RESULTS AND DISCUSSION

### General feature of polyurethane preparation

Keeping the NCO/OH ratio as 1, UPE was mixed with HEMA in different ratios and reacted with IPDI. Preliminary quasi-stoichiometric [NCO]/[OH] showed that the polycondensation of HEMA with IPDI did not occur in the absence of catalysts from 20 to 50°C. The reason can be attributed to (1) steric difficulties related to the encounter of OH and NCO functions; (2) the high viscosity of the medium caused HEMA hard to diffuse.<sup>29</sup> Moreover, the system involved isocyanate moieties, which played the role of crosslinking reagent with respect to the OH groups of HEMA and polydiols. The addition of DBTL to these reaction mixtures will facilitate the condensation and lead to the formation of crosslinked polyurethanes. The positive effect of DBTL on these systems can be related to two cases. First, DBTL is Lewis-acid catalyst for the activation of isocyanate moieties. Second, DBTL is very effective role

**TABLE II**  
**Composition of PUA Using Different Kinds and Content Polymeric Glycols**

Samples	Polyester diol (mol)		IPDI (mol)	HEMA (mol)
	UPE-1	UPE-2		
PUA-0	0.000	0.000	0.225	0.450
PUA-1	0.010	0.000	0.225	0.430
PUA-2	0.015	0.000	0.225	0.420
PUA-3	0.030	0.000	0.225	0.390
PUA-4	0.000	0.010	0.225	0.430
PUA-5	0.000	0.015	0.225	0.420
PUA-6	0.000	0.020	0.225	0.410
PUA-7	0.000	0.030	0.225	0.390
PUA-8	0.000	0.040	0.225	0.370



**Figure 1** IR spectra of unsaturated polyester(UPE-1). 1, MA and PG mixture; 2, unsaturated polyester.

in breaking donor/acceptor interactions,<sup>30</sup> resulting in the activation of the OH groups of HEMA increasing.

### IR study

The linear structure of the unsaturated polyester can be deduced from IR spectra. The curve 2 (Fig. 1) shows the IR spectrum of the unsaturated polyester (UPE-1). The broad peaks at  $1856\text{ cm}^{-1}$ ,  $1783\text{ cm}^{-1}$  are absorption bands of acid anhydride in MA (the curve 1 in Fig. 1), after MA reacted with PG, the two peaks disappear and the intense broad bands at  $1731\text{ cm}^{-1}$  is quite characteristic of the stretching frequency of the carbonyl group ( $\text{C}=\text{O}$ ) of the aliphatic ester (the curve 2 in Fig. 1). The absorption bands at  $1644\text{ cm}^{-1}$ ,  $3000\text{--}2700\text{ cm}^{-1}$  are assigned to the double bond ( $\text{C}=\text{C}$ ) and  $\text{CH}_2$  stretch absorptions (the curve 2 in Fig. 1), respectively.<sup>29</sup> The strong broad absorption band centralized at  $3400\text{--}3500\text{ cm}^{-1}$  characterizes as the stretching frequency of  $\text{OH}$  groups (the curve 2 in Fig. 1).

The curve 1 in Figure 2 is the IR spectrum of UPE-1, HEMA and IPDI mixture. The absorption at  $2267\text{ cm}^{-1}$  indicates the existence of isocyanato-bond  $\text{NCO}$  (the curve 1 in Fig. 2). The macromonomer could be characterized from IR spectra (the curve 2 in Fig. 2). The band at  $1529\text{ cm}^{-1}$  verified the formation of  $\text{O-CO-NH}$  groups. The absorption peaks at  $1644\text{ cm}^{-1}$  implies that double bond ( $\text{C}=\text{C}$ ) still exists. Thus, the double bond had not polymerization. The absorption of isocyanato-bond  $\text{NCO}$  at  $2267\text{ cm}^{-1}$  disappeared, which indicated that isocyanatoes entirely reacted.

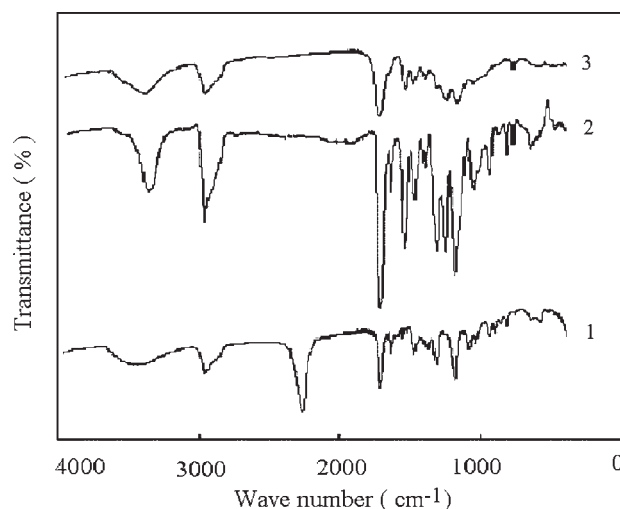
The curve 3 in Figure 2 is the IR spectra of PUA. The IR spectrum of PUA shows that the absorption of double bond ( $\text{C}=\text{C}$ ) at  $1644\text{ cm}^{-1}$  nearly dis-

appears. Thus, the double bonds of the macromonomer polymerized.

### Mechanical-properties measurement

The mechanical properties are very important for materials application. In this section, the mechanical properties of PUA were studied. With the variations of the polydiol and double bond percentage, macromonomer structure would influence tensile strength, impact strength of PUA.<sup>31</sup>

The results of mechanical properties measurement of PUA are presented in Table III. When the content of UPE-1 in PUA was 0.01 mol, 0.02 mol, comparing to PUA-0, the tensile strength of PUA changed slightly. However, impact strength increased very sharply. When the content of UPE-1 increased to 0.03 mol, the tensile strength of PUA increased to 19.80 MPa, and the impact strength increased to  $5.66\text{ kJ/m}^2$ . On adding 0.01 mol UPE-2 the tensile strength and the impact strength of polyurethane sharply increased to 26.58 MPa and  $1.87\text{ kJ/m}^2$ , respectively. Generally speaking, when adding UPE, the degree of PUA crosslinking increases, thus the chain is difficult to slip. With UPE content increasing, the degree of materials crosslinking increases, which leads to materials intensity increase. However, joining 0.015, 0.02, and 0.03 mol UPE-2, with the increase of UPE-2 content, the tensile strength and impact strength of PUA decreased. This case might be the effect of branched chains of UPE-2. With the content of UPE-2 increasing, the content of branched chains increased, and the distance between the molecules increased, so the molecular interaction decreased, which resulted in decrease of PUA intensity. When the content of UPE-2 increased to



**Figure 2** IR spectra of samples. 1, UPE-1, HEMA and IPDI mixture; 2, urethane-acrylate macromonomer; 3, PUA.



**TABLE III**  
Effect of the Content of Unsaturated Polyester (UPE) on  
Mechanical Properties of PUA

Samples	Tensile Strength (MPa)	Impact Strength (kJ/m <sup>2</sup> )	Hardness (HRR)	Transparence (%)
PUA-0	15.41	0.41	124.5	92.5
PUA-1	15.16	1.16	122.0	91.9
PUA-2	15.34	1.18	124.9	92.0
PUA-3	19.80	5.66	128.0	91.2
PUA-4	26.58	1.87	125.2	92.3
PUA-5	23.75	1.13	124.9	91.9
PUA-6	21.14	0.98	122.4	90.9
PUA-7	20.27	0.73	125.3	92.5
PUA-8	11.24	0.47	126.6	90.1

0.04 mol, PUA intensities greatly reduced for the excessive crosslinking.

In this case, the increase in tensile strength could also be attributed to the increased intermolecular cohesive interaction through polar urethane linkages. The concentration of the polar urethane linkages increased with the diol concentration increasing, which can be explained that the concentration of the ester groups increased on the macromonomer chain.<sup>29</sup> An ester group develops an intermolecular force of 3.9 kcal/mol, while a  $-\text{CH}_2-$  group, only 0.68 kcal/mol.<sup>31</sup>

Mechanical-properties analyses evidenced the extent of the supermolecular modifications of PUA as a function of their structural modifications. The greater amount of hard segment would normally lead to the higher stress, and the lower elongations. Reverse effects also occur with more and longer soft segments.

Adding different types and content of UPE, the hardness of the material changed little comparing with PUA-0. However, PUA hardness was higher than polymethyl methacrylate (PMMA), thus, PUA would have more wide application than PMMA in functional materials.

### Optical properties

The optical properties of PUA are shown in Table III. The transmittances of PUA films based on UPE-1 and UPE-2 were about 90%, which indicated that the normalized transparency of all PUA films was excellent and similar to PMMA. The excellent transparency of PUA can be related to its structure. Polyurethane was composed of the soft chain and the hard chain. The soft chain consisted of polydiol, and the hard chain consisted of diisocyanate. The soft chain was difficult to crystallize, meanwhile, its steric hindrance was large and hydrogen bonds density of the hard chain was low. Therefore, PUA was not easy to crystallize and could be behaved as transparent polymers.

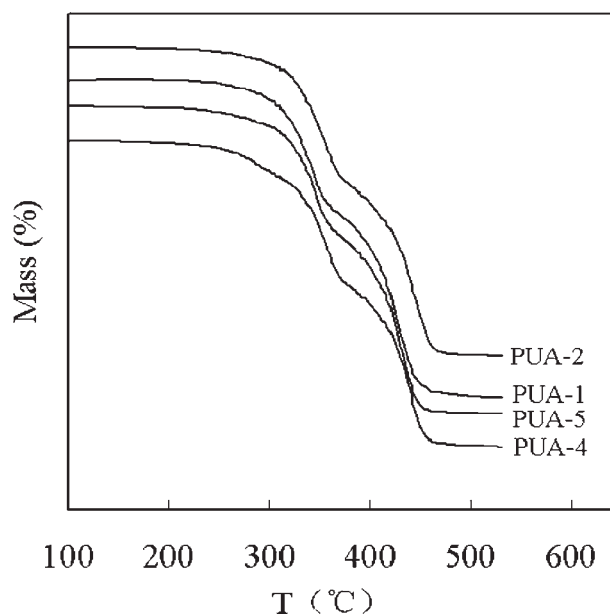
### Thermogravimetric studies

Thermal decomposition patterns of the PUA were determined by TG. Typical thermograms of different PUA are presented in Figure 3. The decomposition patterns for PUA showed almost the same decomposition trend and all the curves displayed two-step decomposition processes, where the procedural decomposition temperatures can be well defined. As indicated, overall thermal stability of the polyurethane system was slightly affected by the incorporation of polyols.

### CONCLUSIONS

Novel PUAs have been synthesized. The effects of soft segment types on their physical and thermal properties have been investigated.

The excellent mechanical properties and the low temperature performance of the polyurethane



**Figure 3** TG curves of PUAs.

systems could be attained by the incorporation of UPE grafts through the macromonomer technique. The tensile strength and impact strength of PUAs increased adding the UPE component. The transparency of all the PUA films was excellent and similar to PMMA. According to thermograms, the thermostability of the polyurethane system was slightly affected by the incorporation of polyols. The novel PUA may be used as optical material because of good thermal, mechanical and optical properties.

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