

# Synthesis and Properties of Graft Copolymer Derived from Polyurethane and Dihydroxyacrylate of Bisphenol A

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**ABSTRACT:** In this investigation, polyurethane was grafted with dihydroxyacrylate of bisphenol A, in basic medium, at 80°C. The grafting process was studied using an acrylate–urethane model compound. The grafting degree of polyurethane with dihydroxyacrylate of bisphenol A was 9% by weight. An alkylation mechanism of the synthesis of the graft copolymer was suggested. The addition of the acrylic double bond to the NH–urethane structures takes place in the first stage, and the reaction can be continued as a transposition in the *ortho* position of the aromatic ring in the second stage. The synthesized graft copolymer was crosslinked at 140°C in the presence of pyridine. The crosslinked copolymer shows high mechanical properties as compared to polyurethane, as well as an improvement of polyurethane's thermal stability. The solubility parameter of the synthesized crosslinked copolymer was estimated to have a value of 11.57 (cal/mol)<sup>1/2</sup>. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1802–1813, 2001

**Key words:** polyurethane; dihydroxyacrylate; alkylation; graft copolymer; mechanical properties

## INTRODUCTION

Thermoplastic polyurethane (PU) possess widely variable applications, being used as a widespread commercial product with extraordinary processability and good mechanical properties.<sup>1</sup> There is a large number of PUs varying in structure, in composition, and in properties.<sup>2</sup> Presently, a growing interest is being given to the interpenetrating PU networks with various glassy polymers.<sup>3–8</sup> Usually, these networks exhibit better mechanical and thermal properties than that of their individual networks. The same importance is accorded to the bloc,<sup>9</sup> graft,<sup>10</sup> and AB cross-linked<sup>11</sup> PU copolymers.

Graft copolymers of PU with vinyl monomers have been synthesized and characterized.<sup>12–14</sup>

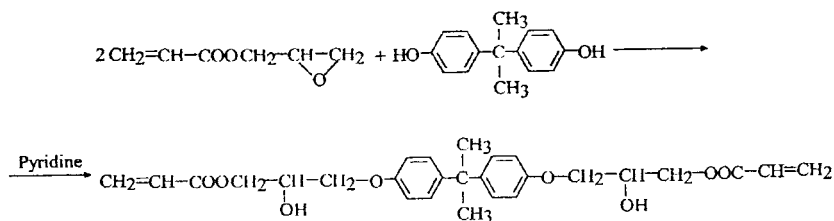
The incorporation of pendent reactive groups on the PU chain provides an approach to subsequent crosslinking to improve the PU chemical and mechanical properties.

In a previous article,<sup>15</sup> we reported the results from an investigation on the synthesis and characterization of some sequential semi-interpenetrating polymer networks based on a crosslinked polyhydroxyacrylate resin of bisphenol A and a linear PU. There was improvement of the PU mechanical properties by incorporation of polyhydroxyacrylate resin, as well as an increase of the PU thermal stability. In this article, PU was grafted with dihydroxyacrylate of bisphenol A (DHABA). The grafting process was evidenced using an acrylate–urethane (A–U) model compound, which was synthesized in our laboratory. The PU–DHABA graft copolymer was crosslinked at 140°C in the presence of pyridine and characterized regarding its mechanical, swelling, and thermal properties.

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Scheme 1 Synthesis of DHABA.

## EXPERIMENTAL

### Synthesis of DHABA

DHABA resin was obtained by an addition reaction of glycidyl acrylate to bisphenol A in the presence of pyridine. The synthesis was carried out in a 500-mL round-bottom flask, fitted with a stirrer, reflux condenser, heating system, thermometer, and oil bath, starting from 114 g bisphenol A, 128.13 g glycidyl acrylate, 6.3 g pyridine, used as catalyst, and 0.74 g hydroquinone, used as thermal polymerization inhibitor. The mixture was stirred at 100°C for 24 h, and the obtained product was washed several times with distilled water, filtered off, and dried in a vacuum at 60°C for 10 h. The yield varied between 80 and 85% by weight.

### Synthesis of PU

The PU polymer used in this investigation was synthesized by fusion condensation of adipic acid, ethylene glycol, and diethylene glycol (1 : 0.5 : 0.6 molar ratio) with 4,4'-diphenylmethane diisocyanate, as previously reported.<sup>16</sup>

### Synthesis of A-U Model Compound

An A-U model compound used to study the grafting reaction of PU with DHABA was synthesized starting from  $\beta$ -hydroxyethylacrylate in reaction with phenyl isocyanate (mol/mol) in anhydrous dimethylformamide (DMF) at 30°C for 12 h. The extent of the reaction was measured using the

band at 2260  $\text{cm}^{-1}$  in infrared spectroscopy (IR), which is specific to the NCO group.

### Synthesis of PU-DHABA Graft Copolymer

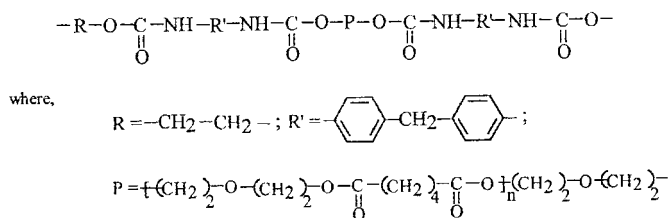
The PU-DHABA graft copolymer was synthesized in basic medium, starting from 30 g PU dissolved in 125 mL fresh distilled DMF. The obtained solution was treated with 9 g DHABA, in the presence of pyridine (pyridine/DHABA molar ratio between 0.678 and 3.402) and hydroquinone (0.1% by weight against DHABA). The mixture was stirred at 60°C for 4 h and continued at 80°C for 1 h to complete the grafting process. The crude final product was purified by successive precipitations from DMF solutions with distilled water, filtered off several times, washed with acetone, and dried in a vacuum at 80°C for 2 h. The unreacted DHABA was removed by extraction with acetone (time: 10 h) using a Soxhlet apparatus.

### Preparation of PU-DHABA Crosslinked Graft Copolymer

The synthesized PU-DHABA graft copolymer was dissolved in DMF. The obtained solution was cast as a film on a glass slides using a doctor-bleading. The slides were heated in an oven at 140°C for 3 h. The traces of solvent were completely removed, and the films, cooled at room temperature, were detached from the glass slides as a crosslinked graft copolymer.

### Characterization

The IR spectrum of the PU-DHABA crosslinked copolymer was recorded on an M 80 Specord spec-



Scheme 2 Structure of PU.



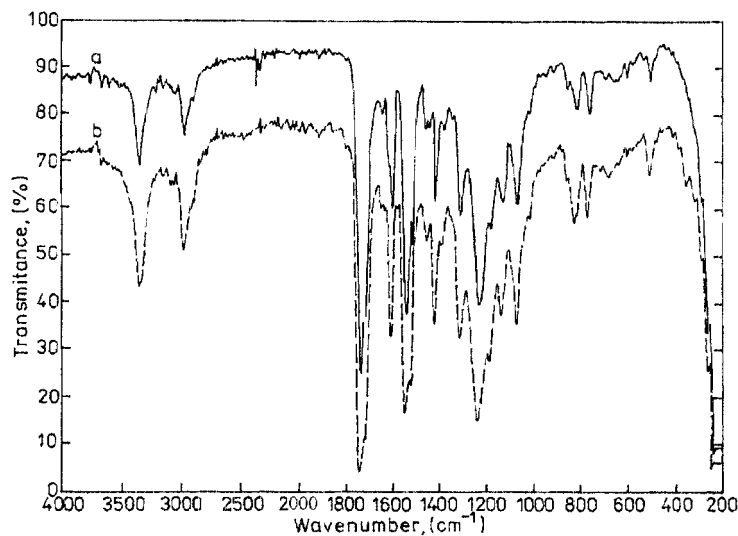


Figure 1 IR spectra (a) of PU-DHABA crosslinked graft copolymer and (b) of PU.

IR spectrum of the synthesized polymer. The  $^1\text{H-NMR}$  spectrum of the A-U polymer, recorded in comparison with the  $^1\text{H-NMR}$  spectrum of the A-U model compound (Fig. 3), evidences the disappearance of the multiplet from 5.9–6.3 ppm, which is characteristic to the double bond.

The data obtained by both IR and  $^1\text{H-NMR}$  techniques in the case of the A-U polymer led us to propose an alkylation mechanism for the polymerization process. In the first stage, the addition of the acrylic double bond to the NH—urethane structures takes place, and the reaction can be

continued as a transposition in the *ortho* or *para* position of the aromatic ring, in the second stage, with formation of an aminobenzoate structure as shown in Scheme 4.

Taking into consideration the results obtained for polymerization of the A-U model compound, the synthesis mechanism of the PU-DHABA graft crosslinked copolymer is proposed in Scheme 5.

The grafting degree (GD) of the synthesized PU-DHABA graft copolymer was calculated using eq. (1):

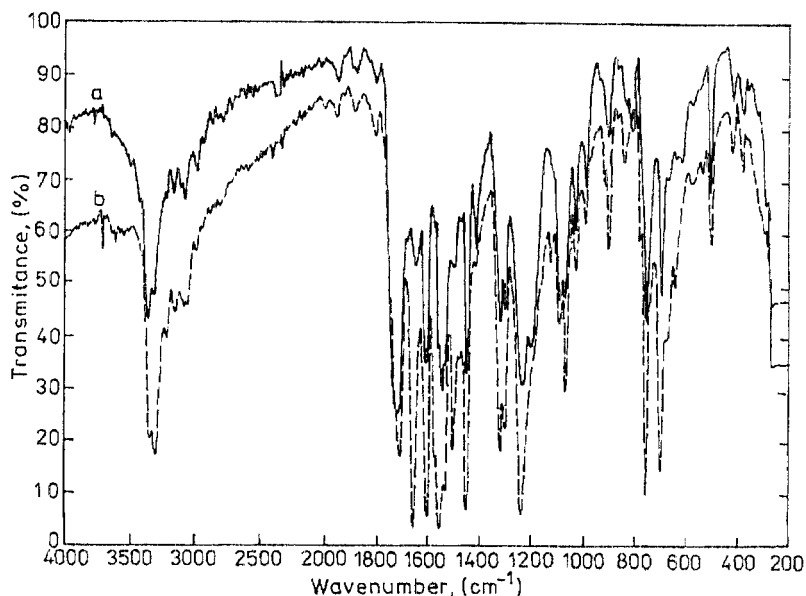
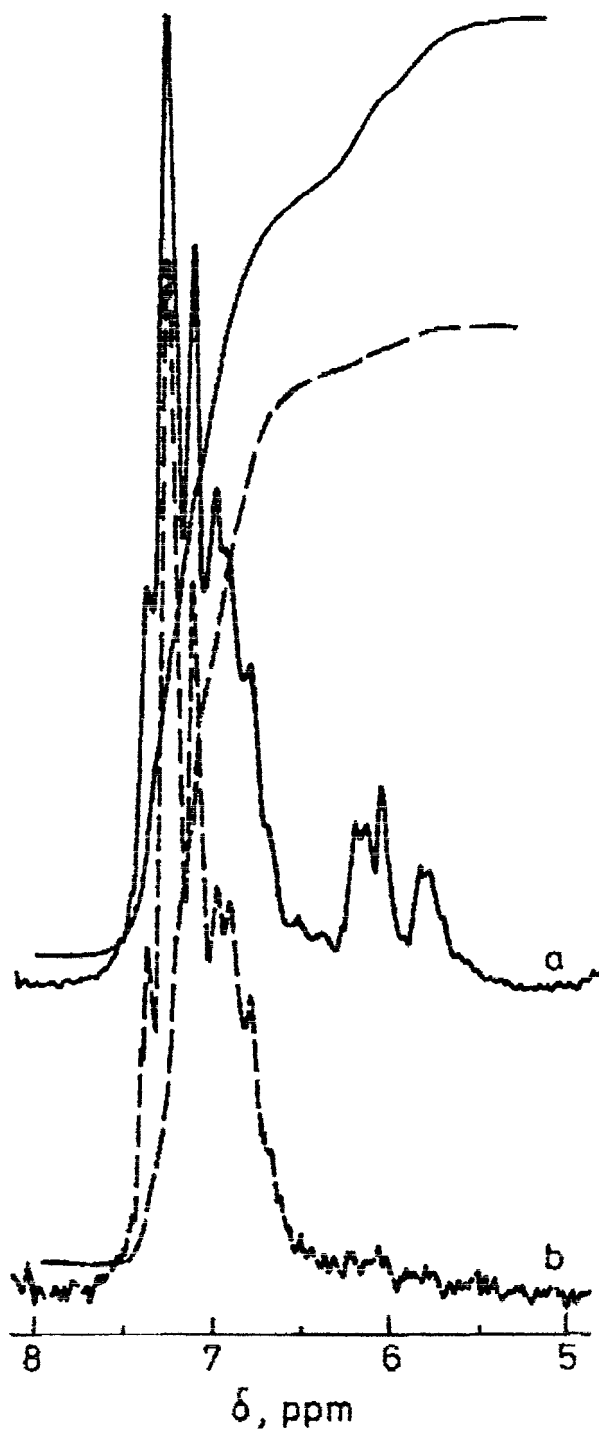


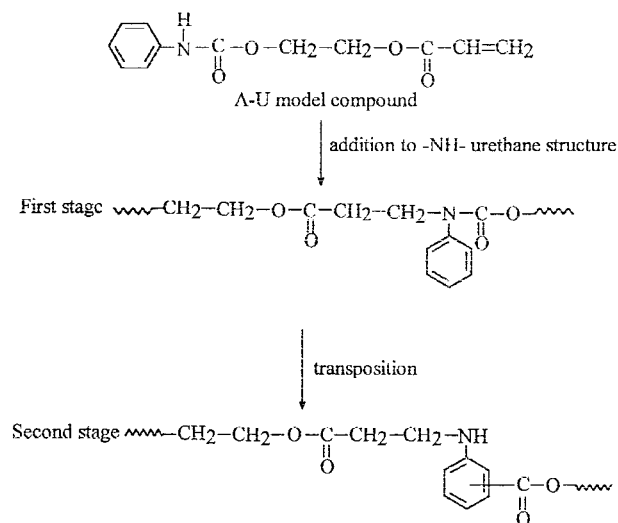
Figure 2 IR spectra (a) of A-U model compound and (b) of A-U polymer.



**Figure 3**  $^1\text{H-NMR}$  (a) of A-U model compound and (b) of A-U polymer.

$$\% \text{ GD} = \frac{W_G - W_{\text{PU}}}{W_G} \cdot 100 \quad (1)$$

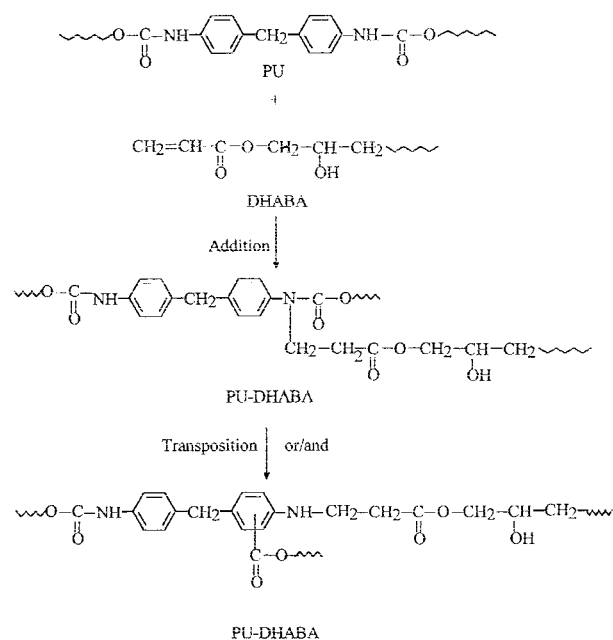
where  $W_G$  is the mass of the graft polymer (g), and  $W_{\text{PU}}$ , the mass of PU (g) subjected to the



**Scheme 4** Poly(acrylate-aminobenzoate).

grafting process. The GD of PU with DHABA was 9% by weight.

The dependence of the GD percentage on both the temperature and the catalyst amount is shown in Figures 4 and 5, respectively. As can be seen, the increase of temperature and of pyridine concentration had as a result an increase of the rate of grafting. At  $80^\circ\text{C}$ , the maximum % GD was reached in 12 h in the presence of a pyridine/DHABA molar ratio around 3.4.



**Scheme 5** Synthesis of PU-DHABA crosslinked graft copolymer.

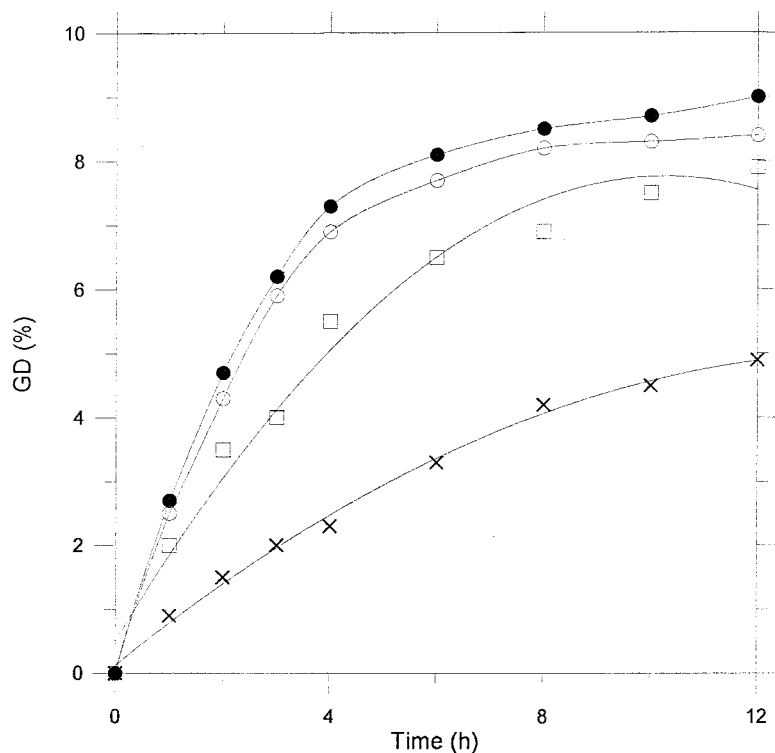


Figure 4 Variation of GD with temperature: (●) 80°C; (○) 70°C; (□) 60°C; (X) 50°C.

### Characterization of PU–DHABA Crosslinked Graft Copolymer

#### Physicomechanical Analysis

The PU–DHABA crosslinked graft copolymer was analyzed regarding its physicomechanical properties. Figure 6 shows the experimental curves obtained by plotting the stress against the strain for the synthesized copolymer in comparison with the curves recorded for PU, as well as for a mixture constituted of PU and 9% DHABA by weight, respectively. Table I lists some of the main physicomechanical properties of the systems mentioned above.

The stress–strain curve in Figure 6, recorded for the PU–DHABA crosslinked graft copolymer, shows a special behavior as against the curves recorded for PU, as well as for the PU–DHABA mixture. Moreover, from Table I, the crosslinked graft copolymer shows, as compared to PU, a high increase of the initial elasticity modulus (57-fold), of the elongation at break (about threefold), the elastic resilience (twofold), and of the resistance to the limit of elasticity (fourfold). Simultaneously, the elongation at break decreases (twofold). These data proved that the synthesized crosslinked graft copolymer was crosslinked by

the chemical bonds as well as by the hydrogen bonds.

#### Swelling Measurements

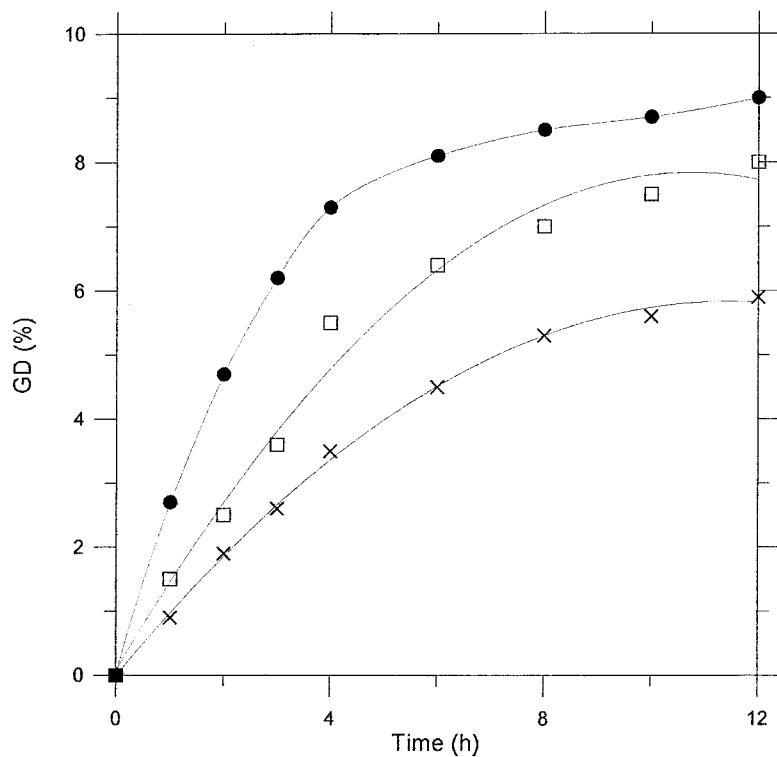
The solubility parameter of the PU–DHABA crosslinked graft copolymer was evaluated by swelling measurements. The swelling procedure is based on an evaluation of the maximum in swelling, using a series of solvents of varying and known solubility parameters. The solvents used in this study with their solubility parameters ( $\delta_s$ ) and other characteristics, namely, molecular weight ( $M$ ), density ( $d_s$ ) and molar volume ( $V_s$ ) are given in Table II. The solubility parameters of the solvents were taken from the literature.

The percentage swelling was calculated by the gravimetric method according to eq. (2):

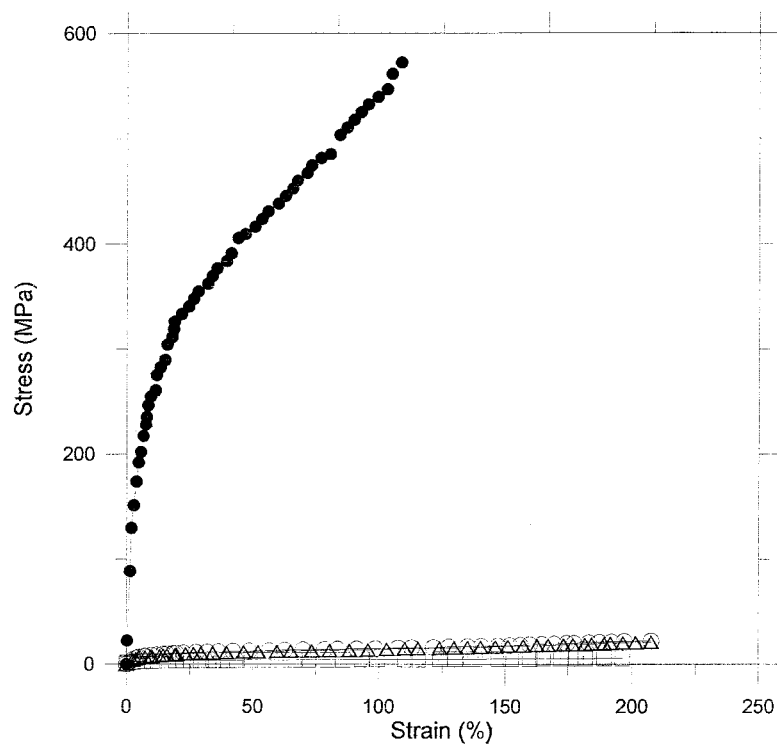
$$Q (\%) = \frac{(W_s - W_0)}{W_0} \times 100 \quad (2)$$

where  $Q$  is the swelling coefficient;  $W_s$ , the weight of the swollen film; and  $W_0$ , the weight of the dry film after swelling.

The relation  $Q$ , determined for PU and for the DHABA crosslinked graft copolymer, versus the



**Figure 5** Variation of GD with the quantity of the catalyst. Pyridine/DHABA (mol/mol): (●) 3.402; (□) 1.701; and (X) 0.678.



**Figure 6** Stress versus strain for (○) PU, (△) PU + 9% DHABA (w/w), (□) PU + 9% DHABA (w/w) mixture, cured at 140°C for 3 h, and (●) PU grafted with 9% DHABA (w/w), cured at 140°C for 3 h.



**Table I Physicomechanical Properties of the Synthesized PU–DHABA Crosslinked Graft Copolymer in Comparison with Those of PU and PU + 9% DHABA Mixture (w/w) Cured at 140°C for 3 h**

Sample	Initial Elasticity Modulus (MPa)	Elongation at Break (%)	Resistance to Break (MPa)	Elastic Resilience (%)	Resistance to the Limit of Elasticity (MPa)
PU–DHABA graft copolymer	68.5	103.3	127.9	33.5	83.8
PU + 9% DHABA mixture (w/w)	1.5	252.3	48.9	15.9	24.0
PU	1.2	212.6	44.5	17.4	20.1

solubility parameters of various solvents is shown in Figure 7. As can be seen, the PU–DHABA crosslinked graft copolymer is insoluble in the solvents listed in Table II, while PU is completely soluble in solvents with  $\delta_s$  around 10.

Starting from the suggestion of Gee,<sup>21</sup> namely, that the maximum swelling occurs when there is an equality between  $\delta_s$  of the solvent and  $\delta_s$  of the polymer, the curves recorded in Figure 7 for the synthesized copolymer were approximated using a regression equation of order 2, as follows:

$$Q (\%) = -5777.85 + 1065 \times \delta_s - 48.89 \cdot \delta_s^2 \quad (3)$$

Using eq. (3), a solubility parameter was evaluated for the PU–DHABA graft copolymer, namely,  $\delta_{\text{PU–DHABA}} = 11.61 \text{ (cal/mol)}^{1/2}$ . The  $\delta_s$

value of the synthesized insoluble copolymer was also evaluated using the value of the swelling coefficient  $Q$ , which, this time, was calculated using eq. (4):

$$Q = \frac{W_s - W_0}{W_0} \frac{1}{d} \quad (4)$$

where  $Q$ ,  $W_s$ , and  $W_0$ , were explained in eq. (2) and  $d$  is the copolymer density ( $\text{g/cm}^3$ ). The  $d$  value, measured by the picnometric method, was  $0.849 \text{ g/cm}^3$ .

By plotting  $Q$  versus  $\delta_s$  of various solvents (Table II), a Gaussian curve was obtained (Fig. 8), whose maximum corresponds to  $Q = Q_{\text{max}} e^{-(\delta_s - \delta_c)^2} V_s$ . Here,  $Q_{\text{max}}$  is the maximum swelling coefficient;  $\delta_s$ ,

**Table II Some Characteristics of the Solvents Used in this Study**

Solvent	Molecular Weight (g)	$d_s$ ( $\text{g/cm}^3$ )	$V_s$ ( $\text{cm}^3$ )	$\delta_s$ ( $\text{cal/cm}^3$ ) <sup>1/2</sup>	References for $\delta_s$ Values
Acetone	58.08	0.7906	73.5	9.75	17
Acetic acid	60.05	1.0492	57.2	10.10	18
Aniline	93.13	1.022	91.1	10.48	17
Benzene	78.11	0.874	89.4	9.02	17
1,3-Butandiol	90.12	1.005	89.7	14.12	17
Chlorophorm	119.38	1.492	80.01	9.3	19
Dimethyl sulfoxide	78.13	1.1014	70.7	12.99	17
Dimethylformamide	73.09	0.944	77.4	12.1	19
Ethyl formate	74.08	0.9117	81.2	9.4	18
Methanol	32.04	0.7911	40.5	14.48	17
<i>n</i> -Butanol	74.12	0.810	91.5	11.4	18
<i>t</i> -Butanol	74.12	0.775	95.6	10.6	18
<i>n</i> -Hexanol	102.17	0.814	125.5	10.7	17
<i>n</i> -Propanol	60.09	0.804	74.7	11.9	18
Pyrrolidone	85.11	1.120	75.9	13.85	17
Nitrobenzene	123.11	1.196	102.9	10.0	18
Carbon tetrachloride	153.82	1.594	96.5	8.6	20
Toluene	94.14	0.865	108.8	8.9	20



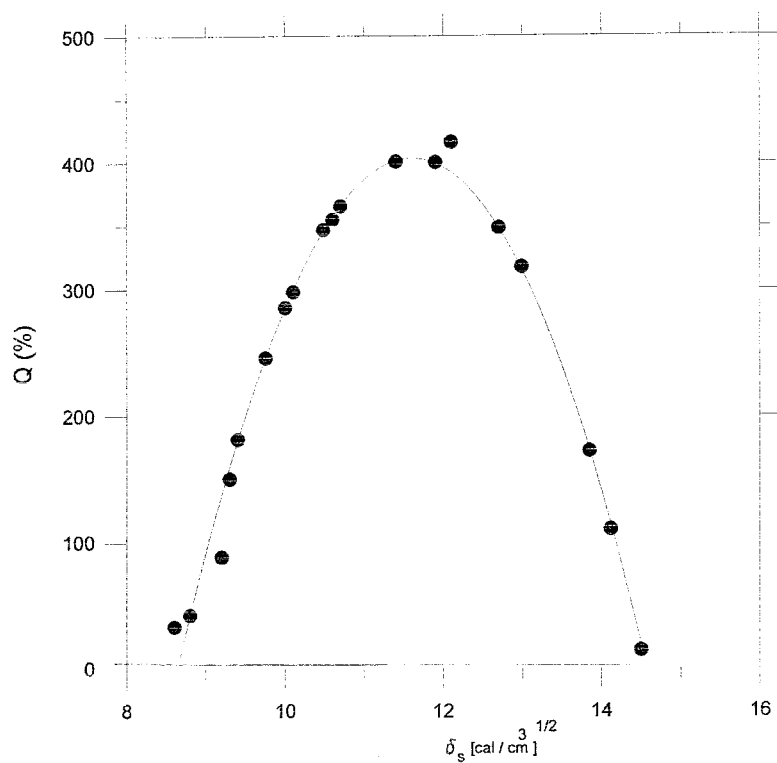


Figure 7 Variation of  $Q$  (%) with  $\delta_s$  of solvents.

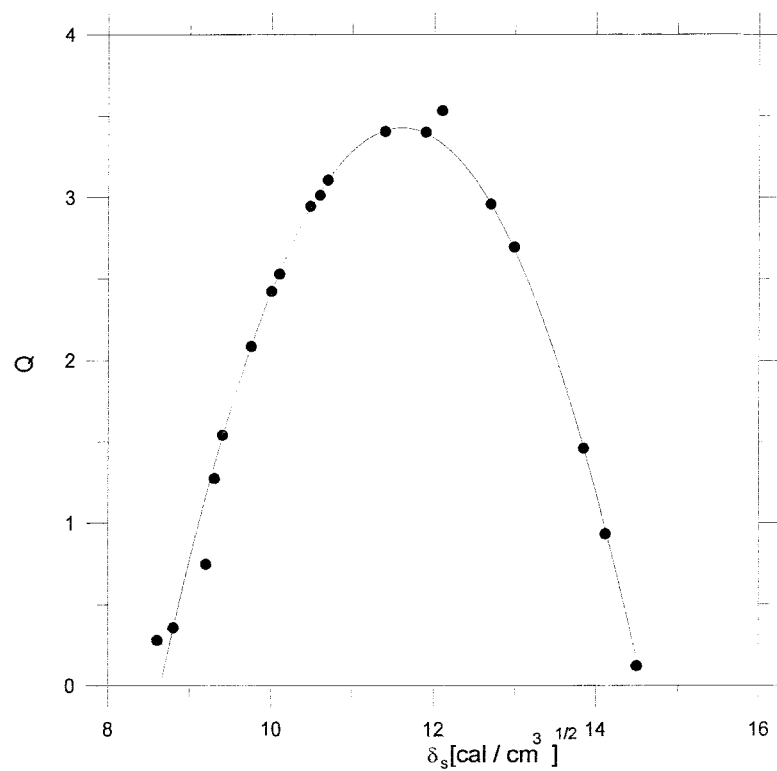
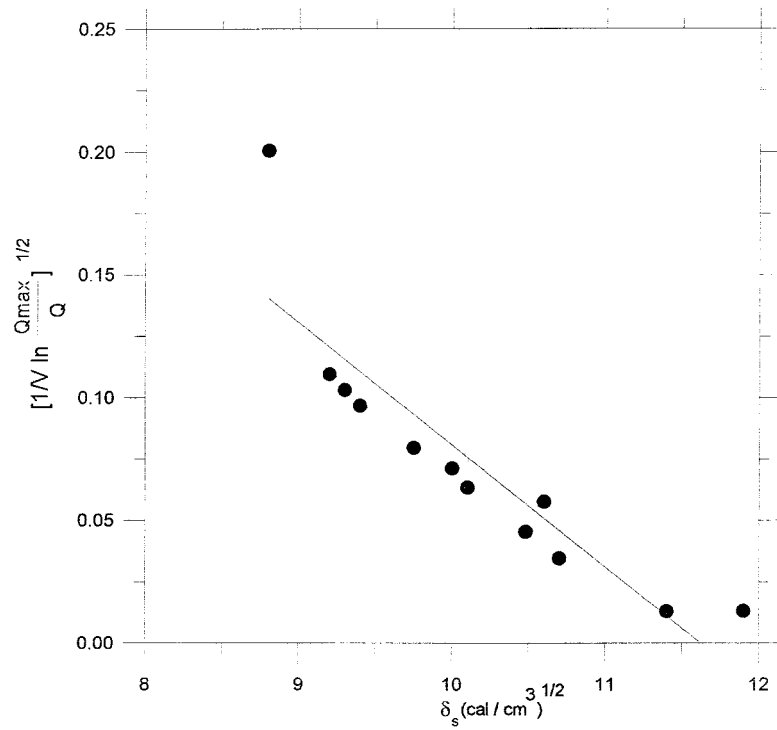
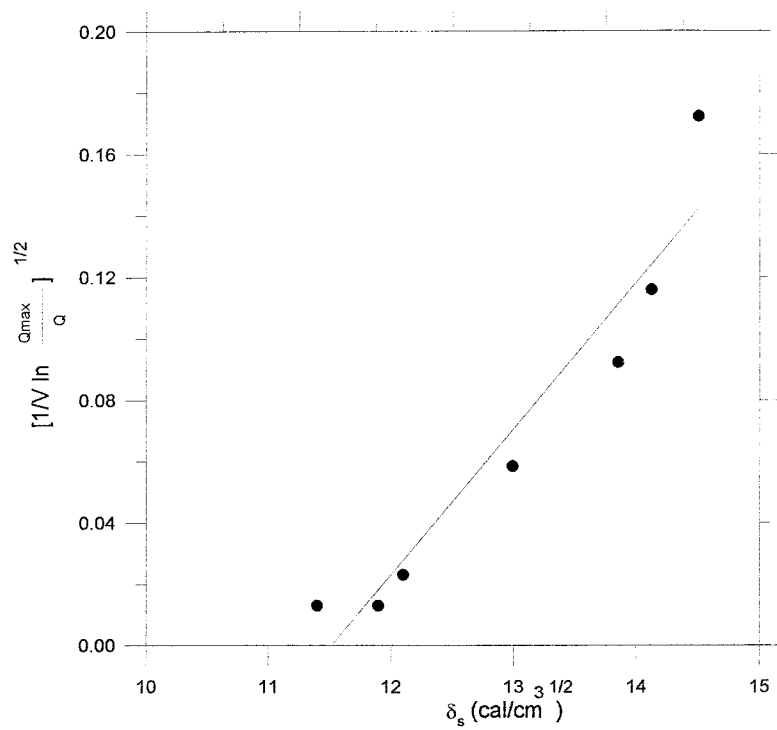


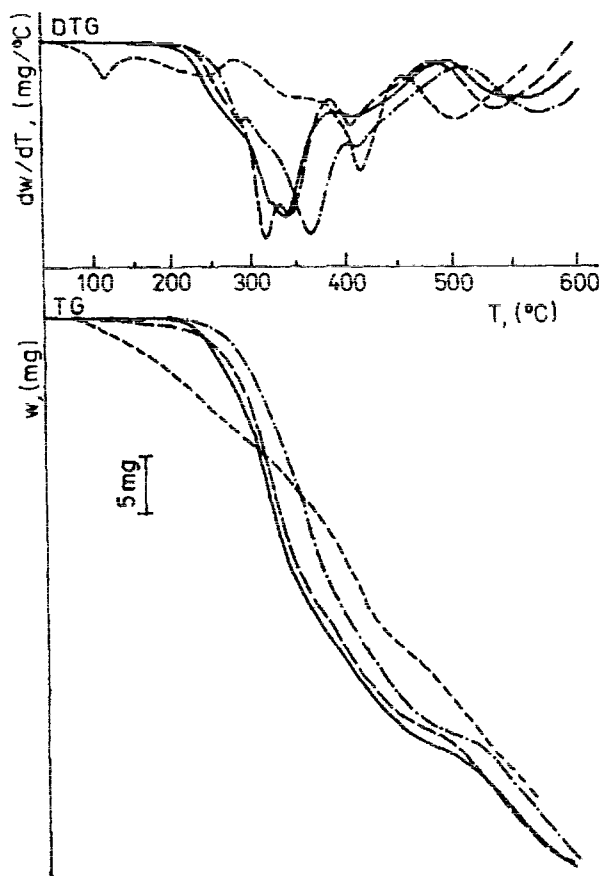
Figure 8 Variation of  $Q$  with  $\delta_s$  of solvents.



**Figure 9** Evaluation of  $\delta_s$  for PU–DHABA crosslinked graft copolymer, using solvents with  $\delta_s < 12$  (cal/cm<sup>3</sup>)<sup>1/2</sup>.



**Figure 10** Evaluation of  $\delta_s$  for PU–DHABA crosslinked graft copolymer, using solvents with  $\delta_s > 10$  (cal/cm<sup>3</sup>)<sup>1/2</sup>.



**Figure 11** TG and DTG curves of PU, DHABA raw materials, and PU-DHABA graft copolymers: (—) PU; (— — —) PU-DHABA graft copolymer; (- · - · -) PU-DHABA crosslinked graft copolymer; (----) DHABA.

the solubility parameter of the solvent;  $\delta_c$ , the solubility parameter of the copolymer; and  $V_s$ , the molar volume of the copolymer.

From the Gaussian curve recorded in Figure 8, a  $Q_{\max} = 4.748$  mol/g was obtained. The plot of the expression  $[(1/V_s)\ln(Q_{\max}/Q)]^{1/2}$  versus  $\delta_s$  of the tested solvents, which values were within the interval between 8 and 12  $(\text{cal}/\text{cm}^3)^{1/2}$  (Fig. 9) and 10–15  $(\text{cal}/\text{cm}^3)^{1/2}$  (Fig. 10), led to the straight lines having an intercept equal to  $\delta_c$  of the copolymer.

The values found for  $\delta_c$  using both Figure 9 [ $\delta_c = 11.62$   $(\text{cal}/\text{mol})^{1/2}$ ] and Figure 10 [ $\delta_c = 11.52$   $(\text{cal}/\text{mol})^{1/2}$ ] are in good concordance with the value found using eq. (3) [ $\delta_c = 11.61$   $(\text{cal}/\text{mol})^{1/2}$ ]. The value of  $\delta_c$  for the PU-DHABA crosslinked graft copolymer proposed by us is 11.57  $(\text{cal}/\text{mol})^{1/2}$ .

### Thermal Analysis

The value of the  $T_g$  evaluated for the PU-DHABA crosslinked graft copolymer was  $-18^\circ\text{C}$ , lower than the  $T_g$  of PU ( $-15^\circ\text{C}$ ).

The TG and DTG experiments show important differences in the thermal behavior of the synthesized PU-DHABA graft copolymers in comparison with the thermal decomposition of PU and of the DHABA resin. Visual inspection of the plots in Figure 10 show four to five decomposition stages for the studied polymers.

The first stage in the range between 100 and 250°C corresponds only to the DHABA resin, and it is probably due to the volatilization of undesirable components present in the starting resin and release of some small molecules. The decomposition of PU was discussed before.<sup>18</sup> The PU-DHABA copolymers decompose starting at about 250°C. A high rate of decomposition is recorded in the range between 280 and 450°C, with important weight losses (around 60–70%). The important conclusion regarding the thermal behavior of the PU-DHABA graft copolymer is that it decomposes after a complex mechanism, with the apparent thermal stability higher as compared with that of PU.

## CONCLUSIONS

In basic medium, the acrylic double bond from DHABA was added to the urethane group from PU with the formation of an alkylated urethane. This urethane can undergo a transposition reaction in the *ortho* position of the aromatic ring (or *para*, but not in the studied systems).

These investigations evidenced that PU grafted with DHABA shows an increase of its mechanical properties. Grafting results in an increase in the initial elasticity modulus, in the break resistance, in the elastic resilience, as well as in the resistance to the limit of elasticity. An improvement of the thermal stability was shown by the grafting process. The solubility parameters of the synthesized PU-DHABA crosslinked graft copolymer has a value placed between 11.52 and 11.62  $(\text{cal}/\text{mol})^{1/2}$ . The value of  $\delta_s$  proposed by us is 11.57  $(\text{cal}/\text{mol})^{1/2}$ .

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