

## PREPARATION AND CHARACTERIZATION OF FUNCTIONAL COPOLYURETHANE WITH MALEIMIDE GROUPS♦

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**Abstract:** Maleimide functionalized copolyurethanes were prepared by the reaction of a binary mixture of dibenzyl diisocyanate and 1-(3,5-diisocyanatophenyl)-1*H*-pyrrole-2,5-dione with a macrodiol (polyethylene-adipate glycol) using diethylene glycol and trimethylolpropane as chain extender and crosslinkers in toluene-dichloromethane solution. Structures of polymers were confirmed by IR and the properties were also studied by thermal and mechanical analysis, and physical methods (contact angle).

**Keywords:** *maleimide, copolyurethane, functional polyurethane*

### INTRODUCTION

Polyurethanes are one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in

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walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interior [1]. Interest in functional polymers is steadily increasing because of their diverse uses as polymeric reagents and catalysts [2 – 4], polymer drugs [5 – 6], etc.

Incorporation of maleimide groups to polymers exhibited effectiveness on increase of crosslinking density, enhancement of thermal stability, and improved of flame retardance [7]. *N*-Substituted polyamides [8] and polymethacrylates [9] with dimethylmaleimide groups has used as photopolymers from microsystem applications. About 20 years ago Mikroyannidis reported on his attempts to prepare polyketones containing maleimide group as functionality [10]. Recently, Liu and coworkers reported multifunctional maleimide oligomers [11], polyamides, polyaminoaspartimides [12] and crosslinked epoxy materials exhibiting thermal remendability and removability [13] from multifunctional maleimide and furan compounds.

In this work, new functional copolyurethanes having maleimide groups were prepared by cycloaddition of a binary mixture of dibenzyl diisocyanate and 1-(3,5-diisocyanatophenyl)-1*H*-pyrrole-2,5-dione with a mixture of polyethyleneadipate glycol (PEGA-2000), diethylene glycol and trimethylolpropane (TMP).

## **EXPERIMENTAL**

### **Measurements**

The FT-IR spectra were recorded on a Bruker Vertex 70 spectrophotometer. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were run on a Bruker 400 MHz spectrometer using DMSO-d<sub>6</sub> as solvent and tetramethylsilane as an internal standard. Melting and softening points were measured with a Gallenkamp hot-block melting point apparatus. Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein Germany. Measurements were run at an extension rate of 46 mm/min, at room temperature 23 °C. All samples were measured three times and the averages were obtained. Thermogravimetric analysis (TGA) was performed under nitrogen flow (15 cm<sup>3</sup>.min<sup>-1</sup>) at a heating rate of 20 °C/min from 25 °C to 500 °C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 4 – 6 mg. Dynamic contact angles were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50 x 8 mm and rate of immersion-emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of 3 contact angle measurements of samples. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10 °C/min, in nitrogen.

### **Reagents and materials**

Maleic anhydride (Aldrich), 5-aminoisophthalic acid (Aldrich), sodium azide (Aldrich), dichloromethane, dibutyltin dilaurate (Aldrich), 4,4'-dibenzylidiisocyanate (DBDI, local mark), trimethylolpropane (TMP, Aldrich), toluene, polyethyleneadipate glycol

(PEGA-2000) with a molar weight of 2000 (Baxenden), diethylene glycol (DEG, Aldrich) were used as received.

**5-Maleimidoisophthalic acid (1)** was prepared from 5-aminoisophthalic acid and maleic anhydride according to the reported method [10], mp = 317 – 320 °C.

**5-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)isophthaloyl dichloride (2)** was prepared by the reaction of **1** with thionyl chloride in 1,2-dichloroethane (DCE). The product was separated by precipitation with *n*-pentane and then filtered. The white solid was recrystallized from ligroin obtaining in 85% yield, mp = 115 – 118 °C [112 - 115°C, lit.10].

**5-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)isophthaloyl diazide (3)** was prepared by interfacial condensation of compound **2** in methylene chloride with an excess of sodium azide in water at 0 – 5 °C for 5 hours. The organic layer was separated and washed two times with 150 mL water, dried over anhydrous magnesium sulfate. The compound **3** was obtained by the evaporation of DCE and resulting in 83% yield, mp = 76 – 79 °C (from ethanol).

FT-IR (KBr, cm<sup>-1</sup>): 3100, 2170, 1740, 1700, 1605, 1490, 1385, 1210, 1160, 840 and 620.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS), δ (ppm): 8.61 (s, 1H, aromatic proton), 8.29 (s, 2H, aromatic protons), 6.94 (s, 2H, maleimide protons).

**1-(3,5-diisocyanatophenyl)-1H-pyrrole-2,5-dione (4)** was prepared by Curtius decomposition of monomer **3** in dry toluene, at reflux, for 5 hours. The product precipitated with *n*-hexane and resulting in 85% yield, mp = 119 – 120 °C.

FT-IR (KBr, cm<sup>-1</sup>): 3100, 2260, 1728, 1600, 1452, 1377, 1148, 840 and 698.

Analysis calculated for C<sub>12</sub>H<sub>5</sub>N<sub>3</sub>O<sub>4</sub> (255.172), %: C, 56.48; H, 1.97; N, 16.46. Found: C, 56.42; H, 1.83; N, 16.08.

### General procedure for the preparation of copolyurethanes C1-C5

*Component I:* PEGA-2000 (50g, 25 mmol) and TMP (0.9 g, 9 mmol) were dehydrated at 120 °C for 4 hours in vacuum before use and then they were dissolved in methylene chloride (46 g). To this solution was added diethylene glycol (3.5 g, 33 mmol).

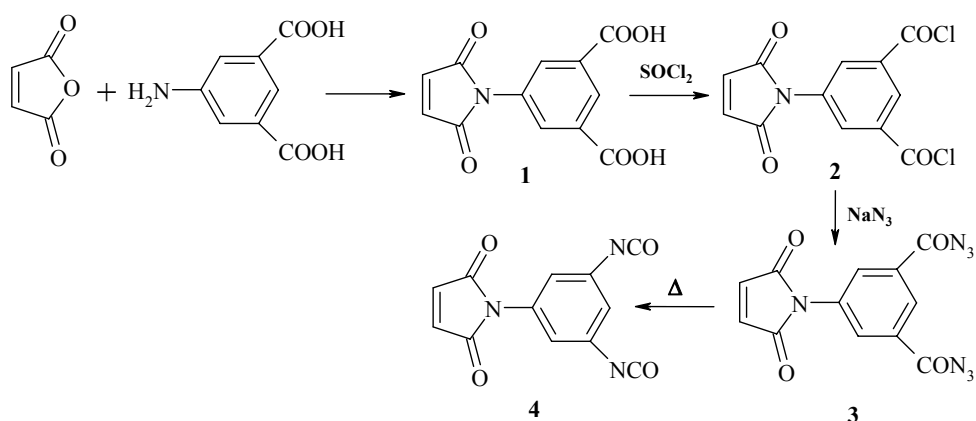
*Component II:* A mixture of DBDI and compound **4** in a molar ratio of 4.5:4.1, 5.5:3.1, 6.6:2, 7.5:1.1 and 8.6:0 was dissolved in a toluene-methylene chloride mixture (10 g), in a weight ratio of 1.8:8.2.

To a mixture of component I (10 g) and component II was added 5 drops of dibutyltin dilaurate as catalyst. The reaction mixture was stirred at room temperature for 2.5 – 3 hours. The polyurethane solution was degassed in vacuum and quickly transferred to a glass plate, using a doctor blade (e = 2 mm). The solvent was evaporated in atmosphere at room temperature for 7 days. The film was removed from the glass plate by soaking in cold water.

## RESULTS AND DISCUSSION

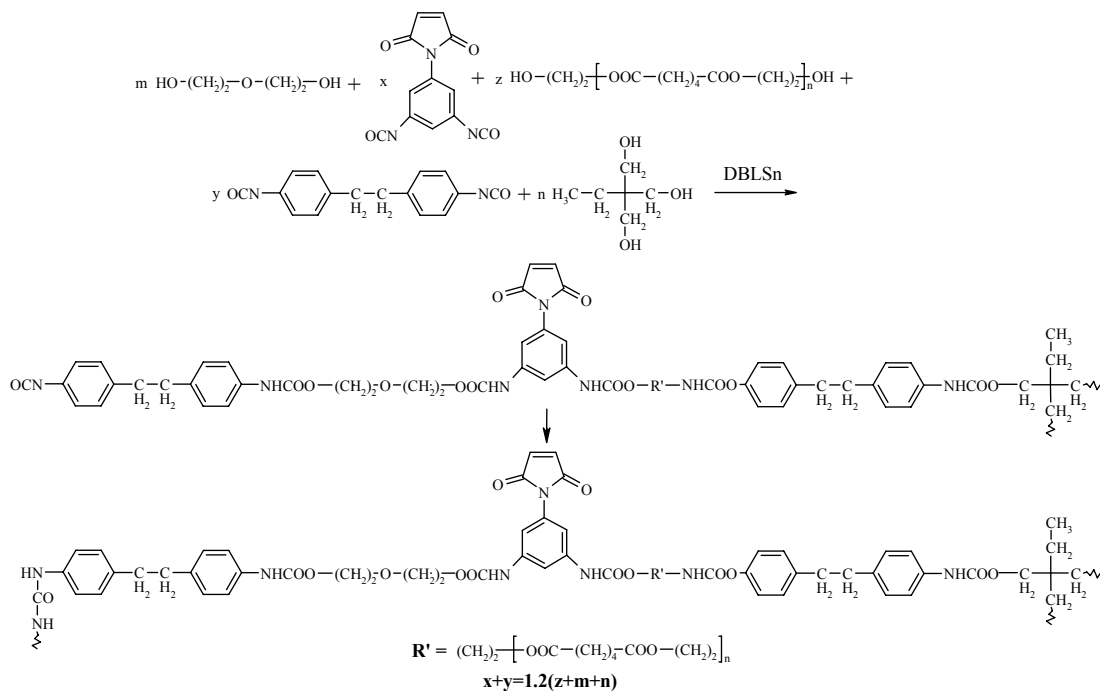
A new maleimide diisocyanate monomer **4** was prepared by Curtius decomposition of compound **3**. Functional maleimides were prepared by the reaction of an equimolecular mixture of maleic anhydride and 5-maleimidoisophthalic acid followed by the

transformation of functional group COOH in acid chloride, azide and isocyanate (Scheme 1). FT-IR,  $^1\text{H-NMR}$  and elemental analysis confirmed the obtained structures. FT-IR spectra of compounds **2** – **4** presented absorption bands at 1710-1720, 1385-1400, 1155-1165 and  $690\text{ cm}^{-1}$  (imide I-IV), 3100, 1605-1610 ( $\text{C}=\text{C}$  double bond of maleimide), 330-2800, 890, 2170 and 2270 corresponding to the functional groups COOH, COCl,  $\text{CON}_3$  and NCO, respectively. The copolyurethane varnishes C1-C5 were prepared by the reaction of two components, a hydroxyl-containing compound (PEGA-2000, diethyleneglycol and TMP) and a mixture of diisocyanates containing dibenzyl diisocyanate and monomer **4**, in the presence of dibutyltin dilaurate, by one-step polymerization process at the ratio  $\text{NCO}/\text{OH}=1.2$ .



Scheme 1

The possible reactions and structure of copolymers C1-C5 are presented in Scheme 2.



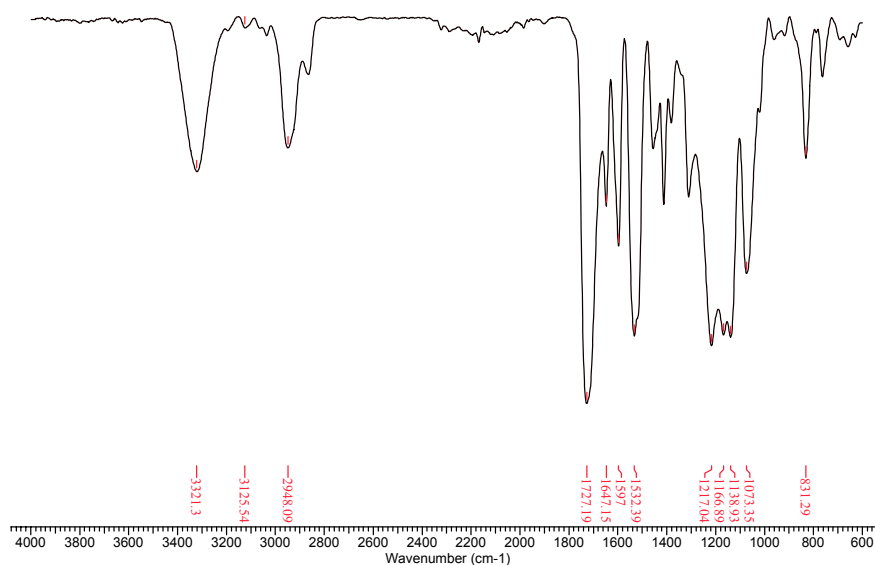
Scheme 2

The composition of copolyurethanes is presented in Table 1.

**Table 1.** Composition of copolyurethanes C1-C5

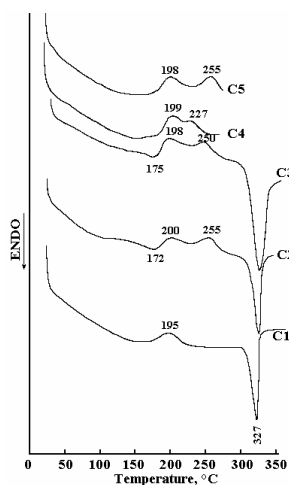
Copolymer	x	y	z	m	n
C1	0	8.6	2.5	0.9	3.3
C2	1.1	7.5	2.5	0.9	3.3
C3	2	6.6	2.5	0.9	3.3
C4	3.1	5.5	2.5	0.9	3.3
C5	4.1	4.5	2.5	0.9	3.3

A representative ATR-FT-IR spectrum of copolyurethane film C5 is shown in Figure 1 and exhibits a broad peak at about  $3340\text{ cm}^{-1}$  due to a combination of urethane NH and urea NH present in the polymer backbone. A strong broad peak was centered at  $1714\text{ cm}^{-1}$  related to the symmetrical stretching of carbonyl groups of urethane, ester and imide groups of polymer. At  $1645\text{ cm}^{-1}$  appeared the carbonyl groups of  $\text{-NH-CO-NH-}$  and at  $1532\text{ cm}^{-1}$  appeared a combination of C-N stretching and NH groups from urethane and urea units. The stretching vibration of C-O-C ester groups appeared as a doublet at  $1067$  and  $1217\text{ cm}^{-1}$ . The peaks corresponding to maleimide groups at  $3100$ ,  $1385$ ,  $1165$  and  $690\text{ cm}^{-1}$  exhibited lower intensity.

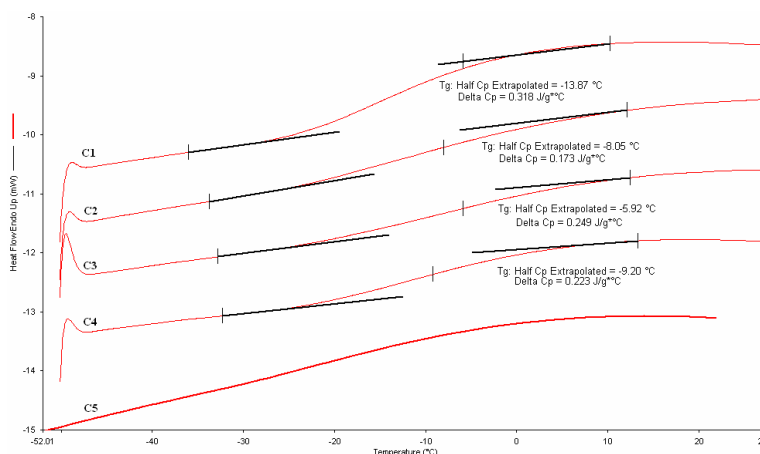


**Figure 1.** The IR spectrum of copolyurethane film C5

The DSC measurements of copolyurethane films are presented in Figure 2. The DSC curve of C1 without a maleimide shows two exothermic peaks centered at  $198$  and  $270\text{ }^{\circ}\text{C}$ , respectively, probably due to complete reaction of NCO groups in excess, and an endothermic peak corresponding to the melting of hard segments. The DSC curves of C2 – C5 present two exothermic peaks at  $198 - 199\text{ }^{\circ}\text{C}$  and  $227 - 255\text{ }^{\circ}\text{C}$  attributed to the complete polyaddition of NCO groups and cure reaction of maleimide groups, respectively, and an endothermic peak at  $323\text{ }^{\circ}\text{C}$ , corresponding to the melting of hard segments. The DSC curves showed a single inflection in the second run, at negative temperature, corresponding to the glass transition temperature of soft segment of copolyurethane that ranged between  $-14\text{ }^{\circ}\text{C}$  and  $-6\text{ }^{\circ}\text{C}$  (Figure 3).



**Figure 2.** The DSC curves of copolyurethane films



**Figure 3.** The DSC curves of copolyurethane films at second heating cycle

$T_g$ 's of soft segment increase with the maleimide content so that the copolyurethane C5 don't show  $T_g$  due to high crosslinking of maleimide groups (Scheme 3, way a).

The ATG curves of copolyurethanes C1 – C5 presented two peaks and two maxima decomposition temperatures ( $PDT_{max1}$  and  $PDT_{max2}$ ) corresponding to the two peaks. The first peak ( $PDT_{max1}$ ) appeared between 339 and 341 °C and is attributed to the depolymerization of the urethane bonds and soft segment decomposition, and the second peak appeared around 425 – 432 °C indicating the hard segment breaking (Table 2).

The polymer having 0% maleimide diisocyanate (C1) presented  $PDT_{max1}$  and  $PDT_{max2}$  values of 340 and 425 °C, respectively, and their corresponding weight losses of 12 and 60%, respectively. Polymers containing maleimide groups (C2 – C5) showed  $PDT_{max1}$  and  $PDT_{max2}$  values ranging between 339 – 341 °C and 426 – 432 °C, respectively and their corresponding weight losses between 12.5 – 16% and 38 – 48%, respectively. The different values of copolyurethanes C2 – C5 could be probably due to the higher thermal stability of the three-dimensional structure of cured maleimide groups.

**Table 2.** Thermal stability of cured films

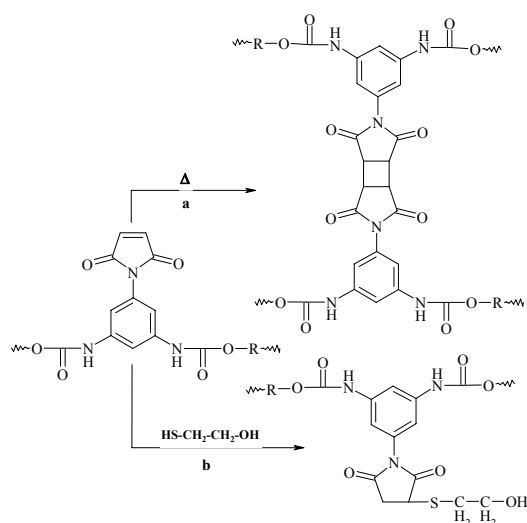
Sample	IDT <sup>a</sup> (°C)	Temperature (°C) for % weight loss <sup>b</sup>		$PDT_{max1}$ <sup>c</sup> (°C)	$PDT_{max2}$ <sup>c</sup> (°C)	$Y_c$ <sup>d</sup> (%)
		$T_5$	$T_{10}$			
C1	260	320	335	340	425	3
C2	260	319	332	340	436	4
C3	260	318	328	339	427	6
C4	265	321	327	341	430	8
C5	270	322	325	340	432	11

<sup>a</sup>Initial decomposition temperature.

<sup>c</sup>Maximum decomposition temperature of cured film.

<sup>b</sup>Temperature for 5 and 10 % weight loss.

<sup>d</sup>Char yield at 500°C.



Scheme 3

Table 3. Water contact angle of copolyurethane varnish films

Sample	Water contact angle			
	untreated films		treated films <sup>a</sup>	
	$\theta_{adv}$ (deg)	$\theta_{rec}$ (deg)	$\theta_{adv}$ (deg)	$\theta_{rec}$ (deg)
C1	96.56 ± 1.01	28.25 ± 0.79	96.00 ± 1.13	29.75 ± 0.69
C2	87.63 ± 1.08	39.42 ± 0.69	81.64 ± 1.01	39.45 ± 0.58
C4	83.18 ± 1.13	41.35 ± 0.53	78.16 ± 1.07	39.75 ± 0.63
C5	53.87 ± 1.08	45.67 ± 0.57	52.47 ± 1.03	37.74 ± 0.37
C5 crosslinked	88.52 ± 1.17	42.96 ± 0.87		

<sup>a</sup>Films were immersed into 10% solution of 2-mercaptoethanol in methanol, for 24 h at room temperature, then they were washed with methanol and dried.

Wettability could be estimated by the determination of the dynamic contact angle. Four samples were immersed and withdrawn into and out the liquid simultaneously measuring the force acting on the samples. The advancing and receding contact angles were determined from the obtained force curve. Advancing and receding contact angle measurements on the casting films from polyurethanes based on monomer 4/dibenzyl diisocyanate/PEGA could provide more information on the hydrophilicity of films and hence the wettability. The advancing contact angle decreases with the increase of the maleimidoisophthalic content (C1 – C5) and with the advance of Michael addition reaction of 2-mercaptoethanol to free maleimide groups (Table 3). The maleimide groups of copolyurethane films (C1 – C5) were modified by the thermal curing and polyaddition reaction of 2-mercaptoethanol (Scheme 3, way b).

## CONCLUSIONS

New maleimide-functionalized copolyurethane films were obtained. Mechanical and thermal properties of copolyurethane films increase with the maleimide content. Also, the copolyurethane films presented an improved hydrophilicity with the increasing of maleimide monomer.

### Acknowledgement

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