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Heterocyclic Poly(Bismaleimide)s. II. Synthesis and Characterization of New Poly(Ether-Bismaleimide)s Containing Parabanic Rings

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NOTES

HETEROCYCLIC POLY(BISMALEIMIDE)S. II. SYNTHESIS AND CHARACTERIZATION OF NEW POLY(ETHER-BISMALEIMIDE)S CONTAINING PARABANIC RINGS

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ABSTRACT

New poly(ether-bismaleimide)s containing parabanic rings were obtained by the nucleophilic substitution reactions of 1,3-bis(4-dichloromaleimido-phenyl)parabanic acid (4) with various bisphenols. The structures of the resulting polymers were confirmed by IR and elemental analysis. The polymers are soluble in aprotic dipolar solvents and showed lower thermal stability than other polymers without parabanic rings.

INTRODUCTION

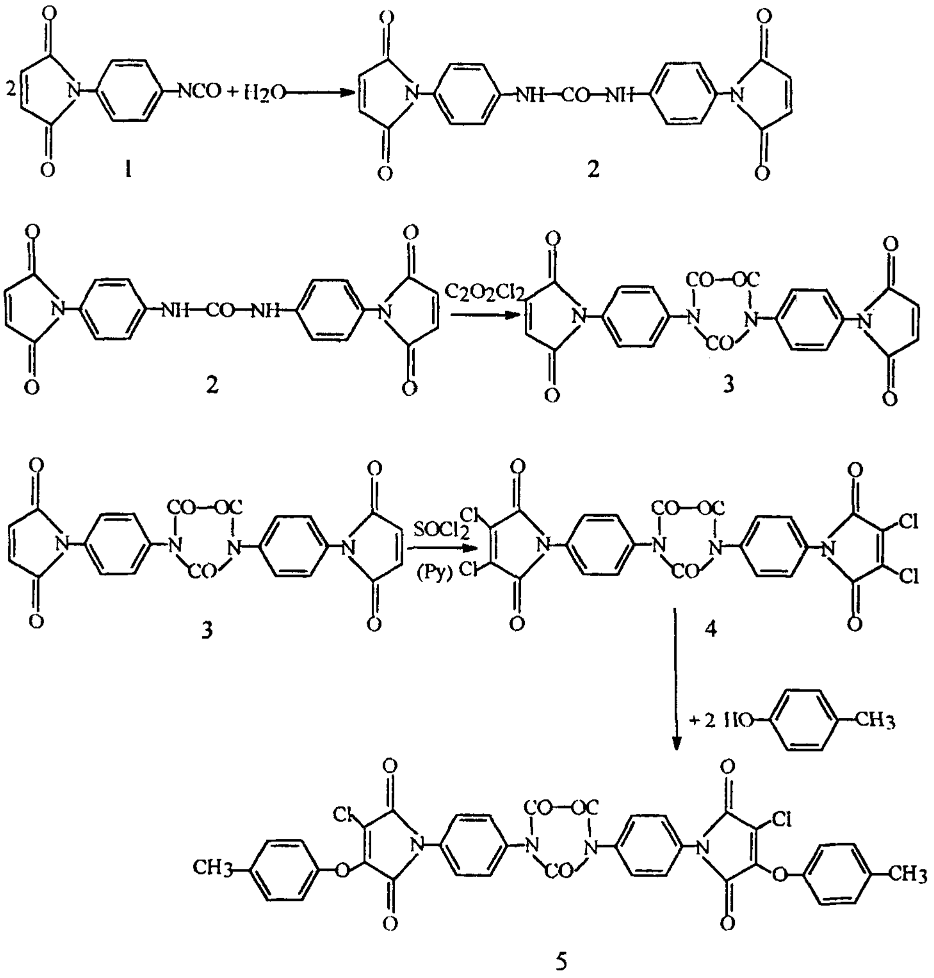
Nucleophilic substitution reactions have been used effectively in the synthesis of several classes of polymers. However, only scanty reports are available in the applications of such reactions to the displacement of chlorine in bis(dichloromaleimides). Relles *et al.* [1] reported, the preparation of poly(maleimide-ethers) by using phenols as nucleophil for the first time. In recent years, poly(chloromaleimide-ethers) [2, 3], poly-(maleimide-amines) [4, 5], and poly(maleimide-amine-ethers) [6], have been prepared by the reaction of bis(dichloromaleimides) (BDCMI) with bisphenols, diamines or tetramines, and p-aminophenol, respectively. The above-mentioned polymers possess good solubilities in aprotic dipolar solvents, little flame retardance [4], good electric properties [2], and are available for further curing reactions due to the presence of olefinic bonds in their structures [5]. In our previous papers [7, 8], poly(maleimide-ester-ethers) and poly(maleimide-amide-amines) were prepared by the reaction of N-(4-chlorocarbonylphenyl)-3,4-dichloro-maleimide and bisphenols with diamine, and their properties were discussed. Polymers containing parabanic rings such as polyurethanes, polyoxadiazolureas, polyimides, polyamides, polybarbiturates, polyhydrazides, polyoxadiazoles and polyureas [9-12], are known as higly thermally stable polymers with improved chemical resistance to organic solvents. Our previous work has been focused mainly on the synthesis and characterization of new poly(aminobismaleimides) containing parabanic rings [13]. The goal of the present paper is to describe the synthesis and characterization of new poly(ether-bismaleimide)s with parabanic rings.

EXPERIMENTAL

Inherent viscosities were measured in a Ubbelohde Suspended Level Viscometer, in DMSO at 30°C at a concentration of 0.5g/dL. The IR spectra were recorded on a Specord M80 Carl Zeiss, Jena Spectrophotometer using the KBr pellet technique. Proton NMR spectra were run on a Jeol 60 MHz NMR Spectrometer at 50°C in DMSO-d_6 using TMS, as the internal reference. Melting and softening points were determined by using a IOR MC1-type polarizing microscope equipped with a heating stage (magnification 150 X). Dynamic weight loss measurements were carried out on a F. Paulik Derivatograph in air, with a heating rate of 10°C/min. All degradation runs were performed using 50 mg sample size. Differential scanning calorimetryc (DSC) measurements were run on a Mettler TA Instrument DSC 12E, in nitrogen with a heating rate of 10/C°min, using a sample size of 5 mg. Polymers solubilities were determined for 12 common solvents at a concentration of 1% (w/v) at room temperature. The solvents studied were (in order of increasing of Hansen solubility parameter, (δ): cyclohexanone, methylene chloride, dioxane, pyridine, m-cresole, dimethyl acetamide (DMA), N-methyl-pyrrolidin-2-one (NMP), hexamethylphosphoramide (HMPA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, water.

Materials

2,5 Bis(4-hydroxybenzilidene)cyclopentanone (**6e**) was obtained as described [13] [mp 317-320(C; Ref. 13, 332°C]. N-Methyl-pyrrolidin-2-one (NMP),



Scheme 1

1,2-dichloroethane (DCE) were dried on P_2O_5 and freshly distilled before use. Thionyl chloride was also freshly distilled before use. Pyridine (Py), triethylamine (TEA), p-cresol, hydroquinone (**6a**), resorcinol (**6b**), bis(4-hydroxy-phenyl)-isopropylidene (**8c**) (Merck) and 4,4'-(hexafluoroisopropylidene)diphenol (**8d**) (Fluka) were used as received.The synthetic route for the monomer (**4**) and model compound (**5**) are shown in Scheme 1.

1,3 Bis(4-maleimidophenyl)parabanic Acid (3) was synthesized from 4-maleimidophenyl isocianate (**1**) through the N,N'-bis(4-maleimidophenylene) urea (**2**) [13].

*1,3 Bis(4-dichloromaleimidophenyl)parabanic Acid **(4)***

A 250 mL three-necked flask equipped with a mechanical stirrer, reflux condenser and dropped funnel was charged with a 9.127 g (0.02 mol) of **3** in 140 mL thionyl chloride. After cooling at 0°C on ice bath, 6.6 mL of dry Py were dropped in over 15 minutes and stirring was maintained for 4 hours at 0°C. After the addition of Py, the initial slurry was converted to a clear yellow solution. The ice bath was removed, then the system was heated at 0°C, at room temperature for 2 hours and at reflux for 2 hours. After the excess of thionyl chloride was removed under vacuum, the solid residue was triturated with methanol, washed with methanol and ethyl ether and dried for 12 hours in vacuum at 60°C. The isolated yield of **4** was 10.32 g (86.88%), mp>350°. Analysis Calcd for $C_{23}H_8Cl_4N_4O_7$ (594.129): C, 46.50; H, 1.36; Cl, 23.87; N, 9.42 %. Found: C, 46.23; H, 1.73; Cl, 23.46; N, 8.96 %. IR (KBr, cm^{-1}): 1745 (C=O, of imidic and parabanic rings), 1385 (imide II), 1140 (imide III), 1620, 1515, 840 (aromatic) and 890 (C-Cl). ^1H-NMR (DMSO-d_6) δ7.75 ppm (s, 8H aromatic).

*1,3 Bis[4-(4-oxytolil)maleimidophenylene]parabanic Acid **(5)***

A 50 mL three-necked flask equipped with magnetic stirrer, thermometer and condenser was charged with 0.9 g (1.5 mmol) **4**, 15 mL NMP, 0.42 mL TEA and 0.324 g (3 mmol) p-cresol, maintained at room temperature for 3 hours, then 2 hours at 60°C. After precipitation with a solution of 5 mL HCl (37.5%) in 80 mL methanol, the reaction mixture was filtered, washed with methanol and Et_2O and dried for 12 hours in vacuum at 60°C obtaining 1g (89.5%) of a brown solid. Analysis Calcd for $C_{37}H_{22}Cl_2N_4O_9$ (737.489): C, 60.26; H, 3.01; Cl, 9.61; N, 7.59 %. Found: C, 60.72; H, 3.14; Cl, 9.35; N, 7.86 %. IR (KBr, cm^{-1}): 2960 ($-CH_3$); 1745 (C=O, parabanic ring), 1730 (C=O, of imidic ring), 1670 (C=O, imidic ring conjugation), 1385 (imide II), 1140 (imide III). ^1H-NMR (DMSO-d_6): δ7.75 (s, 8H aromatic), 7.250 (s, 8H aromatic, p-cresol), 2.40 (s, 6H, CH_3).

Polymer** 7 **a-d Synthesis

The substitution reaction was run under anhydrous conditions using equimolar amounts of tetrachlorobismaleimide (**4**) and various bisphenols (**6 a-d**), in NMP as solvent, with TEA as the acid acceptor. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 10 wt%. A typical reaction was carried out as follows. A 100-mL three-flask, equipped with a mechanical stirrer, thermometer and condenser, was charged with a mixture of 0.6725g (2.0 mmol) of **6d**, 15 mL NMP and 0.52 mL TEA. The mixture was

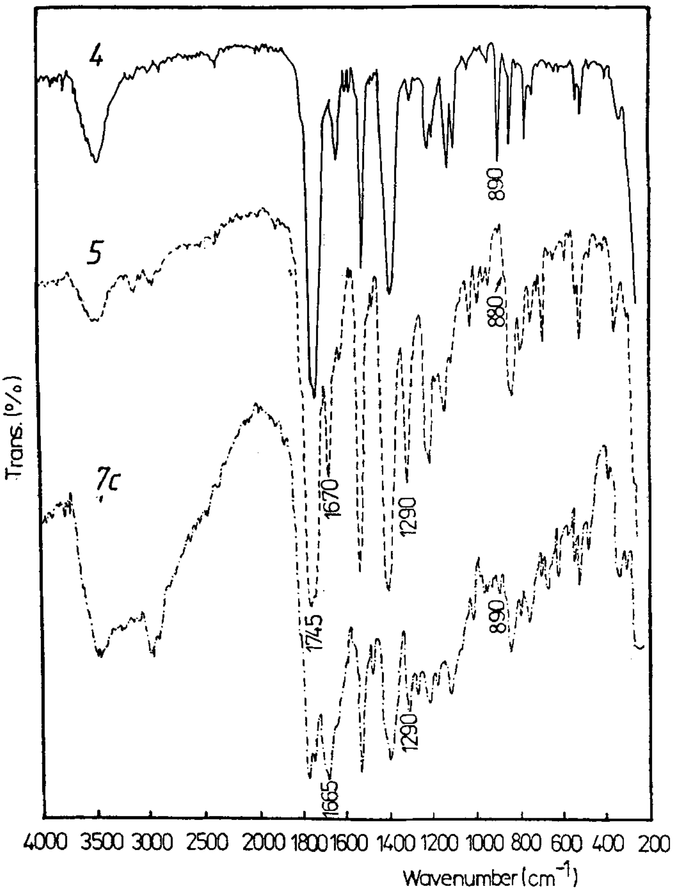
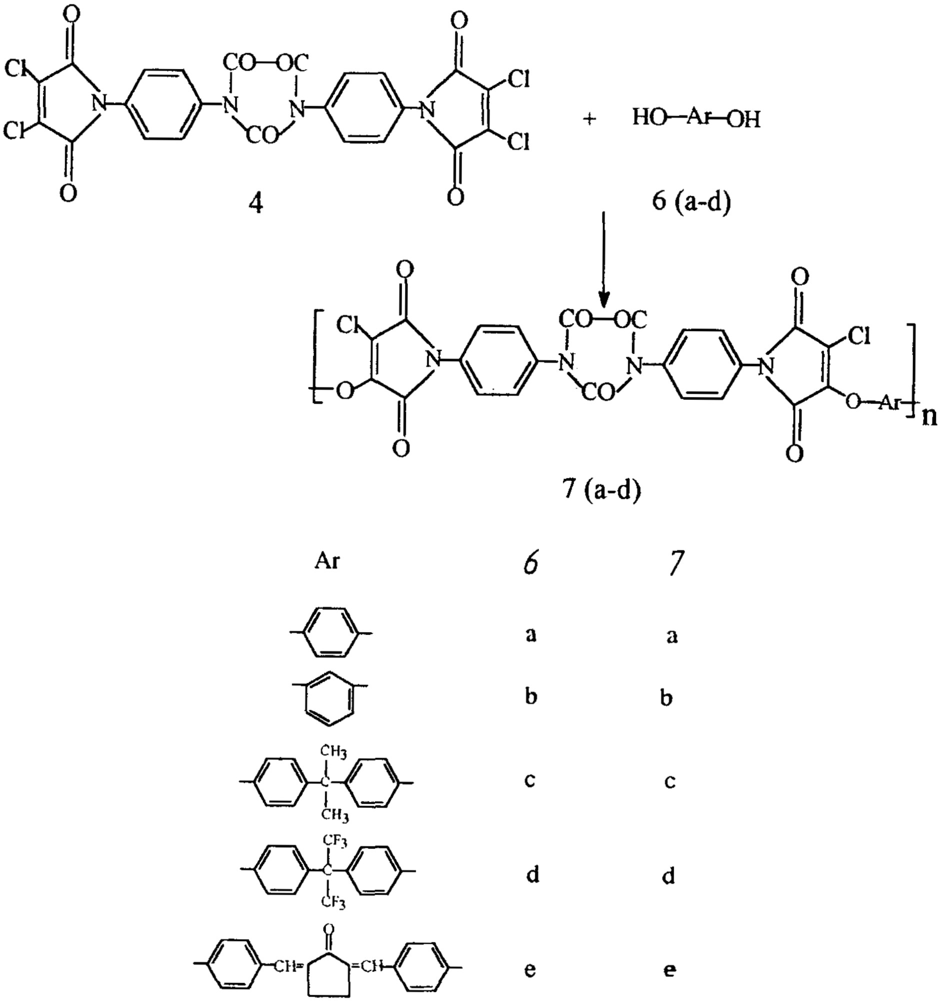


Figure 1. The IR spectra of monomers, model compound and polymer **7c**.

stirred until complete dissolution was accomplished, then 1.188g (2.0 mmol) of tetrachlorobismaleimide (**4**) were added under vigorous stirring. The system was maintained 3 hours at room temperature, then 4 hours at 60°C under vigorous stirring. After cooling and precipitation into 80 mL methanol acidified with 5 mL HCl (37.5%), the solid formed was filtered and washed with methanol, Et_2O and dried for 10 hours under vacuum at 60°C.

RESULTS AND DISCUSSION

A new tetrachlorobismaleimide monomer containing parabanic ring (**4**) was synthesized, using the method of Relles [15] (Scheme 1). The IR, ^{1}H-NMR spectra



Scheme 2

(Figure 1) and elemental analysis confirmed the expected structures. In order to facilitate the assignment of the spectral data, a model compound (**5**) was synthesized from monomer (**4**) and p-cresol as shown in Scheme 1. Linear poly(ether-chlorobismaleimide)s **7(a-e)** were prepared by the nucleophilic substitution reaction of an equimolar mixture of monomer (**4**) with five bisphenols **6(a-e)** in NMP, using triethylamine as acid acceptor (Scheme 2). The structures of the polymers **7(a-e)** were confirmed by IR spectroscopy (Figure 1) and elemental analysis (Table 1). The polymers showed no softening behavior up to 300°C as observed by optical

TABLE 1. Properties of Polymers **7 a-e**.

Polymer	η_{inh}[a] [dL/g]	Elemental Analysis [Calcd/Found] C %	H %	N %	Cl %
7a	0.38	55.17/55.89	1.92/2.17	8.87/8.12	11.23/10.91
7b	0.21	55.17/54.95	1.92/2.30	8.87/7.96	11.23/11.96
7c	0.25	60.89/60.13	2.96/3.14	6.53/6.23	9.16/8.65
7d	0.26	53.23/54.05	1.88/2.12	6.53/6.23	8.27/9.65
7c	0.16	60.25/59.87	2.85/2.55	7.20/6.90	9.12/9.96

[a] Measured at a concentration of 0.5 g/dL in DMSO at 20°C.

TABLE 2. The Thermal Properties of Polymers **7 a-e**.

Polymer	Softening point (°C)	TGA[a] (°C)		Weight loss at 400°C (%)
		T5	T10	
7a	>320	318	338	25
7b	>320	332	350	22
7c	>320	333	352	24
7d	>320	328	348	20
7e	>320	330	350	19

[a] TGA measurements in air,at a heating rate of 12°C/min.

microscope. IR spectra of polymers (Figure 1) showed the complete disappearance of C-Cl absorption peak at 890 cm^{-1} and the appearance of the characteristic absorption bands at 1665 cm^{-1} (conjugation), 1290 cm^{-1} (aromatic ether) confirming the presence of 4-chloromaleimide moieties in the polymer backbone. The inherent viscosities of the polymers (**7 a-d**) ranged between 0.16 and 0.38 dL/g. Their thermal behavior was monitored by DSC. The DSC curves (first heating cycle at a heating rate of 20°C/min) showed similar thermal behaviour for all the studied polymers. No glass transition temperatures (T_g) or melting endotherms were detected up to about 250°C. At this temperature, a broad exotherm occurred. Samples analyzed under optical microscope showed no melting or softening behavior up to 320°C. The thermooxidative stability of the polymers was studied in air by TGA with a heating rate of 12°C/min (Table 2). The polymers showed

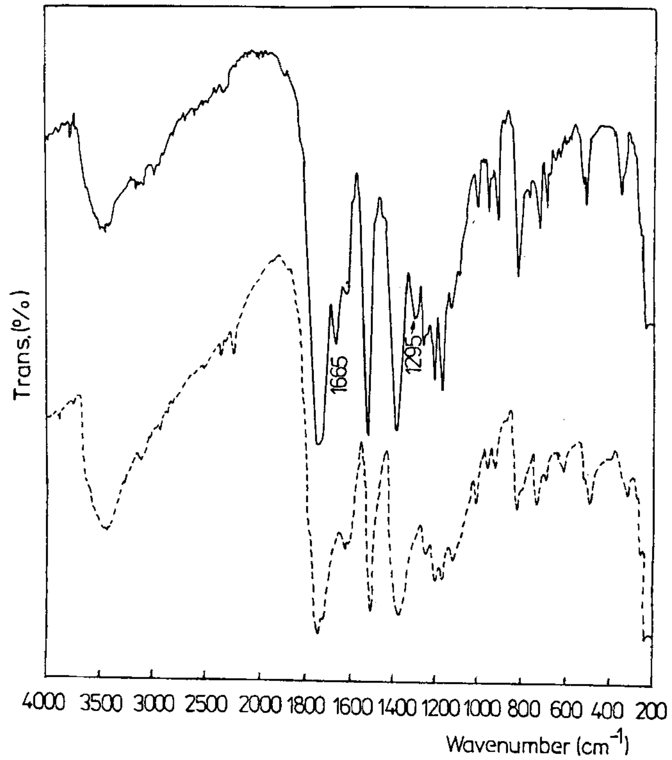


Figure 2. The IR spectra of polymer **7d** (————) and (-----) after heated over 300°C for 30 minutes.

similar decom-position patterns, and the temperature at which 5% weight loss occured (T_5) ranged between 318 and 333°C, comparable with T_5 of poly(amino-bismaleimides) containing parabanic rings in our previous paper [13], but lower than the poly(maleimide-ethers) obtaining of the classic tetrachlorobismaleimides with bisphenols [1,4].

The influence of the bisphenol nature on the thermal stability of the polymers is not significant. The polymers heated over 300°C for more 30 minutes, became insoluble and the IR spectra showed the disappearance of the characteristic peaks at 1665 cm^{-1} and 1295 cm^{-1} assigned to the ether links (Figure 2). Room temperature solubilities of polymers **7 a-e** are given in Table 3. As can be seen, the polymers were soluble in dipolar aprotic solvents such as NMP, DMF, DMSO. The polymer **7a** is soluble only in DMF and DMSO, probably of its rigid structure. The solubility of the polymers increased with the introduction of the m-phenylene or strong polar

TABLE 3. The Solubility of Polymers **7 a-e**[a].

Test Solvent	Solubility Parameter[b] δ	Polymer 7a	7b	7c	7d	7e
Cyclohexanone	9.89	I	I	I	SW	I
Methylene chloride	9.90	I	I	I	SW	I
Dioxane	10.01	I	I	I	PS	SW
Pyridine	10.60	SW	SW	PS	S	PS
m-Cresol	11.12	SW	PS	PS	S	PS
DMAc	11.12	SW	PS	S	S	S
NMP	11.17	PS	PS	S	S	S
HMPA	11.35	PS	S	S	S	S
DMF	12.15	S	S	S	S	S
DMSO	13.038	S	S	S	S	S
Methanol	14.49	I	I	I	I	I
Water	23.43	I	I	I	I	I

[a] I=insoluble, SW=swollen, PS=partially soluble, S=soluble.

[b] Solvent solubility parameter in $(\mathrm{cal/cm^3})^{1/2}$[16].

groups. In that case, the polymer became soluble even in Py. The solubilities of poly(ether-bismaleimides) were better that those of poly(amino-bismaleimide), previously reported [13]. Brittle films were obtained by casting from solutions in DMF.

CONCLUSIONS

New tetrachlorobismaleimides containing parabanic ring and their polymers with bisphenols were synthesized. The polymers showed lower thermo-oxidative stability than of the similarly polymers obtaining of the classic tetrachloro-bismaleimides. This is probably, due to the thermal stability of the parabanic ring.

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