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SYNTHESIS OF METAL CONTAINING POLYUREAS WITH A PARABANIC STRUCTURE

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Abstract—A new diisocyanate containing a parabanic ring was synthesized via a Curtius rearrangement reaction. The direct reaction of this diisocyanate with the Mg salt of p-aminobenzoic acid, or with a mixture of aromatic diamines gave ionic polyureas with a parabanic structure. A detailed study of inherent viscosities of these polymers was achieved.

INTRODUCTION

There are known metal-containing polymers having ionic links on the main chain [1–3]. The introduction of an ionic linkage in the polymer structures was accompanied by new characteristic properties [4]. Parabanic ring containing polymers has been our field of investigation for about 10 yr [5–9] due to their interesting properties. These polymers are characterized by the presence of the heterocycle 2,4,5-imidazolinetrione in the main chain with the American Registry number [120-89-8]. In the present work we proposed to study the influence of the metallic ion linkage in the main chain of the polymer.

The incorporation of a parabanic ring into a polymer chain was achieved by intermolecular reaction between polyureas and oxalyl chloride or by reaction between monomers containing a preformed parabanic ring. In this paper such a monomer was synthesized; a new diisocyanate containing preformed parabanic ring: 1,3-bis(isocyanatophenyl)parabanic acid, by a Curtius rearrangement reaction. The polyaddition reaction between this diisocyanate and the bivalent Mg salt of p-aminobenzoic acid or with mixture of 4,4′-diaminodiphenyloxide (DADO) or 4,4′-diaminodiphenylmethane (MDA) lead to polyureas containing ionic groups in the main chain. Divalent salts of p-aminobenzoic acid containing an ionic bond formed between —COO$^-$ and Mg^{2+} [3] and two terminal amino groups are able to react with diisocyanate to form polyureas.

EXPERIMENTAL

The spectra were recorded on a Specord M80 Carl Zeiss Jene spectrophotometer by using the KBr pellet technique. The inherent viscosities of the polymers were monitored by using appropriate solvents (20°C, conc. 0.5% w/v Ubbelohde viscometer). The thermal behaviour of the polymers (TGA) was examined on a F. Paulik Derivatograph (in air, heating rate 12°C/min). Dichloroethane (DCE) was dried on P_2O_5 and freshly distilled before use. N,N′-dimethylformamide (DMF) was dried on P_2O_5, 4,4′-dibenzyldiisocyanate freshly distilled. Commercial 4,4′-diaminodiphenylmethane (MDA) and 4,4′-diaminodiphenyloxide were purified and dried in the usual manner.

Monomer synthesis

The divalent salt of p-aminobenzoic acid (DS) was prepared as described [3].

1,3-Bis(p-chloroformylphenyl)parabanic acid (CP) was prepared easily in our laboratory from p-aminobenzoic acid and phosgene in aqueous solution when a urea intermediate was formed. The reaction of this intermediate with oxalyl chloride led to chloride terminal groups formation and simultaneously to the closing of a parabanic ring [5].

1,3-Bis(p-phenylisocyanate)parabanic acid (DIP)

The diazide preparation. Into a flask equipped with a stirrer, were introduced 0.1 mol CP in 40 ml dichlorethane (DCE). To an ice cold suspension a solution of 0.025 mol activated sodium azide in 20 ml water was dropped during 2 hr, and stirred for 2 hr. Finally 50 ml water was added and the mixture reaction was filtered. The collected precipitate was washed with water and acetone, dried at 50°C under vacuum. A 90% yield of the product was obtained.

1,3-Bis(p-phenylisocyanate)parabanic acid. Into a 250 ml round bottomed three necked flash equipped with stirrer were introduced 0.1 mol azide derivative and 150 ml anhydrous DCE. The flask was fitted with a condenser, thermometer and gas outlet tube. The mixture was heated at a reflux temperature when a Curtius degradation takes place. The progress of reaction was followed by N_2 evolution. Finally, the reaction mixture became clear. The warm solution was filtered and allowed to stand at room temperature, when a crystalline white product was formed, which was purified by recrystallization from DCE. The crude yield was 95% (m.p. 296–298°C).

Analysis calculated for $C_{17}H_8N_4O_5$: C,588; 63%; H, 3.3%; N, 16%.

Found: C, 59.02%; H, 2.19%; N, 15.7%.

Synthesis of Metal Containing Polyureas–Parabanic Polymers

Polymer PUB

Into a 100 ml three necked flask fitted with a mechanical stirrer, nitrogen inlet tube and condenser, were placed 0.03 mol DS in 10 ml dried DMF and 0.25 ml Pyridine (Py). A stream of nitrogen was introduced into the flask cooled

Table 1. Polymer characterization

Absenation	Formula (molecular weight)		Elemental analyses C (%)	H (%)	N (%)	MgO (%)	η_{inh}[a] dl g^{-1}	Decomposition temperature max. DTG (°C)	Electrical conductivity in pellets (Ω^{-1}/cm^{-1})
PUB	$C_{31}H_{20}N_6O_9Mg$	Calculated	57.74	3.13	13.03	6.24	0.33	330	$9.72 \cdot 10^{-11}$
	(664.82)	Found	56.04	3.89	12.54	8.50			
PUFB	$C_{60}H_{42}N_{12}O_{14}Mg$	Calculated	61.50	3.55	14.11	3.38	0.41	350	$7 \cdot 10^{-11}$
	(1191.35)	Found	60.62	3.22	14.79	4.89			
PUDADO	$C_{60}H_{40}N_{12}O_{15}Mg$	Calculated	60.60	3.39	14.13	3.39	0.45	350	—
	(1189.3)	Found	59.30	3.40	13.80	5.07			

[a] Inherent viscosity, measured in solution water/DMF = 0.5 (in volume), and has a temperature of 20°C.

at −15 and −20°C. At this temperature 0.03 mol of DIP was gradually added in five portions over a period of 1 hr, with stirring. After 1 hr at room temperature the viscous solution was poured into a large amount of acetone.

The solid product was filtered, washed with acetone and dried.

Polyurea PUFB

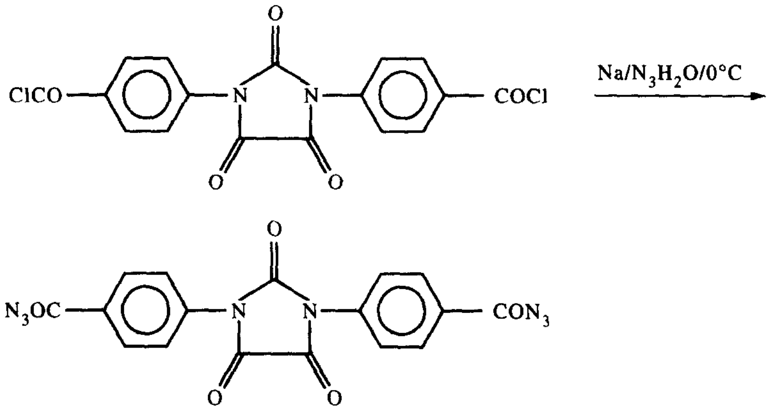
A mixture of 0.02 mol DS, 0.02 mol MDA or DADO, 0.35 ml Py in 37 ml DMF was cooled at −15 and −20°C under a stream of dry nitrogen; 0.04 mol of DIP was gradually added in portions over a period of 1 hr.

The viscous solution was poured into a large amount of acetone. The solid polymer was filtered; washed and dried.

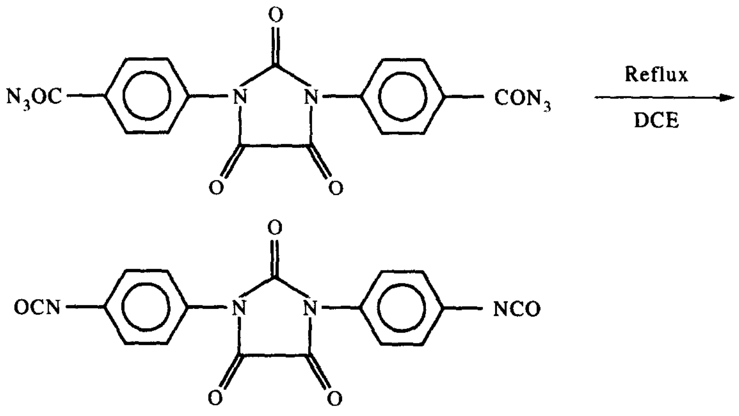
The elemental analyses and the characterization of the polymers are shown in Table 1.

RESULTS AND DISCUSSION

1,3-Bis(p-phenylisocyanate)parabanic acid (DIP), was prepared by a succession of reactions starting from 1,3-bis(p-chloroformylphenyl)parabanic acid 4 and sodium azide by boiling the azide derivative in dichlorethane (DCE). On reflux a Curtius rearrangement takes place:



Scheme 1



Scheme 2

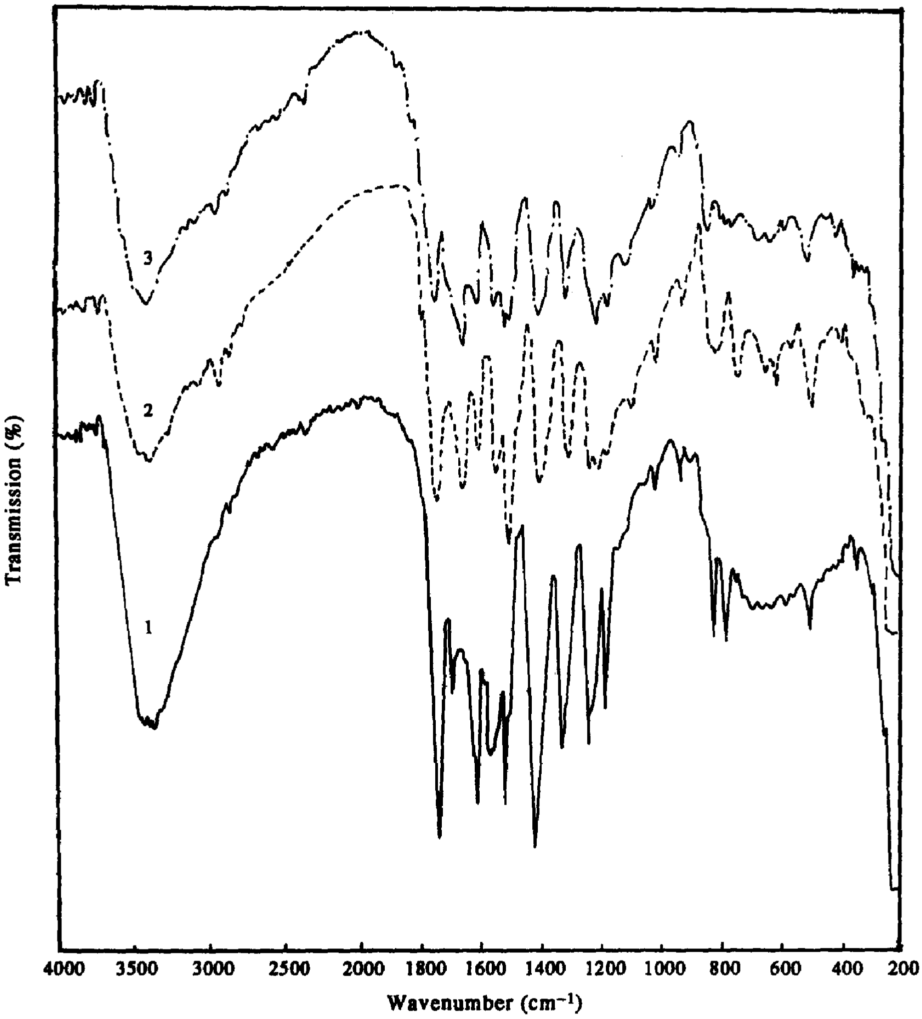


Fig. 1. IR spectra of polymers: 1, polymer PUB; 2, polymer PUFB; and 3, polymer PUDADO.

DIP was characterized by elemental analyses, IR and ^{1}H-NMR spectra.

The IR absorption spectra show the disappearance of the azide doublet from 2135 and 2190 cm^{-1}, and the appearance of an NCO absorption band at 2290 cm^{-1}. The absorption band characteristic of a parabanic ring is present at 1730 cm^{-1} in both spectra.

DIP was also characterized by treating DIP with MeOH by conventional procedure and analysed by ^{1}H-NMR spectra. The CH_3 groups from urethane derivative at 3.85 ppm were observed. The ratio of areas corresponding to CH_3 urethane protons and aromatic protons (7.23–7.75) agree well with calculated values.

Polyureas with a parabanic ring containing Mg in the macromolecular chain were prepared directly by a polyaddition between DIP and divalent salt of p-aminobenzoic acid (PUB) or with mixture of 4,4′-diaminodiphenyl methane (PUFB) and 4,4′-diaminodiphenyl oxide (PUDADO). The structures of the divalent salt of p-aminobenzoic acid was confirmed by the Mg content which corresponds with the calculated values. The structure and the characterization of the polymers are shown in Table 1.

IR investigation of the polymers revealed a spectrum which exhibit absorption bands characteristic of carboxylate groups at 1420 cm^{-1} as well as absorption bands at 3400 cm^{-1} (—NH stretching) 1690 cm^{-1} (carbonyl urea stretching) and 1740 cm^{-1} (parabanic ring) (Fig. 1).

The ionic character of the polymers

As was expected the polymers exhibit a pronounced polyelectrolyte character. Due to this fact, the polymers are insoluble in polar solvents such as N,N′-dimethylformamide (DMF); due to the organic radicals, the polymers are insoluble in water. However, a zone exists, in which the polymers are soluble. This zone differs from one polymer to another; for PUB polymer this region is ranged between 0.12–0.55 water/DMF (volume). The state of the polymers in this range is very different. Figure 2 shows the variation of inherent viscosities.

When the water content is increased, the inherent viscosity is increased until the value of 0.44 dl g^{-1}.

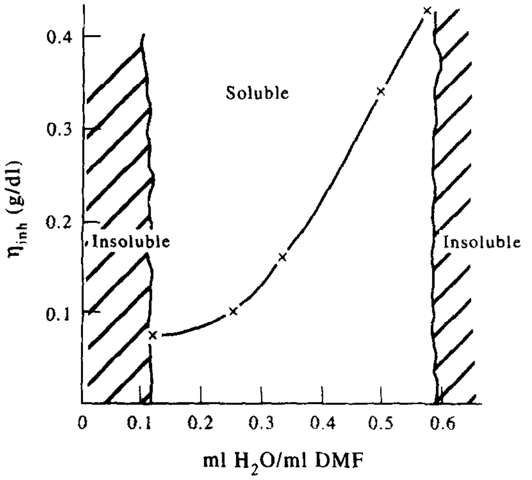


Fig. 2. Inherent viscosity (η_{inh}) report water/DMF (in volume). Concentration of polyureas PUB = 0.3418 g/100 ml.

This increase of viscosity can be attributed to the trend of molecules to adopt a linear shape, the interaction between the ionic groups of the polymers being diminished by polymer–water interaction. Another manifestation of ionic properties of the polymers can be evidenced by the influence of the addition of ionic salts having small molecules. Figure 3 shows the inherent viscosity variation of PUB polymer at different concentrations in solutions containing different quantities of LiCl. It can be seen that in the absence of LiCl, inherent viscosity increased with the concentration of the polymer, due to the tendency of ionic association of the polymers. The addition of LiCl has probably an unbinding action on ionic bonding inter and intra to the macromolecular chain, leading to a noteworthy decrease of the inherent viscosity.

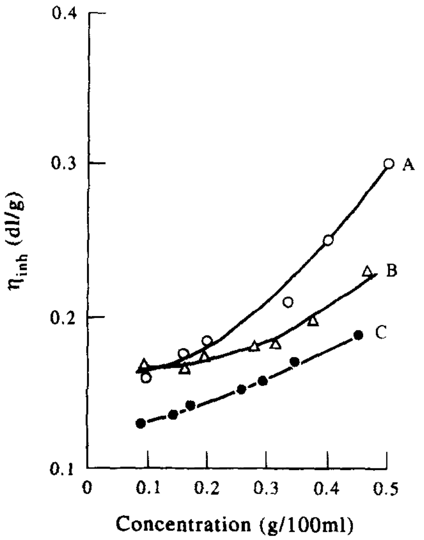


Fig. 3. Inherent viscosity (η_{inh}) vs concentration of polyureas PUB in mixture water/DMF = 0.25 (in volume), with various salt (LiCl) concentrations. LiCl amount: A, none; B, $1.5 \cdot 10^{-3}$ mol/l; and C, $3 \cdot 10^{-3}$ mol/l.

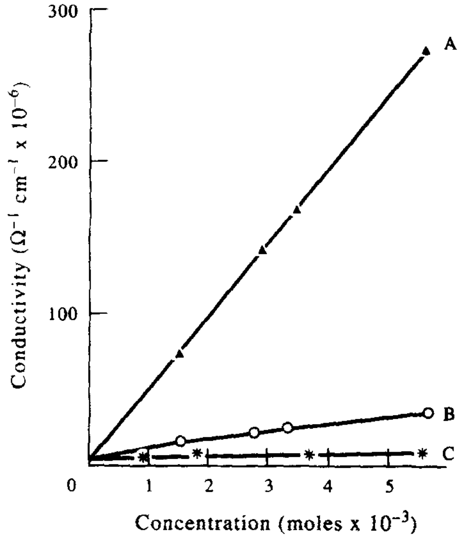


Fig. 4. Electrical conductivity vs concentration of: A, $MgCl_2$; B, Mg benzoat; and C, polymer PUFB in mixture water/DMF = 0.20 (in volume).

In the last part of this paper, the electrical properties of a polymer solution in water—DMF 0.20 (vol.) have been studied. In Fig. 4 the electrical conductivity in solution of the polymer PUFB is indicated, in comparison with Mg benzoate and $MgCl_2$, the content of Mg being expressed in equivalents. In all cases an increase of the electrical conductivity simultaneously with an increase of the equivalent content is observed. There is a difference of the values of this conductivity due to the different dissociation degrees (benzoate $MgCl_2$), as well as, probably due to the mobility of the anion. The macromolecular anion resulting from macromolecular chain scission has a smaller mobility than that of a benzoate anion.

Figure 5 presents the variation of the conductivity in the case of PUFB polymer. From this figure results show that from an increase of the concentration the tendency to association decreases due to the opposite effect of increase of the ionic interaction. In the more concentrated solution we can observe agreement

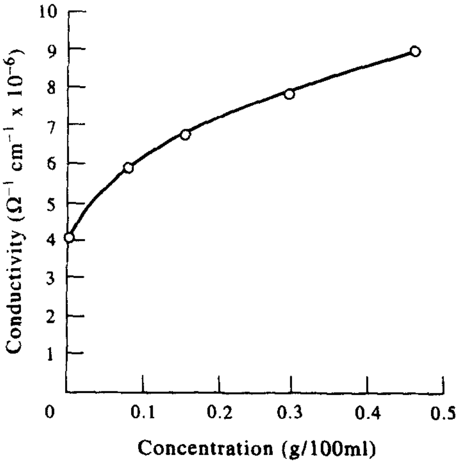


Fig. 5. Electrical conductivity vs concentration of polymer PUFB in mixture water/DMF = 0.20 (in volume).

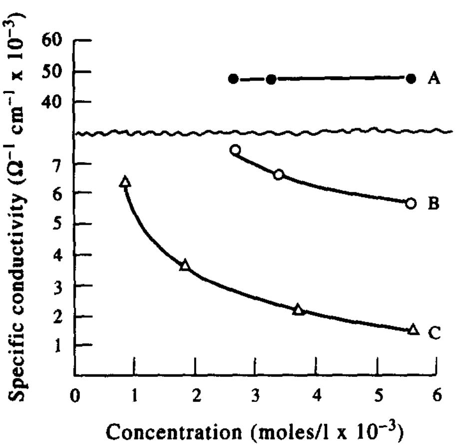


Fig. 6. Specific conductivity vs concentration of: A, $MgCl_2$; B, Mg benzoat; and C, polymer PUFB in mixture water/DMF = 0.20 (in volume).

between the above-mentioned phenomenon of increased inherent viscosity (Fig. 6).

In the very dilute solutions the carboxylates are dissociated leading to a considerable increase of the electrical conductivity when the concentrations of the polymer in solution are increased; the reassociation tendency is also increased which leads to a reduced dissociation.

Electrical conductivity in the solid state (in pellets) is ranged between $1.10^{-10}\,\Omega^{-1}\,cm^{-1}$ for PUB polymer and $7.10^{-10}\,\Omega^{-1}\,cm^{-1}$ for PUFB. Due to this fact these polymers are situated in the class of medium semiconductor polymers.

CONCLUSIONS

A new diisocyanate containing a preformed parabanic ring was achieved via a Curtius rearrangement reaction. By the reaction with the divalent salt of p-amino benzoic acid in a mixture of aromatic diamine, ionic polyureas with a parabanic structure were obtained. A detailed study of the determination of inherent viscosities was achieved. All the compounds were characterized by elemental analyses, IR spectra, inherent viscosities. The obtained polyurea–parabanic polymers containing Mg^{2+} on the main chain are situated in the class of the medium semiconductor polymers.

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