

AROMATIC POLYAMIDE WITH PARABANIC STRUCTURE

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Abstract—A new monomer containing preformed parabanic ring, 1,3-(*p*-chloroformylphenyl) parabanic acid (II), can be obtained easily by the reaction between *p*-aminobenzoic acid and phosgene in aqueous solution. The urea acid intermediate was reacted with oxalyl chloride to obtain II. Aromatic polyamides with parabanic structure were synthesized from II and aromatic diamines in dimethylacetamide. From polymer solutions flexible films can be obtained with good electrical insulating properties and good thermal stabilities.

INTRODUCTION

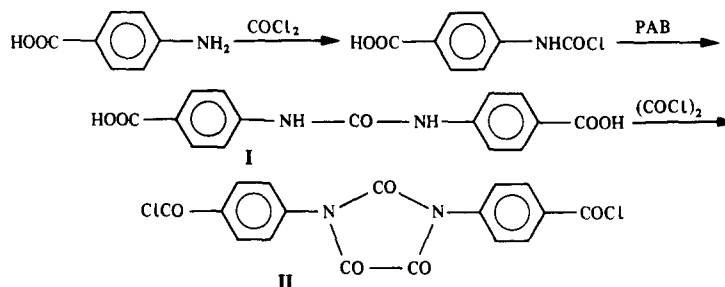
Polymers having parabanic rings in the main chain have been prepared by the reaction between polyureas and oxalyl chloride or from monomers containing preformed parabanic ring as diisocyanate parabanic or diisocyanate diparabanic [1, 2].

In continuation of the study of parabanic polymer synthesis, aromatic parabanic polyamides were prepared by low temperature solution polycondensation of a new monomer containing parabanic ring, 1,3-(*p*-chloroformylphenyl) parabanic acid II, with aromatic diamines in amidic solvents.

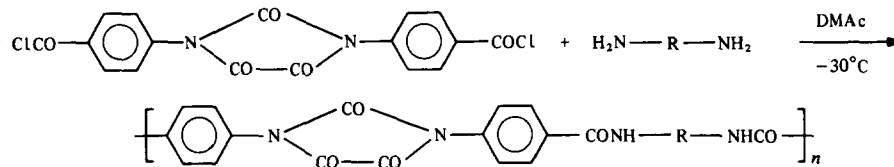
Polyamide solution was poured directly onto glass plates and dried in vacuum to give tough films. Alternatively, the polymer solution was poured into methanol to obtain solid polyamides.

RESULTS AND DISCUSSION

The monomer 1,3-(*p*-chloroformylphenyl) parabanic acid was prepared easily from *p*-aminobenzoic acid (PAB) with phosgene in aqueous solution when an urea acid intermediate I was formed. The reaction of I with oxalyl chloride lead to acid chloride groups and simultaneously to the closing of parabanic ring II.



The polyamides were prepared by low temperature solution polycondensation from II with aromatic diamines in dimethylacetamide.



where :

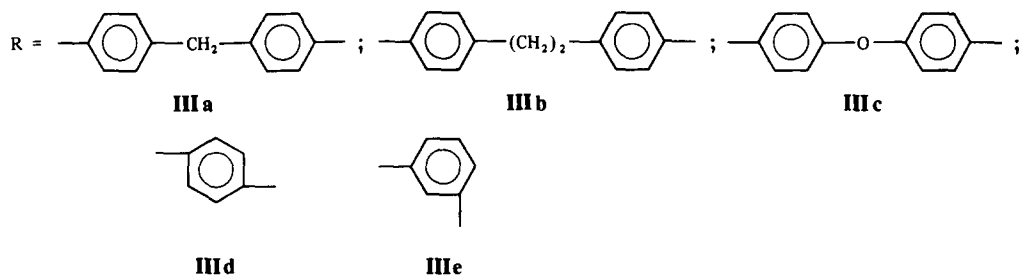


Table 1. Qualitative information on films obtained from aromatic polyamide with parabanic structure

Polymer	Structural units	Qualitative information on solutions and films
IIIa		Viscous, clear solution, flexible films
IIIb		Viscous, opaque solution, brittle films
IIIc		Viscous clear solution, flexible films
IIId		Polymer precipitated
IIIe		Viscous clear solution, flexible films

Table 1 shows the structures and qualitative information on solutions and films. In the polyamides IIIa and IIIc, the aromatic rings are inclined to one another at an angle; because of steric hindrances, there is no rotation around the axes of the methylene carbon–aromatic ring or oxygen–aromatic ring bonds. In contrast, the presence of the ethylene group between the aromatic rings in polyamide IIIb, allows the ring to rotate. In this conformation, the macromolecular chains readily pack to form fully hydrogen-bonded sheets, resulting in high crystallinity and low flexibility. This behaviour resembles that of polyurethanes having similar structures [3].

All the polymers are soluble in amidic solvents due to the parabanic ring and in contrast with other types of aromatic polyamides.

Polymer IIIc has a high decomposition temperature, good solubility in amidic solvents and good mechanical properties (tensile strength 670–845 kgf/cm²).

ELECTRICAL PROPERTIES

The films of aromatic polyamide with parabanic structure have good electrical insulating properties such as volume resistivity and dielectric constant. Such properties make these polymers useful as insulators in motors and transformers. Table 2 shows these values for polyamides IIIa, b, c with highest inherent viscosity.

EXPERIMENTAL

Materials

N,N'-Dimethylacetamide was purified by vacuum distillation; dichloroethane was purified by vacuum distillation over CaH₂; aromatic diamines were purified by recrystallization from appropriate solvents. Commercial oxalyl chloride and *p*-aminobenzoic acid were used as received.

Monomers

1,3-*p*-(chloroformylphenyl)parabanic acid was prepared in a two step reaction as follows: in a flask equipped with mechanical stirrer, reflux condenser and phosgene inlet and outlet were placed 15 g *p*-aminobenzoic acid in 30 ml water. Then the phosgene was bubbled for 3–4 hr at reflux temperature with stirring. After cooling to room temperature, the precipitated crystalline urea acid I was filtered and purified by successively passing from sodium salt into free acid. The yield was 90%. The IR spectrum (KBr) exhibited absorptions as 3300 cm⁻¹ and 1630 cm⁻¹ (N—H), at 1655 cm⁻¹ (C=O) and 2500–3000 cm⁻¹ (COOH).

Analysis calculated for C₁₅H₁₂N₂O₅: C 60%; H 4%; N 9.3%; found C 60.61%; H 3.99%; N 9.06%.

Synthesis of diacylchloride II was performed as follows: in a flask equipped with mechanical stirrer and reflux condenser, were introduced 15 g I in 400 ml dichloroethane (DCE). Then, 63 ml oxalyl chloride were added in the presence of a few drops of dimethylformamide as catalyst.

The mixture reaction was heated at reflux temperature with stirring until the solution became clear. After cooling to room temperature, the precipitated crystalline product was filtered, washed with DCE and dried. The yield was 98–99%. Recrystallization from DCE gave white crystals; m.p. 252–253° (by capillary tube).

The IR spectrum (KBr) exhibited absorptions at 1730 cm⁻¹ (parabanic C=O), 1770 cm⁻¹ (diacylchloride

Table 2. Electrical properties

Polymer	Dielectric constant	Dissipation factor	Volume resistivity ($\Omega \times \text{cm}$)	Dielectric strength (kV/mm)
IIIa	1.95–2	8.5×10^{-3}	8.14×10^{15}	125–135
IIIb	2.75	$(3.7\text{--}4.9) \times 10^{-2}$	$(2.04\text{--}8.14) \times 10^{11}$	65–70
IIIc	2.21	8×10^{-3}	$(1.4\text{--}1.7) \times 10^{16}$	200–230

Table 3. Polyamide parabanic polymer

Monomers			Analysis (C%)	Calculated (H%)	(Found) (N%)	MPT (°C)	Decomposition temperature ^a (°C)	η_{inh} (g/dL)
Diacyl parabanic chloride	Aromatic diamine	Polymer						
II	MDA	IIIa	69.77 (67.69)	3.87 (3.88)	10.85 (10.50)	> 400	280	0.68
II	DBDA	IIIb	70.18 (69.27)	4.18 (4.34)	10.56 (10.22)	> 400	350	2.03
II	DADO	IIIc	67.18 (67.25)	3.5 (4.05)	10.81 (10.82)	> 400	320	1
II	p-PDA	IIId	64.79 (62.74)	3.29 (3.31)	13.15 (13.43)	> 400	250	0.63
II	m-PDA	IIIe	64.79 (62.08)	3.29 (3.30)	13.15 (12.01)	> 400	280	0.45

^aDetermined by ATG in air at a heating rate of 12°/min.

C=O) and 880 cm^{-1} (C—Cl). The IR demonstrated also the disappearance of the band characteristic of COOH from $2500\text{--}3000\text{ cm}^{-1}$.

Analysis calculated for $\text{C}_{17}\text{H}_8\text{O}_5\text{Cl}_2$: C 52.2%; H 2.06%; Cl 18.13% found C 52.24%; H 2.06; Cl 18.28%.

Polycondensation

Equimolecular amounts of diacylchloride II and aromatic diamines were introduced in a flask equipped with a stirrer. Then, a quantity of solvent needed to give a concentration of about 15% was added. The solution was cooled to -30° . The reaction mixture was stirred rapidly for 30 min; the cooling bath was removed and the solution was allowed to rise to room temperature. Stirring was continued for 2 hr.

The polyamide parabanic polymers were isolated by pouring the viscous solution into rapidly stirred methanol.

The solid polymers were filtered, washed with ethanol and dried at 60° .

The characteristics of the polymers are indicated in Table 3. The melting point temperature (MPT) was determined in capillary tube and decomposition temperature by thermogravimetric analysis.

REFERENCES

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