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Synthesis and Properties of Poly(Benzoxazines): Poly[6,6'-Methylene(4H-3,1-Bibenzoxazine) 2,2'-Diylphenylenes

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ABSTRACT

A new class of benzoxazine polymers were synthesised from bis(4-amino-3-hydroxymethylphenyl)methane with substituted phthalic acids by solution polycondensation in polyphosphoric acid. The model compound bis(4H-3,1-benzoxazine)2,2'-p-phenylene was also synthesised. The polymers were characterised by UV and IR spectra, viscosity measurements and thermal analysis.

INTRODUCTION

In the past years, investigations concerning the organic heterocyclic polymers such as benzimidazoles (VOGEL and MARVEL, 1961), benzoxazoles (KUBOTA and NAKANISHI, 1964), benzthiazoles (HERGENROTHER et al., 1965), oxadiazoles (FRAZER et al., 1964) and imides (BOWER and FROST, 1965) have been reported. Further some other heterocyclic polymers with six membered bicyclic units such as quinoxalines (STILLE et al., 1965) quinazolinediones (YODA et al., 1966a, 1967a) and benzoxazinones (YODA et al., 1966b, 1967b) have also been reported. These polymers are found to possess excellent thermal stability and outstanding hydrolytic stability. STILLE and FREEBURGER (1968) reported the synthesis of ladder poly(phenoxazines), which had less thermal stability. In this paper we report the synthesis and thermal properties of two poly(benzoxazines) prepared from bis(4-amino-3-hydroxymethylphenyl)methane with terephthalic and isophthalic acids in polyphosphoric acid as the polymerisation solvent and cyclising reagent.

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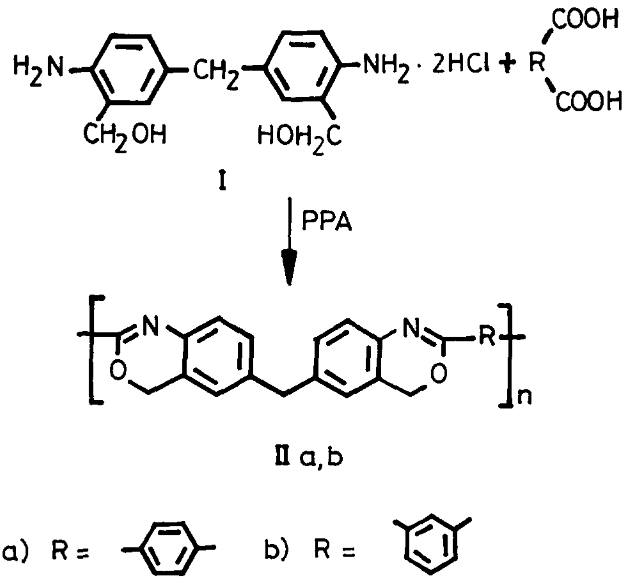


EXPERIMENTAL

Orthophosphoric acid (BDH), phosphorus pentoxide (BDH), terephthalic and isophthalic acids (Fluka AG) samples were used as such. The polyphosphoric acid was prepared just before use by dissolving phosphorus pentoxide (15g) in orthophosphoric acid (20 ml) at 120°C for 6 hours.

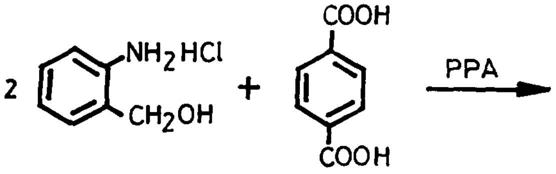
The Ultra-Violet (UV) spectra of the model compound and the polymers were recorded in a Carl-Zeiss DMR 21 spectrometer (concentrated sulphuric acid) and the infra-red (IR) spectra were recorded in a Perkin-Elmer 257 spectrometer (KBr pellets). The density measurements were made in a small pycnometer with hexane at 30°C and the intrinsic viscosities were measured in an Ostwald viscometer in concentrated sulphuric acid at 30°C (C = 0.1g/dl). The thermogravimetric analysis were carried out in a Stanton thermobalance at a heating rate of 8°C/min. and the differential thermal analysis were carried out with a Stanton Redcroft Thermal Analyser at a heating rate of 10°C/min. in air.

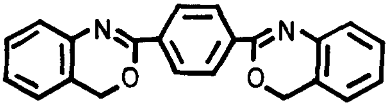
Synthesis of bis(4-amino-3-hydroxymethylphenyl)-methane(I):

The 5,5'-methylenedimethylanthranilate was prepared by the reaction of methyl anthranilate with aqueous formaldehyde (40%) and concentrated hydrochloric acid (KHOFBAUER and LEONOVA, 1971) m.p.146°C (lit.147°C). 9.5g of the diester (0.03 mole) was treated with 3.5g of lithiumaluminiumhydride (0.09 mole) in tetrahydrofuran under ice-cold conditions and then refluxed for five hours. After usual work up, 5.4g of I was isolated after recrystallisation from chloroform, m.p.161°C. The IR spectrum of the compound(I) showed a doublet at 3380, 3300 cm^{-1} (ν NH_2) and a broad band at 3240-3180 cm^{-1} (ν OH hydrogen bonded) and the ^1H NMR spectrum of the compound in $CDCl_3/F_3CCOOH$ showed a singlet at δ 4.12, 2H, ($-CH_2-$), a singlet at δ 5.13, 4H, ($-CH_2-O-$), and a broad multiplet, 6H at δ 7.3-7.5 (aromatic protons). The amine and hydroxyl protons merged with the offset trifluoroacetic acid protons.

Synthesis of bis(4H-3,1-benzoxazine)2,2'-p-phenylene:

A mixture of 3.2g 2-amino-benzylalcohol hydrochloride and 60g of polyphosphoric acid was heated at 120°C in nitrogen atmosphere. During the heating hydrogen chloride was evolved and eliminated with nitrogen. To this solution 1.66g of terephthalic acid was added and the mixture was heated to 120°C with stirring for ten hours, cooled and precipitated into ice-cold water. The precipitates were washed successively with dilute solution of sodium carbonate, water and methanol (2.25g yield 70%). It was recrystallised from N,N'-dimethylformamide and methanol mixtures. The compound(III) did not melt upto 220°C and then started decomposing. The UV spectrum of the compound(III) showed the following absorption maxima at 210 nm (ε=174.4), 263 nm (ε=95.48), 310 (ε=61.65) and 360 nm (ε=54.13) and the IR spectrum of the compound showed the following peaks at 1615, 1500, 1280, 1150, 820 and 740 cm^{-1}.





III

Polymerisation:

A mixture of 1.65g of the hydrochloride of I and 75g of polyphosphoric acid was heated at 120°C in nitrogen atmosphere. After hydrogen chloride was eliminated with nitrogen, 0.83g of terephthalic or isophthalic acids were added and the mixture was heated with stirring at 160°C for four hours and at 220°C for ten hours. The viscous mass was precipitated in ice-cold water, filtered, washed with dilute sodium carbonate solution, water and methanol. It was then dried at 110°C for four hours.

RESULTS AND DISCUSSION

HERGENROTHER et al., (1965) have reported the preparation of poly(benzthiazoles) in polyphosphoric acid, the polycondensation temperature had influence on the molecular weight of the polymers and a reaction temperature of 240°C yielded a polymer with an intrinsic viscosity value as high as 1.5 dl/g. The poly(benzoxazines) obtained in our case also had an intrinsic viscosity values of 1.31 and 1.20 dl/g. The UV spectra of the polymers showed the following absorption maxima at 195 nm (ε=92), 262 nm (ε=69), 310 nm (ε=54) and 360 nm (ε=46) and the IR spectra of the polymers showed the following peaks at 1615, 1500, 1270, 1150, 820 and 770 cm^{-1}. The absence of any other functional groups such as -NH- and hydroxyl groups indicates the cyclisation has gone to the maximum extent. The data on yields, viscosity, density, polymer decomposition temperatures and the weight loss are presented in the TABLE.

TABLE

Properties of poly(benzoxazines)

Property	Polymer IIa	IIb
Yield (%)	55	48
Intrinsic viscosity dl/g	1.31	1.20
Density g/cm^3	1.497	1.410
Polymer decomposition temperature °C	300	265
Weight loss in %		
18	320	310
55	405	375
79	440	435

The polymers were soluble only in concentrated sulfuric acid, chlorosulfonic acid and were almost insoluble in most organic solvents including HMPT, DMAc, DMF and DMSO. The TG analysis of the polymers in air showed that they were stable upto 300°C (IIa) and 260°C (IIb) and started decomposing to give a weight residue at approximately 440°C (IIa) and 435°C (IIb) respectively. The final residues were stable upto 700°C. The low thermal stability may be due to the reactive methylene group present in the benzoxazine units. The DT analysis of the polymers showed a strong endotherm at 280-285°C (IIa), 240-245°C (IIb) and two exothermic peaks at 310°C, 332°C (IIa) and 274°C, 312°C (IIb) respectively. The strong endotherm at the lower temperatures may be due to the decomposition of polymers as evidenced by TG analysis.

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