**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Malcolm B. Polk[a]; Fidelis C. Onwumere[a]
[a] Department of Chemistry and Polymer Research Center, Atlanta University, Atlanta, Georgia

**To cite this Article** Polk, Malcolm B. and Onwumere, Fidelis C.(1985) 'The Synthesis and Characterization of Poly Oxy(2-methyl-1,3-phenylene) oxyisophthaloxyl-b-Oxy(2-methyl-1,3-phenylene)oxyterephthaloxyl', Journal of Macromolecular Science, Part A, 22: 10, 1371 — 1378

**To link to this Article: DOI:** 10.1080/00222338508063341

**URL:** http://dx.doi.org/10.1080/00222338508063341

J. MACROMOL. SCI.–CHEM., A22(10), pp. 1371-1378 (1985)

# The Synthesis and Characterization of Poly Oxy(2-methyl-1,3-phenylene) oxyisophthaloxyl-b-Oxy(2-methyl-1,3-phenylene)oxyterephthaloxyl

MALCOLM B. POLK and FIDELIS C. ONWUMERE

Department of Chemistry and Polymer Research Center
Atlanta University
Atlanta, Georgia 30314

## ABSTRACT

The syntheses and characterizations of poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] and the corresponding homopolymers are described. The synthesis involves the coupling of dihydroxy-terminated homopolymers with terephthaloyl chloride. The resulting block copolyester was characterized by infrared spectroscopy, proton and carbon-13 nuclear magnetic resonance spectroscopy, solution viscosity, differential scanning calorimetry, and thermogravimetric analysis.

## INTRODUCTION

For several years our research group has been involved in the synthesis and characterization of block copolyesters containing liquid crystal blocks [1-4]. Poly[oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl-b-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (I); poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,

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4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II); poly[oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl-b-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl] (III); and poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) (IV) have been synthesized and shown to form mesomorphic solutions. As expected, we have demonstrated that the oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl moiety is responsible for the liquid crystalline properties of block copolyesters I and II. Poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) homopolymer has been shown to form lyotropic solutions in o-chlorophenol [5]. Because of decomposition of the cycloaliphatic blocks at temperatures below the melting points of the aromatic blocks, none of the block copolyesters combining cycloaliphatic and aromatic blocks displayed thermotropic properties.

Thermotropic aromatic polyesters are well known in the chemical literature [6-12]. In order to expand our studies to include the preparation of systems that would exhibit thermotropic liquid crystal properties, we chose to investigate strategies for the preparation and characterization of poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl]. The syntheses and characterizations of the corresponding homopolyesters are described in earlier papers [2, 3].

Our plan involved the preparation of the aromatic homopolyesters by the reaction of 2-methylresorcinol and isophthaloyl chloride in one case and 2-methylresorcinol and terephthaloyl chloride in the other case. The 2-methyl resorcinol was added in 10% excess in each case to the corresponding diacid chloride to generate homopolyesters with predominating dihydroxy endgroups. The homopolyesters with hydroxy endgroups were reacted with terephthaloyl chloride to form the corresponding block copolyesters.

## EXPERIMENTAL SECTION

Inherent viscosities were measured at 30°C with a Cannon-Fenske viscometer at a concentration of 0.5 g/100 mL in a 3:1 v/v mixture of chloroform and trifluoroacetic acid. Melting points were determined with a differential scanning calorimeter (Du Pont 990 thermal analyzer with the Du Pont 910 differential scanning calorimeter). Carbon-13 NMR spectra were determined on deuteriochloroform solutions of the polyesters with a Bruker WM-250 spectrometer with carbon-13 spectra taken at 62.860 MHz. The chemical shifts are reported relative to tetramethylsilane. Infrared spectra were obtained on KBr disks with a Beckman 4240 infrared spectrophotometer.

The o-dichlorobenzene solvent used in the polyesterification was purified and dried by fractional distillation and stored over molecular sieves. Terephthaloyl chloride, isophthaloyl chloride, and 2-methylresorcinol were commercial products. Terephthaloyl chloride and isophthaloyl chloride were purified by recrystallization from dry hexane. 2-Methylresorcinol was purified by recrystallization from deoxygenated water.

### A. Preparation of Poly[Oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-Oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] with a 1:1 Molar Ratio of Starting Materials

A 500-mL three-necked round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and either a potassium or sodium hydroxide trap, was charged with 13.37 g (0.1078 mol) of 2-methylresorcinol and 100 mL of dry o-dichlorobenzene. To this stirred solution was added 20.0 g (0.0980 mol) of terephthaloyl chloride in a nitrogen atmosphere. The mixture was heated for 1 h at 130°C. The temperature was increased to 165°C and the mixture was heated under reflux for 7 h.

To the same apparatus described above was charged 13.37 g (0.1078 mol) of 2-methylresorcinol and 100 mL of dry o-dichlorobenzene. To this stirred mixture was added 20.0 g (0.0980 mol) of isophthaloyl chloride in a nitrogen atmosphere. As before, the mixture was heated for 1 h at 130°C, and after the temperature was raised to 165°C, the mixture was refluxed for 7 h.

After cooling, the two solutions were mixed in a 500-mL three-necked round-bottom flask equipped with a magnetic stirrer, condenser, nitrogen inlet, thermometer, and either a potassium or sodium hydroxide trap. To this mixture was added 27.6 g (0.136 mol) of terephthaloyl chloride. The mixture was heated for 1.5 h at 120°C, and after the temperature was raised to 165°C, the mixture was refluxed for 7.5 h. After cooling, the polymer was precipitated by pouring the reaction mixture into 450 mL of acetone. The polymer was allowed to stand in acetone for 1 day. After filtering and washing twice with acetone and deionized water repetitively two or three times, and drying the polymer in a vacuum oven for 48 h at 120°C, 40.0 g of the block copolyester was obtained.

### B. Preparation of Poly[Oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-Oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] with a 1:2 Molar Ratio of Starting Materials

The procedure described in preparation A for the preparation of the poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer was repeated.

A 500-mL three-necked round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and either a potassium or sodium hydroxide trap, was charged with 6.62 g (0.0530 mol) of 2-methylresorcinol and 50 mL of dry o-dichlorobenzene. To this stirred solution was added 10.0 g (0.0490 mol) of isophthaloyl chloride. The mixture was heated for 1 h at 130°C, and after the temperature was raised to 165°C, the mixture was refluxed for 7 h.

After cooling, the two solutions were mixed in a 500-mL three-necked round-bottom flask equipped with a magnetic stirrer, condenser, nitrogen inlet, thermometer, and a potassium hydroxide trap. To this mixture was added 27.6 g (0.136 mol) of terephthaloyl chloride. The mixture was heated for 1.5 h at 120°C, and after the temperature was raised to 165°C, the mixture was refluxed for 7.5 h. After cooling, the polymer was precipitated by pouring the reaction mixture into 450 mL of acetone. The polymer was allowed to stand in acetone overnight. After washing as described above and drying in a vacuum oven for 48 h at 120°C, 32.0 g of the block copolyester was obtained.

### Modification of Block Copolyesters A and B with Terephthaloyl Chloride

Block copolyester B (11.0 g) and terephthaloyl chloride (6.0 g, 0.029 mol) were added to 100 mL of o-dichlorobenzene and the mixture was refluxed for 8 h at 170°C. After cooling, the polymer was precipitated by pouring the reaction mixture into a 450 mL of acetone. The polymer was allowed to stand in acetone for 1 day. After filtering and washing twice with acetone and with deionized water repetitively three times, the polymer was dried in a vacuum oven for 48 h at 140°C.

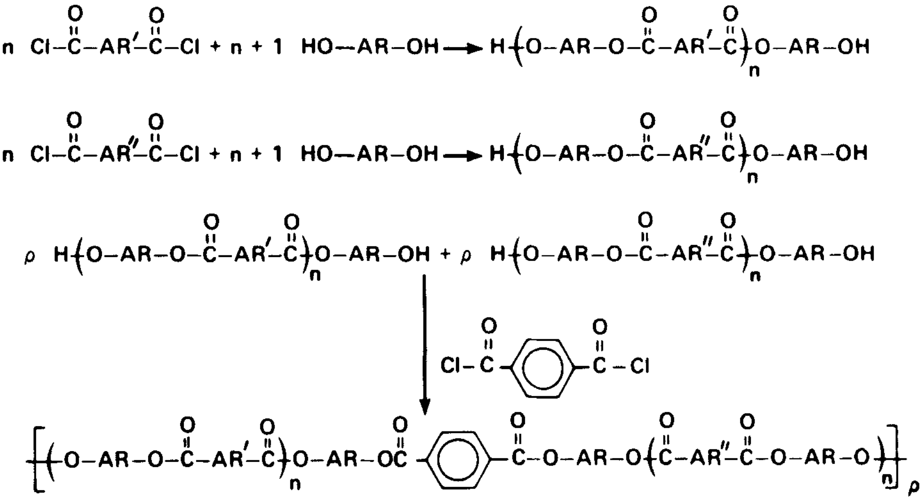
Block copolyester A (2.0 g) was modified with 1.8 g of terephthaloyl chloride.

## RESULTS AND DISCUSSION

Block copolyesters were formed by the step-reaction polycondensation of reactive ester oligomers capped with dihydroxy endgroups and terephthaloyl chloride. The block copolyesters subsequently underwent further reaction with terephthaloyl chloride to form higher molecular weight block copolyesters. The synthetic scheme is shown in Scheme 1. The general structure of the block copolyesters is shown in Fig. 1.

### Properties of Poly[Oxy(2-methyl-1,3-phenylene)-oxyisophthaloyl-b-Oxy(2-methyl-1,3-phenylene)-oxyterephthaloyl]

The inherent viscosities for block copolyester A, modified block copolyester A, block copolyester B, and modified block copolyester B



SCHEME 1. Synthesis of block copolyester.

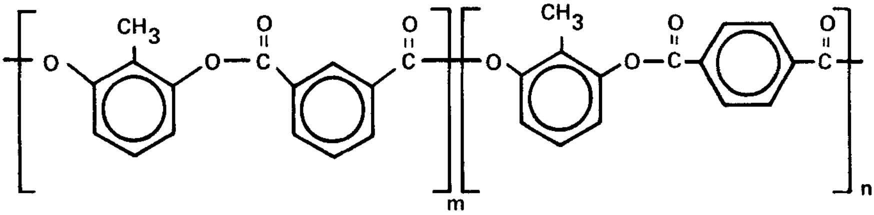


FIG. 1. Structure of poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl].

were 0.40, 0.58, 0.37, and 0.60 dL/g in a 3:1 v/v mixture of chloroform and trifluoroacetic acid at 30°C.

The infrared spectra of block copolyesters A and B showed peaks at 3420 (O–H stretch), 1730 (ester C=O stretch), 1600, 1460, and 1400 (aromatic nucleus), and 1250, 1075, and 1000 (C–O stretch) $\mathrm{cm}^{-1}$.

The differential scanning calorimetry thermogram of block copolyester A showed a glass transition temperature of 176°C and a crystalline melting point of 328°C. Thermogravimetric analysis showed a decomposition temperature of 450°C. Thermal analysis of block copolyester B showed a glass transition temperature of 195°C, a crystalline melting point of 325°C, and a decomposition temperature of 415°C.

Modified block copolyester B showed a crystalline melting point of

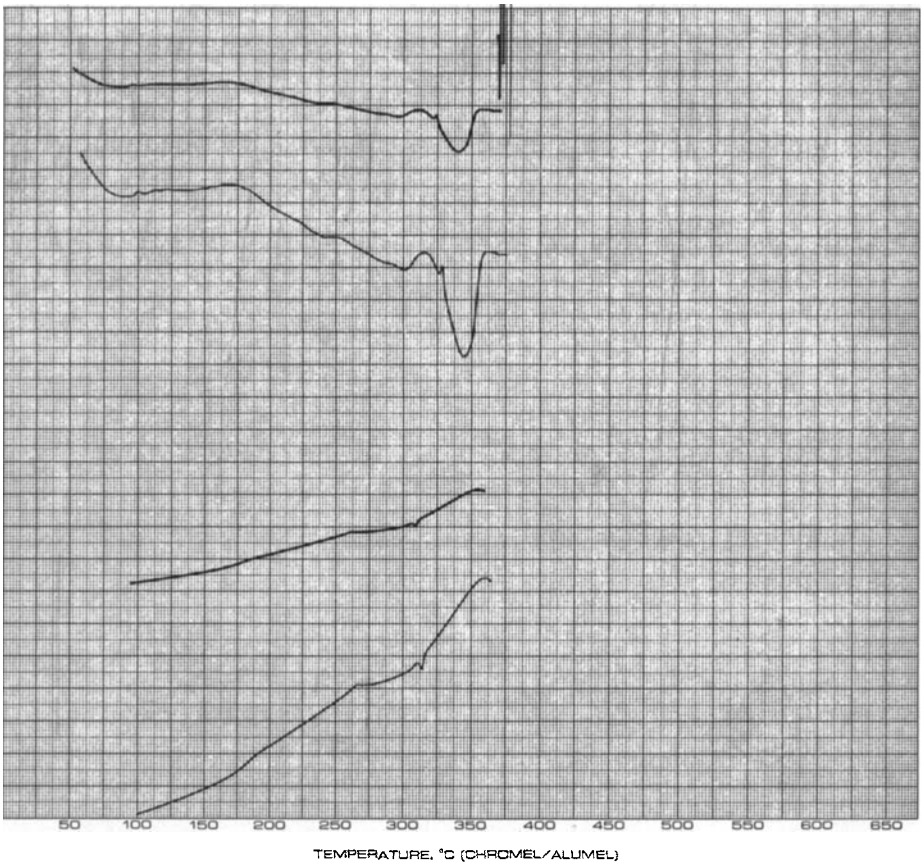


FIG. 2. DSC thermogram of modified block copolyester B.

340°C and a decomposition temperature of 430°C. An interesting low enthalpic transition at 297°C also appeared (see Fig. 2).

The proton-decoupled natural-abundance $^{13}C$-FT-NMR spectrum of block polyester A is shown in Fig. 3. The $^{13}C$-FT-NMR spectrum of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] has been reported recently [4]. The resonances at δ 10.2, 123.9, 150.3, 120.2, and 127.0 are assigned to the methyl carbon and the carbons α, ortho, meta, and para to the methyl group, respectively, in the oxy(2-methyl-1,3-phenylene)oxy ring system. The resonances at δ 133.8 and 130.6 were assigned to the carbons α and β to the carbonyl, respectively, in the terephthaloyl ring system. The resonances at δ 135.2, 130.2, 131.9,

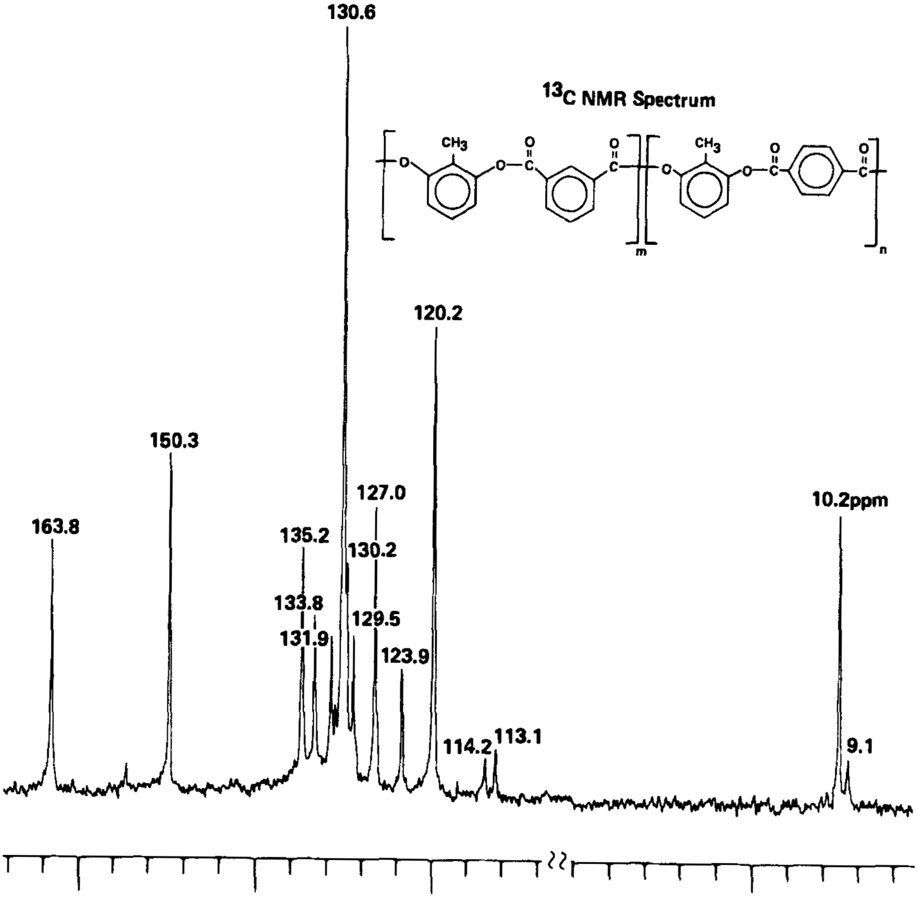


FIG. 3. $^{13}$C-NMR spectrum of block copolyester A.

and 129.5 were assigned to the carbon between the carbonyl groups and the carbons α, ortho, and meta to the carbonyl groups, respectively, in the isophthaloyl ring system based on the corresponding assignments for di-n-butylisophthalate [13] (δ 133.6, 130.7, 131.2, and 128.5). The resonance at δ 163.8 was assigned to the carbonyl carbon.

None of the block copolyesters or modified block copolyesters depolarized plane-polarized light on heating to temperatures as high as 400°C. However, the block copolyesters turned a red color on heating to ~300°C, and strong, tough fibers were successfully pulled from the molten polymer.

## CONCLUSION

In summary, synthetic procedures have been developed for the preparation of all-aromatic block copolyesters. The preparation of a block copolyester by the linking together of dihydroxy-terminated oligomers with terephthaloyl chloride yielded block copolyesters with terminal hydroxy endgroups which underwent additional step-growth polycondensation on reaction with terephthaloyl chloride as evidenced by the corresponding increases in inherent viscosity.

## ACKNOWLEDGMENTS

We thank Mr William Lewis for obtaining the NMR data. We thank Mr Ogburubi Ibe-Uro for obtaining the thermal analysis data. Support from the Office of Naval Research under Grant No. N00014-80-0577 is gratefully acknowledged.

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Accepted by editor June 3, 1984
Received for publication June 19, 1984