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# Synthesis and Characterization of Some New Polyarylates Derived from Two Heterocyclic Monomers

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## ABSTRACT

New polyarylates were synthesized by phase-transfer catalyzed two-phase polycondensation of benzofuro[2,3-b]benzofuran 2,9-dicarbonyl chloride with bisphenols of various derivatives and 2,13-dihydroxy[7a,14c]dihydronaphtho[2,1-b]naphtho[1',2':4,5]furo[3,2-d]furan with various aromatic dicarboxylic acid chlorides. All of these polyarylates dissolve readily in a wide range of organic solvents such as *N,N'*-dimethylacetamide, *N,N'*-dimethylformamide, and hexamethyl phosphoramide. These polyarylates have inherent viscosities of 0.14–0.30 dL/g and 10% weight loss between 302.9–455.8 °C in nitrogen atmosphere.

**Key Words:** polyarylates, polycondensation, benzofuro[2,3-b]benzofuran-2,9-dicarbonyl chloride, bisphenols, 2,13-dihydroxy[7a,14c]dihydronaphtho[2,1-b]naphtho[1',2':4,5]furo[3,2-d]furan

## INTRODUCTION

There has been a continuing and strong effort since the late 1950's to synthesize thermally stable polymers. The physical and chemical parameters that lead to increased heat resistant polymers also present problems with respect to the synthesis of polymers with good solubility behaviour [1]. There are two general approaches to this compromise. One approach involves the introduction of some flexible linkages, such as isopropylidene, C=O, and SO<sub>2</sub> into the rigid polymer chain by using an appropriate monomer or comonomer.

The other approach involves the introduction of a bulky unit into the polymer main chain, such as

tetraphenylethylene [2], 2,2'-binaphthalene [3] and benzopinacolone units [4].

Polyarylates are one of the most important kinds of thermally stable polymers that are used as high performance engineering plastics. The main target of researches in this field lay on providing new monomers and polymers in such a manner that these polymers have good solubility and high molecular weight in addition to good thermal properties.

This article deals with the preparation and characterization of polyarylates both from benzofuro[2,3-b]benzofuran-2,9-dicarbonyl chloride **1** [5] and various bisphenols and from 2,13-dihydroxy[7a,14c]dihydronaphtho[2,1-b]naphtho[1',2':4,5]furo[3,2-d]furan **4** [6] and various aromatic dicarboxylic acid

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chlorides by phase-transfer catalyzed two-phase polycondensation method.

## EXPERIMENTAL

### Materials

Benzofuro[2,3-b]benzofuran-2,9-dicarbonyl chloride **1** was prepared [5] from corresponding diacid compound that was prepared by oxidation of corresponding dimethyl compound, which itself was prepared from condensation of glyoxal with *p*-cresol in acidic media.

2,13-Dihydroxy[7a,14c]dihydronaphtho[2,1-b]-naphtho[1',2':4,5]furo[3,2-d] furan **4** was prepared [6] from condensation of glyoxal and 2,7-naphthalene diol in acidic media. 4,4'-Dicarbonyl chloride diphenyl sulphone (**5-a**) was prepared [7] in three steps, starting with toluene and chlorosulphonic acid. 4,4'-Dichloroformyl diphenyl ether (**5-b**) was prepared [8] in three steps, starting from diphenyl ether and acetyl chloride. 4,4'-Dibenzoyl chloride (**5-c**) was also prepared [9] in three steps, starting from biphenyl and acetyl chloride. Other diacid chlorides were synthesized by the reaction of the corresponding dicarboxylic acids with thionyl chloride in the presence of a few drops of *N,N'*-dimethylformamide (DMF). They included terephthaloyl chloride (**5-d**), and isophthaloyl chloride (**5-e**).

Various bisphenols were obtained commercially and used as received. They included 2,7-naphthalene diol (**2-a**), 1,5-naphthalene diol (**2-b**), 2,2-bis(4-hydroxyphenyl) propane (bisphenol A, **2-c**), 1,1-bis-2-naphthol (**2-d**), 1,8-dihydroxy anthraquinone (**2-e**), and 1,4-dihydroxy anthraquinone (**2-f**). Tetrabutylammonium bromide (TBAB) was used as received.

All the solvents employed were purified by distillation before use.

### Polymerization

Typical example of a phase-transfer polymerization is described as the following procedure.

*Polymer 4-a* Synthesized from Compounds **4** and **5-a** in a flask fitted with a stirrer, were placed compound **4** (0.855 g, 2.5 mmol), tetrabutylammonium bromide

(20 mg), and 1M aqueous sodium hydroxide (5.1 mL).

To the stirred solution was added a solution of **5-a** (0.857 g, 2.5 mmol) in dichloromethane (10 mL) all at once. The two-phase mixture was vigorously stirred at room temperature for 10 h under nitrogen. The mixture was then poured into 300 mL of hot water, containing a small amount of HCl.

The precipitated polymer was collected by filtration, washed thoroughly with refluxing methanol, and dried at 90 °C under vacuum. The yield was 92% and the inherent viscosity ( $\eta_{inh}$ ) of the polymer in DMF was 0.259 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (KBr) showed characteristic ester carbonyl absorb ion at 1740  $\text{cm}^{-1}$

$(\text{C}_{36}\text{H}_{18}\text{O}_6\text{S})_n$	C (%)	H (%)	S (%)
Analytical calc.	70.58	3.26	5.23
Found	70.35	3.18	5.16

Other polymers of **3** and **4** series were prepared by similar procedure.

### Measurements

IR Spectra were obtained using a Perkin-Elmer spectrometer 781.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were obtained using a Bruker Avance DPX 250 spectrometer. Mass spectra were recorded using a Shimadzu G. CMA-QP 1000 mass analyzer, and UV spectra using Unicam PU 8750 spectrometer. The inherent viscosities of polymers were determined by using a Cannon-Fenske viscometer No 100.

## RESULTS AND DISCUSSION

### Polymer Synthesis

All of the polyarylates are shown in Schemes I and II.

These polyesters were synthesized by phase-transfer catalyzed two-phase polycondensation method, under the same condition. The effect of the catalyst was found to be very important but it is still poorly understood. In this work tetrabutylammonium bromide (TBAB) was used as a phase-transfer agent in the preparation of polyarylates.

In order to choose the best method for

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**Table 1.** Different methods of polymerization.

Method of polymerization	Yield (%)	$\eta_{inh}$ (dL/g)
High-temperature method	43	0.081
Low-temperature method	62	0.094
Two-phase method (CH <sub>2</sub> Cl <sub>2</sub> as organic media)	86	0.232

**Table 2.** Optimization of two-phase method with different organic media.

Organic media	Yield (%)	$\eta_{inh}$ (dL/g)
Dichloromethane	86	0.232
Nitrobenzene	74	0.176
Chloroform + 1,2-dichloroethane	82	0.190

preparation of the polyarylates, two other methods were carried out in the polymerization of bisphenol A with compound 1. These methods included high and low temperature solution polycondensation methods.

In the high-temperature solution method [10], a mixture of compound 1 (2 mmol) and bisphenol A (2 mmol) in *o*-dichlorobenzene (20 mL) was heated with stirring at 200 °C for 15 h under nitrogen. In the low-temperature solution method [11], to a mixture of bisphenol A (2 mmol), pyridine (10 mL), and *sym*-tetrachloroethane (10 mL), mixture of compound 1 (2 mmol) in *sym*-tetrachloroethane (15 mL) was added dropwise.

The mixture was stirred at room temperature for 12 h under nitrogen.

**Table 3.** Solubility of the polyarylates.

Polymers Solvents	Polymers											
	3-a	3-b	3-c	3-d	3-e	3-f	6-a	6-b	6-c	6-d	6-e	6-f
DMAc	++	++	++	++	±	++	++	++	++	+	±	++
DMF	++	++	++	++	-	++	++	+	++	-	+	++
HMPA	+	+	++	++	-	++	+	+	+	-	-	++
1,1,2,2-Tetrachloroethane	++	+	++	++	+	++	+	++	-	-	+	++
1,2-Dichloroethane	+	+	++	++	-	++	-	-	-	-	-	+
H <sub>2</sub> SO <sub>4</sub> (conc.)	++	++	++	++	++	++	++	++	++	+	±	++

(++) Soluble at room temperature; (+) Soluble on heating; (±) Partially soluble or swelling; (-) Insoluble.

Both methods produced polymers with low yield and low inherent viscosities, as compared with two-phase polycondensation method. The results are summarized in Table 1.

Thus, in this work the two-phase polycondensation method was chosen as a very effective method for the synthesis of all of the polyarylates. On the other hand, the polymerization of bisphenol A with compound 1, by two-phase polycondensation method, was optimized by use of different solvents as organic media. The solvents that were examined for this optimization included dichloromethane, nitrobenzene, and a mixture of chloroform and 1,2-dichloroethane. The results that are summarized in Table 2 showed that dichloromethane are the best organic media.

### Polymer Characterization

Most of these polyarylates dissolve readily in a wide range of organic solvents such as: DMAc, DMF, HMPA, and concentrated H<sub>2</sub>SO<sub>4</sub>. They are, however, insoluble in solvents such as ethanol and methanol.

These solubility behaviours are summarized in Table 3.

IR bands, inherent viscosities ( $\eta_{inh}$ ), yield (%), 10 % weight loss (TGA), and UV ( $\lambda_{max}$ ) of these polyesters are summarized in Table 4. The IR spectra of all the polyesters showed characteristic ester carbonyl absorption at around 1750 cm<sup>-1</sup>. Inherent viscosities were obtained at 0.5 g/dL in DMF or concentrated H<sub>2</sub>SO<sub>4</sub>, at 30 °C, and  $\lambda_{max}$  was obtained in DMF solution of polymers. Elemental analysis of

Table 4. Characteristics of polyesters.

Polymers	Yield (%)	$\eta_{inh}$ (dL/g)	$\lambda_{max}$ (nm)	IR bands ( $cm^{-1}$ )	Temperature of 10 % wt. loss ( $^{\circ}C$ )
3-a	87	0.176 (DMF)	269.4	1740, 1625, 1520, 1490, 1290, 1270, 1230, 1210, 1100, 760	347.06
3-b	78	0.204 (DMF)	271.2	1740, 1620, 1520, 1490, 1400, 1290, 1270, 1230, 1210, 1100, 780, 760	352.9
3-c	86	0.232 (DMF)	272.6	2990, 1740, 1620, 1510, 1290, 1270, 1220, 1180, 840, 760	397.06
3-d	78	0.191 (DMF)	270.4	1740, 1620, 1520, 1490, 1290, 1270, 1210, 1100, 810, 750	364.7
3-e	52	0.281 (H <sub>2</sub> SO <sub>4</sub> )	268.5	1750, 1680, 1630, 1600, 1500, 1450, 1340, 1300, 1270, 1220, 1100, 740	-
3-f	65	0.148 (DMF)	269.8	1750, 1660, 1630, 1600, 1500, 1450, 1340, 1300, 1270, 1220, 1100, 740	302.9
6-a	92	0.259 (DMF)	269.5	1740, 1630, 1520, 1460, 1410, 1280, 1160, 1070, 830, 690, 620	420.8
6-b	95	0.301 (H <sub>2</sub> SO <sub>4</sub> )	274.1	1740, 1640, 1600, 1510, 1460, 1370, 1250, 1180, 1060, 840, 760, 690	455.8
6-c	90	0.232 (DMF)	273.1	1740, 1640, 1620, 1400, 1380, 1260, 1170, 1070, 830, 750	-
6-d	87	insoluble	270.9	1740, 1640, 1520, 1450, 1370, 1250, 1160, 1060, 1020, 830, 720	-
6-e	89	insoluble	271.8	1740, 1640, 1520, 1450, 1370, 1250, 1160, 1060, 1020, 830, 720	-
6-f	78	0.218 (DMF)	268.2	1740, 1640, 1620, 1400, 1290, 1200, 1170, 1100, 840, 760	432.3

Table 5. Elemental analysis of polyesters.

Polymers	Calculated			Found		
	C (%)	H (%)	S (%)	C (%)	H (%)	S (%)
3-a	72.28	2.88	-	73.98	2.90	-
3-b	72.28	2.88	-	69.1	3.20	-
3-c	76.22	4.13	-	70.2	4.30	-
3-d	79.12	3.32	-	75.4	3.80	-
3-e	72.01	2.42	-	69.6	2.80	-
3-f	72.01	2.42	-	72.1	2.40	-
6-a	70.58	3.26	5.23	70.35	3.18	5.16
6-b	76.59	3.54	-	76.63	3.48	-
6-c	78.83	3.65	-	78.54	3.48	-
6-d	78.27	3.41	-	76.4	3.80	-
6-e	76.27	3.41	-	76.12	3.38	-
6-f	75.75	3.01	-	75.2	3.50	-

polyesters is presented in Table 5.

## CONCLUSION

New polyarylates containing benzofuro and naphthafuro units were synthesized by two-phase method. IR and UV spectrophotometers were employed for the confirmation of the chemical structures of these polymers. Inherent viscosities and their thermal behaviour were studied, and finally the elemental analysis was carried out as well. The synthesized polyarylates exhibit excellent solubility in organic solvents and good thermal properties.

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