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Copoly(Aryl Ether)s Containing 1,10-Phenanthroline Moieties

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ABSTRACT

Poly(aryl ether)s were synthesized by reaction of 4,7-dichloro-3,8-diphenyl-1,10-phenanthroline and 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline with bisphenol A (BPA) in the presence of potassium carbonate in *N,N*-dimethylacetamide or *N*-methylpyrrolidinone. High molecular weight homopolymers could not be prepared because of the insolubility of the polymers resulting in premature precipitation from the reaction mixture. Soluble, high molecular weight copolymers were readily prepared containing up to 70 mol% of the 1,10-phenanthroline moieties. The copolymers were all highly fluorescent with blue emission.

Key Words: Copoly(aryl ether)s; Phenanthroline; Fluorescence.

INTRODUCTION

Schmittel recently described the synthesis of some 4,7-dihalogenated 1,10-phenanthrolines for use as soluble precursors for the preparation of macrocyclic oligophenanthrolines. The halide groups were shown to be readily displaced in high yield by a nucleophilic substitution reaction with phenoxide ions or by a Heck coupling reaction with

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acetylenes.^[1] He later described the synthesis of some macrocycles joined by ethynyl linkages.^[2]

Phenanthrolines are of current interest for use in electroluminescent (EL) cells because they are electron transport materials,^[3,4] as well as having blue light-emitting electroluminescence.^[5] Bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is also often used as a barrier layer to confine radiative recombinations in the hole transport layer in EL cells.^[6] Furthermore, metal chelates of phenanthrolines that emit at much longer wavelengths have been extensively studied.^[7,8]

We have described the synthesis of poly(aryl ether)s that contain hole transport, electron transport, and electroluminescent functionalities.^[9-11] This paper will describe the synthesis of some copoly(aryl ether)s that incorporate 1,10-phenanthroline moieties into the high molecular weight linear polymers by reaction of 4,7-dihalogenated 1,10-phenanthrolines with bisphenoxides.

EXPERIMENTAL

Materials

Bis(4-fluorophenyl)sulfone and bisphenol A (BPA) were purchased from Aldrich Chemicals Inc. *N,N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were refluxed and distilled over P₂O₅ and then kept over molecular sieves in nitrogen. Acetic acid, potassium carbonate, reagent grade, toluene, DMAc, chloroform, and methanol were obtained from commercial sources.

Measurements

The glass transition temperatures and 5% wt. loss temperatures were determined on Seiko 5200 TGA/DTA and Seiko 220 differential scanning calorimetric (DSC) instruments at a heating rate of 20°C min⁻¹ under nitrogen. The reported *T_g* and *T_d* values were recorded after first holding the samples at 150°C for 10 min in the thermogravimetric analysis (TGA). The ¹H NMR spectra were recorded on a Varian Mercury 300 spectrometer with CDCl₃ or DMSO-d as solvent vs. tetramethylsilane. Mass spectra were measured on a Kratos MS25RFA at an ionization energy of 70 eV. Melting points were determined on a Fisher-Johns melting point apparatus. Inherent viscosity measurement was determined by using a Ubbelohde dilution viscometer. UV-VIS absorption spectra were recorded on a Cary 50 spectrophotometer. Photoluminescence (PL) measurements were performed on a SPEX FL-3 fluorescence spectrometer.

General Procedure for Synthesis of Polymers and Copolymers from Bisphenol A

A typical example for preparation of polymers is as follows. To a 25 mL three neck round-bottom flask equipped with a magnetic stirrer, a Dean-Stark trap full of toluene and condenser and a nitrogen inlet, was added BPA (0.2000 g, 0.876 mmol) potassium carbonate (0.2679 g, 1.927 mmol), 2 mL DMAc and 2 mL toluene. The reaction mixture



was heated until the toluene began to reflux with the reaction mixture maintained at 130–140°C. During this stage of the reaction, the solution underwent a color change from transparent to slight pale yellow. The toluene was then removed by distillation and the reaction mixture was cooled. After cooling, bis(4-fluorophenyl)sulfone and dichloro-monomer (**5** or **10**) were added. The mixture was heated to 160–170°C and kept at low reflux until a very viscous solution was obtained. After cooling, 1 mL DMAc or chloroform was added to dilute the reaction mixture, and then the viscous solution was slowly dropped into 50 mL of methanol containing several drops of acetic acid with vigorous stirring. The polymer precipitated out as a fine fiber and was dissolved in 20 mL of chloroform followed by filtration through a thin layer of celite. The filtrate was concentrated and dropped into 40 mL methanol with stirring followed by filtration to isolate the polymer. The purified product, a white fiber, was dried at 80°C under vacuum for 24 h.

When NaH was used as a base the procedure was as follows. To a 25 mL three neck round-bottom flask equipped with a magnetic stirrer, condenser and with nitrogen flowing, was added BPA (**12**; 0.2000 g, 0.876 mmol), sodium hydride (0.0921 g, 3.52 mmol), and 2 mL DMAc were charged to the flask. The reaction mixture was heated to 80–90°C and refluxed for 1 hr, and then cooled down. After cooling, the bis(4-fluorophenyl)-sulfone and dichloro-monomer (**5** or **10**) were added. The mixture was heated to 100–110°C and kept at low reflux until a very viscous solution was obtained. The resulting polymer was purified as described above.

Homopolymers were synthesized by a similar method.

General Procedure for Synthesis of Polymers from the Biscarbamate of Bisphenol A 11

A typical example is given as follows. A 25 mL three-necked round-bottomed flask with nitrogen inlet, a magnetic stirrer, and a condenser was flushed with nitrogen and then charged with biscarbamate of BPA **11** (0.4000 g, 1.004 mmol), bis(4-fluorophenyl)sulfone and dichloro-monomer (**5** or **10**), K₂CO₃ (0.3069 g, 2.208 mmol), and DMAc (4 mL). The reaction mixture was heated to 140–150°C under nitrogen. After 2–3 h, the solution became very viscous and the reaction was stopped. After cooling, the polymer solution was diluted with 2 mL of DMAc and poured into 80 mL of methanol containing several drops of acetic acid to precipitate out the polymer. The resulting polymer was purified as described above.

Homopolymers were synthesized by a similar method.

RESULTS AND DISCUSSION

Synthesis of Poly(Arylene Ether)s from Monomer **5** (Table 1)

The monomer 4,7-dichloro-3, 8-diphenyl-1, 10-phenanthroline **5** was prepared according to the literature^[1] (Sch. 1). The biscarbamate of BPA **11** was prepared as previously described.^[12]

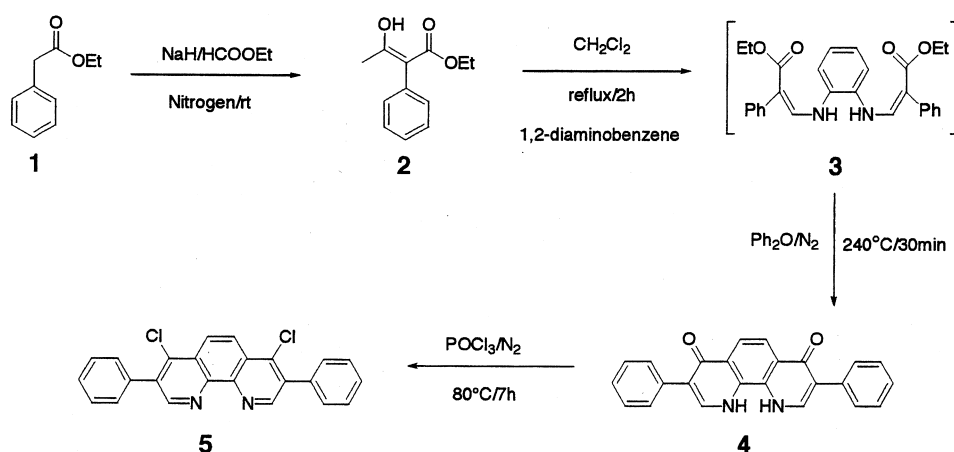


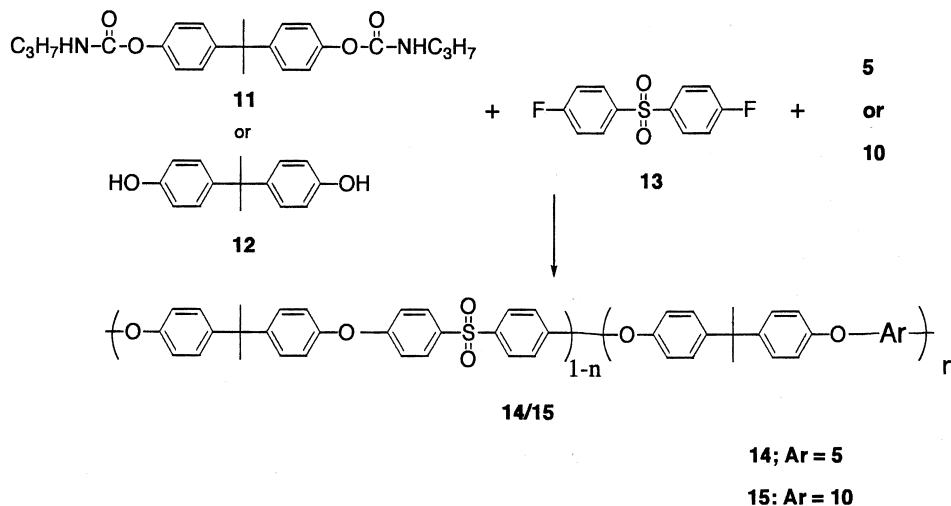
Table 1. Polymers and copolymers from monomer **5**.

Polymer	<i>n</i>	Bisphenol	Solvent	Yield (%)	η_{inh}	T_g (°C)	$T_d -5\%$ (°C)
14a	0.1	BPA	DMAc	94	0.31	203	474
14b	0.3	BPA	DMAc	93	0.39	218	462
14c	0.7	BPA	DMAc	87	0.18	244	469
14d	0.7	Biscarbamate	DMAc	95	0.55	247	486
14e	1.0	Biscarbamate	DMAc	88 ^a	0.03	247	476
14f	1.0	BPA	NMP	71 ^a	0.12	264	455

^aPolymer precipitated from reaction mixture.

When BPA reacted with the monomer **5** and *bis*(4-fluorophenyl)sulfone **13** to prepare the copolymers **14** (Sch. 2) DMAc was used as a solvent and stringently anhydrous conditions had to be used to remove the water in the solvent or that formed during the reaction. All of the polymerization reactions proceeded satisfactorily until the content of monomer **5** reached 70 mol% (Table 1). However, the yield of polymer **14c** was less than 90%, and the solution viscosity was only 0.18 dL g⁻¹. We thought the reason for the low molecular weight might be traces of water in the solvent or water formed during the reaction resulting in hydrolysis of some of the monomer. In order to find out if water can really interfere with the monomer **5**, we added one drop of water and K₂CO₃ to **5** in chloroform at reflux for several hours. The NMR spectrum of the product was complicated indicating that water did affect **5**. In order to remove the effect of water completely, we dried the potassium carbonate at 350°C in vacuum for 14 h to remove the moisture and utilized the biscarbamate instead of the bisphenol. Wang et al. had demonstrated that by using a masked biphenol such as a biscarbamate^[12] polymerization reactions proceeded without the usual dehydration step since there is no water formed during the reaction but only highly volatile propylamine that does not interfere with the reaction. We later demonstrated that much cleaner polymers with much lower molecular weight dispersities

**Scheme 1.** Synthesis of monomer **5**.



Scheme 2. Preparation of copolymers **14** and **15**.

were obtained when the a bis-carbamate was used.^[10] When the bis-carbamate of BPA was used, copolymer **14d** was obtained with η_{inh} of 0.55 compared to **14c** with η_{inh} 0.18 when BPA was used. However, attempts at synthesis of the homopolymer (**14e** and **14f**) with or without the bis-carbamate gave only low molecular weight polymers since the homopolymer precipitated from the reaction mixture prematurely. We tested several other solvents for the polymerization reaction, but none of them gave solutions of the homopolymer.

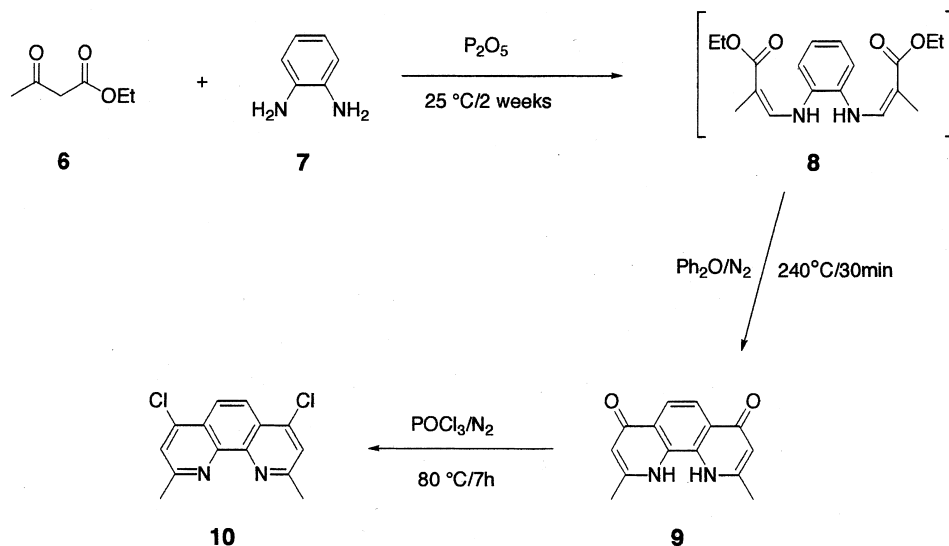
Synthesis of Poly(Arylene Ether)s from Monomer 10

The monomer 4,7-dichloro-2, 9-dimethyl-1,10-phenanthroline **10** was prepared by the method described previously^[13] (Sch. 3). The synthesis of poly(arylene ether)s from **10** showed similar phenomena as those of polymers from **5**. The polymerization went smoothly with copolymers containing 10–30% of **10**, but when the content of **10** was increased to 70% difficulties were encountered and only low molecular weight polymer **15c** was obtained (Table 2). This monomer was also shown to be sensitive to water. In order to avoid the water effect entirely an excess of NaH was used as base and high molecular weight copolymer **15e** was obtained in good yield. Homopolymer **15f** was prepared in the same way but a small amount of precipitate appeared in the reaction mixture during the reaction. When NMP was used as solvent, homopolymer **15g** with higher yield and viscosity was obtained. After cooling the reaction mixture the homopolymer separated from the solution.

Properties of Poly(Arylene Ether)s 14 and 15

Copolymers containing up to 70% of the phenanthroline moieties (**14a, b, d, and 15a, b, e**) were soluble in chloroform and could be cast into tough, flexible films. The





Scheme 3. Synthesis of monomer 10.

homopolymers did not give flexible films. We were not able to obtain molecular weight data by gel permeation chromatography since the polymers were strongly adsorbed on the columns.

The T_g s of the copolymers increased with increasing amount of monomer 5 or 10 as expected since the phenanthroline containing monomers are large, rigid groups (Tables 1 and 2). The T_g s of the homopolymers are the highest in each series of polymers, 253 °C and 279 °C, respectively.

From TGA, all the T_d s (−5% wt. loss) of polymers 14 series were above 450 °C and the T_d s decrease with increasing amounts of the monomer 5 in the polymerization reaction (Tables 1 and 2). Polymer 15 shows similar behavior but all of the T_d s were lower than those of 14, which are all around 400 °C. The stability of polymers from 10 would be expected to be lower than those from 5, since it is a completely aromatic structure.

Table 2. Polymers and copolymers from monomer 10.

Polymer	<i>n</i>	Base	Bisphenol	Solvent	Yield (%)	η_{inh}	T_g (°C)	T_d −5% (°C)
15a	0.1	K ₂ CO ₃	BPA	DMAc	96	0.30	205	436
15b	0.3	K ₂ CO ₃	BPA	DMAc	93	0.36	218	426
15c	0.7	K ₂ CO ₃	BPA	DMAc	87	0.18	250	347
15d	0.7	NaH	BPA	DMAc	94	0.33	250	391
15e	1.0	NaH	BPA	DMAc	87 ^a	0.31	264	391
15f	1.0	K ₂ CO ₃	BPA	NMP	92	0.35	279	386

^aPolymer precipitated from reaction mixture.



Table 3. UV absorption and fluorescent properties of polymers **14** and **15**.

Polymer	λ_{UV} (nm) ^a	λ_{em} (nm) ^b
14a	270	390, 406
14b	276, 308	390, 405
14c	280, 308	370, 395, 410
15a	268	380, 400
15b	267, 310	367, 381, 401
15d	266, 311, 330, 347	360, 375, 390, 410
15f	266, 310, 330, 346	365, 380, 410

^aMaximum UV–VIS spectra absorption wavelength.^bMaximum emission wavelength.

UV Absorbance and Photoluminescence Properties

Copolymers **14** and **15** derived from monomers **5** and **10** have similar UV absorption, indicating that the absorption at the longest wavelength can be ascribed to the phenanthroline moieties (Table 3).

The polymers show strong blue photoluminescence in chloroform when excited at their absorption maximums.

CONCLUSION

Two phenanthroline-containing monomers **5** and **10** were prepared according to the literature.^[1,13] Two series of poly(arylene ether)s were synthesized from these monomers. The monomers are very sensitive to water so that careful removal of the water, the use of sodium hydride as base, or the use of carbamates of the bisphenol was necessary in order to obtain high molecular weight polymers. The copolymers and homopolymers synthesized exhibited high glass transition temperatures and good thermal stability. The highest T_g and 5% wt. loss temperatures T_d for this series of polymers were 278°C and 479°C, respectively. The glass transition temperatures of the copolymers increase with the increasing amount of phenanthroline moieties, but the T_d s decrease. The two series of poly(arylene ether)s copolymers were colorless and could be cast from chloroform solution to give pale yellow, transparent and tough films. All of the polymers showed strong blue fluorescence.

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