Articles

Colored Poly(arylene ether)s Containing Benzoylenebenzimidazole, Phthaloperinone, and Phthalocyanine Moieties

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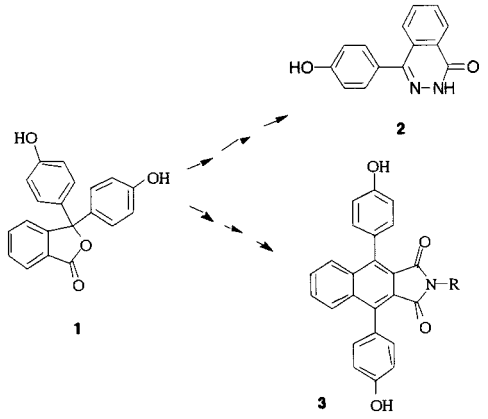
ABSTRACT: The synthesis of a novel biphenol from phenolphthalein that contains an anhydride group is described. The biphenol readily undergoes further reactions. Two biphenols that contain the 1,2-benzoylenebisbenzimidazole or phthaloperin-12-one moiety, respectively, were prepared from the biphenol anhydride by reaction with aromatic diamines, *o*-phenylenediamine, and 1,8-diaminonaphthalene. Two series of poly(arylene ether)s were synthesized from these heterocyclic containing biphenols. The polymers and copolymers synthesized exhibited extremely high glass transition temperatures and excellent thermooxidative stability. The highest T_g and 5% weight loss temperatures of these polymers were almost 360 and 600 °C, respectively. The two series of poly(arylene ether)s were yellow and orange in color, respectively. These poly(arylene ether)s have good solubility and can be cast from solution into tough films. The glass transition temperatures of the copolymers increased with increasing heterocycle content, while the solubilities decreased. We have also synthesized, utilizing a biphenol containing the dicyanoarylene moiety, a polymer that contains the phthalocyanine copper(II) moiety that has a blue color. Copolymers containing all three moieties have been synthesized that have a permanent black color since they absorb over the entire visible spectral region from 300 to 750 nm. All of the polymers were highly fluorescent materials with emission wavenumbers ranging from 400 to 750 nm.

Introduction

Phenolphthalein (**1**) is potentially an inexpensive material that is readily synthesized from phthalic anhydride and phenol in the presence of acid catalysts, such as zinc chloride.[1,2] More environmentally friendly processes using cation-exchange resins as catalysts have also been reported.[3,4] Phenolphthalein is a biphenol with a lactone group between the two phenolic groups, and it has been used to synthesize aromatic polyesters,[5] aromatic polycarbonates,[6] and poly(arylene ether ketone)s or sulfones.[7] These polymers generally have high glass transition temperatures, but probably because of possible reactions involving the lactone ring, problems have often arisen in the processing of the resulting polymers.

We have previously reported the synthesis of two new classes of monomers which are derived from phenolphthalein and can be polymerized to give polymers with very high glass transition temperatures which are very thermooxidatively stable. (Scheme 1) The phthalazinone **2** has an NH group which is acidic and behaves like a phenol so that under conditions that produce poly(arylene ether)s high molecular weight polymers can be prepared which have glass transition temperatures in the range 250−350 °C.[8,9] The polymers contain O−C and N−C linkages. Extensive studies on the processing and modification of these polymers have been carried out.[10−14] Polymers that contain only N−C linkages have also been synthesized from bisphthalazinones.[15]

Scheme 1. Synthesis of Monomers 2 and 3



We have also reported the synthesis of biphenol monomers, e.g., **3**, 3,8-bis(4-hydroxyphenyl)-*N*-phenyl-1,2-naphthalimide, from phenolphthalein. From these biphenols with different N-substituents, high molecular weight poly(arylene ether)s with very high T_gs have been prepared.[16,17] The imidoaryl group can undergo transimidization reactions with amino compounds to form *N*-amino, *N*-alkyl, and *N*-aliphatic acid derivatives.[18]

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We report herein the synthesis of the parent 3,8-bis-(4-hydroxyphenyl)-1,2-naphthalic anhydride **7** from phenolphthalein. This biphenol has an anhydride pendant group; therefore, it is very easily functionalizable and can readily react with amines. From the biphenol, two novel biphenols have been synthesized via reaction with aromatic *o*-diamines. They can be utilized to synthesize a new class of fluorescent yellow to orange-colored amorphous, thermally stable polymers with very high T_gs. In this paper, by incorporation of monomeric units containing phthalocyanine moieties, we have also demonstrated the preparation of polymers which absorb over the complete range of the visible spectrum and are, therefore, black.

Experimental Section

Materials. 4,4′-Difluorobenzophenone, bis(4-fluorophenyl)-sulfone, 1,2-diaminobenzene, 1,8-diaminonaphthalene, maleic anhydride, and *o*-phthalonitrile were purchased from Aldrich Chemicals Inc. Phenolphthalein was purchased from TCI America and used as received. 1,3-Bis(4-fluorobenzoyl)benzene was synthesized according to the published procedure.[14] Bis-(4-fluorophenyl)phenylphosphine oxide was prepared by a Grignard technique.[15] 2,3-Dicyano-1,4-(4-hydroxybenzene) was made according to the procedure developed in this laboratory.[16] Sulfuric acid, anhydrous potassium carbonate, reagent-grade *N*-methylpyrollidinone (NMP), sulfolane, quinoline, toluene, *N*-cyclohexylpyrrolidinone, chloroform, methanol, and acetic acid were obtained from commercial sources and used as received.

Instrumentation. The glass transition temperatures and 5% weight 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 under nitrogen flow. The reported T_g values were recorded from the second scan after first heating and quenching. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI−TOF−MS) analyses were performed on a Kratos KOMPACT MALDI−TOF−MS. The analyte consisted of 1:4:2 (by weight) of sample, lithium bromide, and 1,8,9-trihydroxy-anthracene (dithranol) matrix. All spectra were obtained in the reflectron mode. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. NMR data were recorded at 270 MHz on a Gemini 270 Hz NMR instrument (JEOL-270-CPF) and are listed in parts per million downfield from tetramethylsilane (TMS). Melting points were taken on a Fisher-Johns melting point apparatus. UV−visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescent spectra were performed on a Fluoro Max-2 spectrophotometer.

Preparation of Isobenzofuran 5. To a dry 250 mL round-bottom flask equipped with a mechanical stirrer was added 20 g (62.4 mmol) of dry, finely powdered phenolphthalein (**1**). The flask was immersed in an ice−acetone bath for 10 min, and then concentrated sulfuric acid (65 mL, also cooled to 0 °C) was poured into the flask. The mixture was vigorously stirred for 2−3 min to dissolve all of the solids The mixture was then stirred for another 7−8 min at this temperature. The inner temperature of the flask was kept at around 5 °C. The resulting yellow-brown slurry was quickly poured into a 2 L beaker containing 1200 mL ice−water and the remaining solids in the flask were removed with a spatula, while washing with small aliquots of cold water (20−30 mL × 4). The green-yellow solids were combined, separated by filtration, and washed with 200 mL cold water and dried on the filter for 5−15 min before being used directly in the following Diels−Alder reaction.

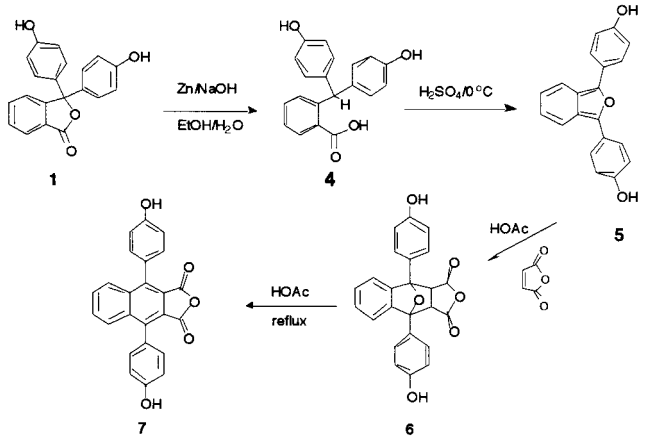
Preparation of Anhydride Biphenol 7. To a 500 mL round-bottom flask containing 6.0 g (61.22 mmol) of maleic anhydride in 130 mL of acetic acid was added the isobenzofuran **5**. The mixture was quickly heated to the temperature of reflux. After 15−20 min, a yellow product **6** precipitated out from the reaction mixture. This product was not isolated since the Diels−Alder adduct undergoes further dehydration to form final product **7** in the presence of residual sulfuric acid from the acid-catalyzed rearrangement. The reaction was continued at this temperature for another 2 h to complete the reaction. The product was isolated by filtration and washed twice with a minimum amount of acetic acid. The final product was dried under vacuum at 70−80 °C for 48 h. Pure yellow powder **7** was obtained in 73.5% yield. (mp 245−247 °C (dec). ^{1}H NMR (DMSO): δ (ppm) 9.82 (s, 2H, −OH), 7.94 (m, 2H), 7.82 (m, 2H), 7.31 (d, 4H, J = 9.60 Hz), 6.98 (d, 4H, J = 9.60 Hz). MALDI−TOF−MS: single peak found, 382.40; calcd for $C_{24}H_{14}O_5$, 382.36; hplc, 99.7%.

Preparation of 8. To a 100 mL round-bottom flask containing 4.0 g (10.46 mmol) of biphenol **7** in 45 mL of NMP was added 1.2 g (11.10 mmol) of 1,2-diaminobenzene. The mixture was slowly heated to the temperature of reflux. The color of the reaction mixture changed from yellow (60 °C) to green-yellow (90 °C), deep green (100 °C), and finally brown-red (130 °C). The reaction was kept at the temperature of reflux for 12 h, and the reaction was followed periodically by HPLC. After 12 h the reaction mixture was cooled to room temperature, and a yellow product precipitated from the reaction mixture. The product was isolated by filtration and washed with a minimum amount of NMP followed by recrystallization from NMP. The solid was dried under high vacuum at 130 °C for 24 h. A yellow powder **8** was obtained in excellent yield (99.3%). No mp below 320 °C. ^{1}H NMR (DMSO): δ (ppm) 9.79 (s, 1H, −OH), 9.76 (s, 1H, −OH), 7.82−7.60 (m, 6H), 7.45−7.25 (m, 6H), 7.01 (t, 4H, J = 8.00 Hz). MALDI−TOF−MS: single peak found, 454.50; calcd for $C_{30}H_{18}N_2O_3$, 454.48; hplc, 99.4%.

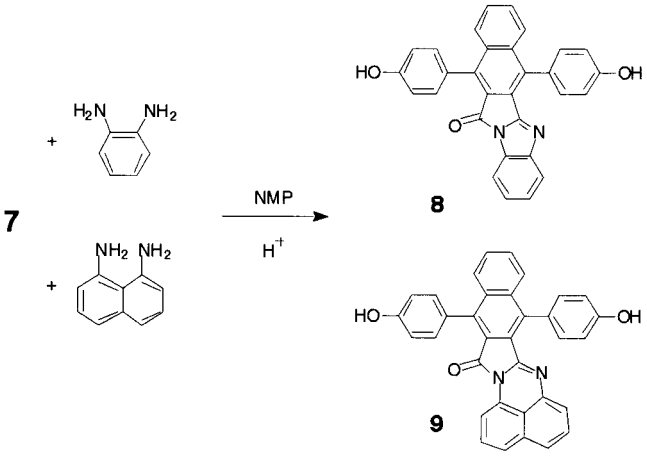
Preparation of 9. To a 100 mL round-bottom flask containing 4.0 g (10.46 mmol) of biphenol **7** in 40 mL of NMP was added 1.76 g (11.10 mmol) of 1,8-diaminonaphthalene. Two drops of methanesulfonic acid were added as catalyst, and then the mixture was slowly heated to 100 °C and kept at that temperature for 0.5 h. The mixture was heated to the temperature of reflux and maintained at that temperature for another 24 h. The reaction was periodically followed by HPLC. After 24 h, the dark-red reaction mixture was cooled to room temperature, and an orange product precipitated out from the reaction mixture. The product was isolated by filtration and washed with a minimum amount of NMP followed by recrystallization from NMP. The solid was dried in vacuuo at 130 °C for 24 h. An orange powder **9** was obtained in quantitative yield (∼100%). No melting point was observed below 420 °C. ^{1}H NMR (DMSO): δ (ppm) 9.75 (s, 1H, −OH), 9.56 (s, 1H, −OH), 7.92−7.64 (m, 8H), 7.53−7.25 (m, 6H), 6.98 (d, 4H, J = 7.87 Hz). MALDI−TOF−MS: single peak found 504.60; calcd for $C_{34}H_{20}N_2O_3$, 504.53; hplc, 99.6%.

General Procedure for Synthesis of Polymers. A typical example for polymer **11a** is given as follows. To a 25 mL three-neck round-bottom flask equipped with a magnetic stirrer, a Dean−Stark trap and condenser, and a nitrogen inlet were added bis(4-fluorophenyl)sulfone (0.2288 g, 0.9 mmol) and biphenol **9** (0.4541 g, 0.9 mmol). Then 7 mL of sulfolane, 7 mL of toluene, and potassium carbonate (0.1932 g, 1.26 mmol) were charged to the reaction flask. Under an atmosphere of nitrogen, the solution was heated to 145 °C and maintained at that temperature for 2 h to remove all water by means of a Dean−Stark trap using toluene. The polycondensation was continued for 1−3 h at 180 °C (oil bath temperature). When the reaction mixture became too viscous, 2−3 mL of sulfolane was added into the reactor. The reaction mixture was diluted three more times with sulfolane, and then the viscous solution was slowly poured into 100 mL of methanol with vigorous stirring. The polymer **11a** precipitated out as a fine fiber, and the material was redissolved in 50 mL of chloroform followed by filtration through a thin layer of Celite. The filtrate was slowly poured into 200 mL of methanol with stirring, and then the resulting polymer was separated by filtration. The purified product, an orange-red fiber, was dried at 110 °C under vacuum for 24 h.

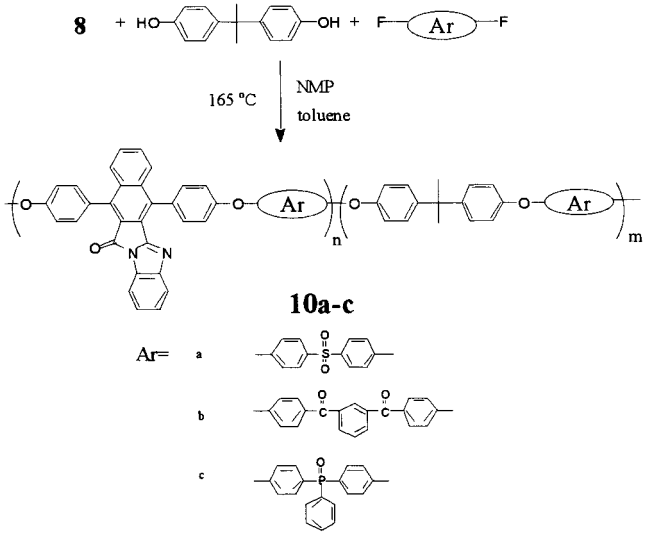
Scheme 2. Synthesis of Anhydride-Containing Biphenol 7



Scheme 3. Synthesis of Biphenols 8 and 9



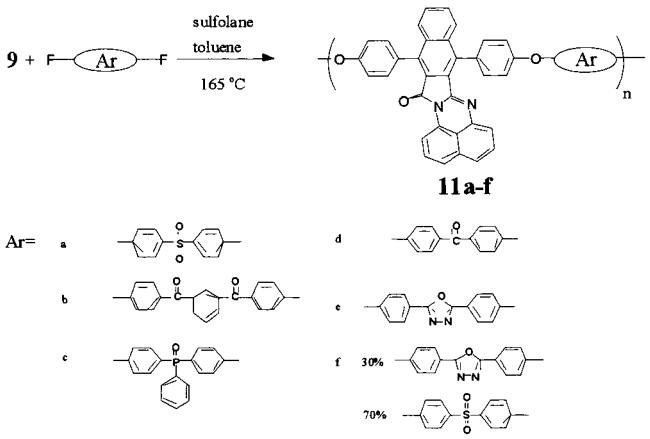
Scheme 4. Synthesis of Copolymers 10a−c



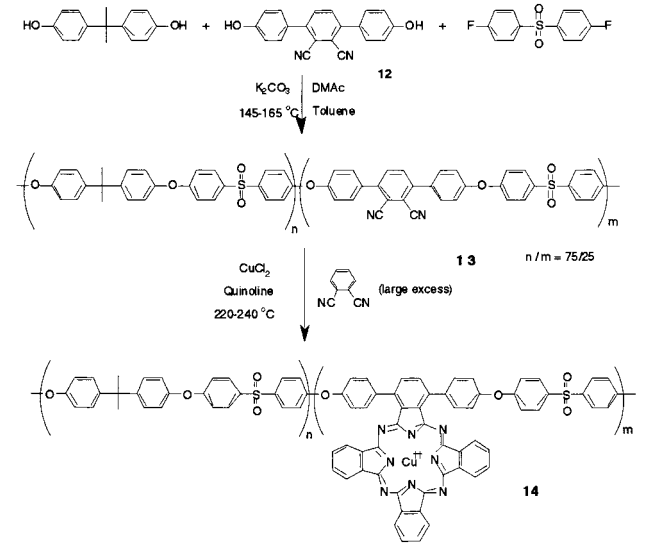
Homopolymers and copolymers **10a−c** were synthesized by a similar method except that NMP was used as solvent.

Procedure for Synthesis of Polymer 13. As shown in Scheme 6, the procedure for the synthesis of the precursor polymer **12** containing a dicyanoarylene group is similar to that for polymers **10** and **11**. For the synthesis of polymer **13**, to a 250 mL three-neck flask equipped with a condenser and argon gas inlet were added the above dicyanoarylene group containing precursor polymer (1.0 g; 0.539 mmol), *o*-phthalonitrile (1.0 g, 7.805 mmol), $CuCl_2$ powder (0.6 g), and 150 mL of quinoline. Under an atmosphere of argon, the mixture was heated to 210−230 °C for 3 h. During this period, the reaction mixture became dark blue and some dark blue solids (copper phthalocyanine) separated. The mixture was poured into a mixture of 300 mL of methanol and 20 mL of hydrochloric acid (36%), with vigorous stirring. The deep-green to blue particles were washed with acetone and ethanol, and then the polymer was separated from the copper phthalocyanine by chloroform, using a Soxhlet extractor. The deep-green to blue chloroform solution was concentrated and precipitated into methanol. A dark blue fibrous material was produced and dried at 130 °C in vacuo.

Scheme 5. Synthesis of Polymers 11a−f

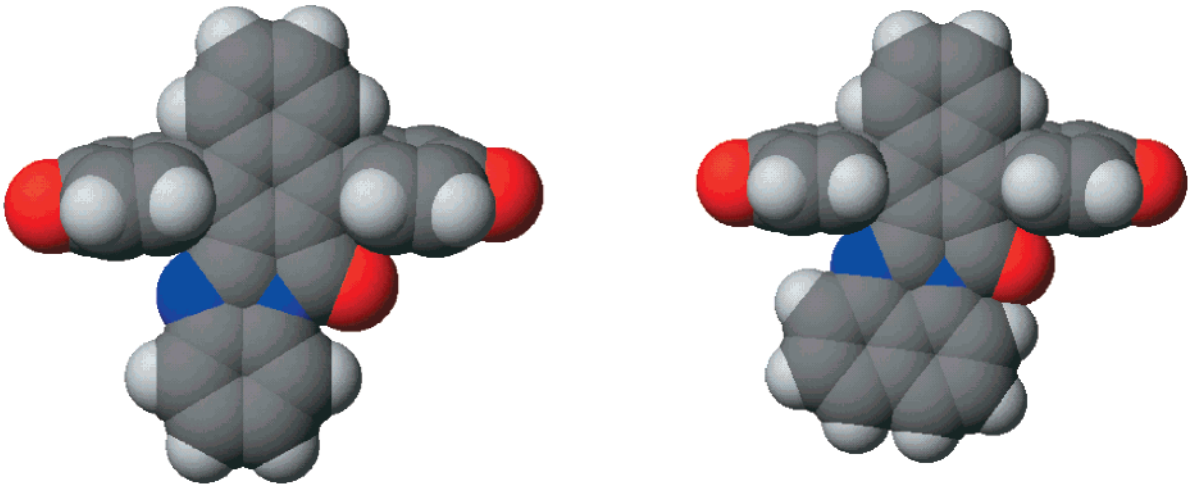


Scheme 6. Synthesis of Polymers 13 and 14



Results and Discussion

Synthesis of Anhydride Biphenol 7. Phenolphthalein (**1**) has been used as a biphenol in the synthesis of polymers.[5−7] The resulting polymers are not thermooxidatively stable at high temperature due to the instability of the lactone group. Blicke[19,20] demonstrated that phenolphthalein could be quantitatively reduced to phenolphthalin **4** (Scheme 1) by zinc metal. The phenolphthalin was then rearranged in a strong acid, such as sulfuric acid, into isobenzofuran **5** in a reasonable yield. To minimize the sulfonation of isobenzofuran **3**, the sulfuric acid was cooled to about 0 °C, and then poured quickly into compound **4**. A minimum amount of sulfuric acid should be used for the reaction (generally 1.25:1.00 volume/mass of H_2SO_4/**4**). The reaction was run at about 0 °C for 5−10 min. Longer reaction times result in the sulfonation of **3**. The isobenzofuran **5,** was



8 **9**

Figure 1. Energy-minimized molecular models of biphenols **8** and **9**.

isolated by filtration and washed only once with ice−water as rapidly as possible. The green solids were dried on the filter for 5−20 min before being directly used for the next reaction step.

The Diels−Alder reaction with N-substituted maleimides was carried out a number of years ago to produce imidobiphenols.[16,17] At that time we attempted to prepare the anhydride biphenol **7** directly by reaction with maleic anhydride, but we were unsuccessful.[21] In this work, we have carried out this reaction in a number of solvents, i.e., anhydrous ethanol, benzene, and ethyl acetate giving a mixture of products with a low yield of **7**. We have now found that when acetic acid is used as solvent, a very clean reaction was achieved to produce anhydride biphenol **7** in an overall yield of 73.5% based on the starting material **1**. Biphenol **7** is fluorescent under UV light at 360 nm.

Synthesis of Biphenols 8 and 9. The reaction of *o*-phenylenediamine with phthalic anhydride has been extensively studied as a model for the formation of polymers containing the 1,2-benzoylenebis(benzimidazole) ladder structure that can be obtained by reaction of dianhydrides with tetraamines.[22,23]A similar reaction with 1,8-diaminonaphthalene yields phthaloperin-12-one.[24]

The reaction of biphenol anhydride **7** with *o*-phenylenediamine or 1,8-diaminonaphthalene in NMP and in the presence of acid catalyst yields biphenols **8**, which contains a benzoylenebenzimidazole moiety, and **9**, which contains a phthaloperinone moiety (Scheme 3) in quantitative yield. Biphenol **8** does not have a melting point, and biphenol **9** has a melting point of 418.7 °C with decomposition. Biphenols **8** and **9** are yellow and orange-red in color, respectively and they are both highly fluorescent. The energy minimized molecular models of **8** and **9** are shown as Figure 1. The two phenolic moieties are almost perpendicular to the planes of the very bulky heterocyclic moieties. The bukyl heterocyclic groups are unsymmetrical therefore the chemical shifts of the two −OH protons in both **8** and **9** are separated from each other. Random arrangement of these A−B unsymmetrical monomers in poly(aryl ether)s might therefore be expected to enhance the solubility of the polymers derived from these two novel biphenols.

Synthesis of Poly(arylene ether)s from Biphenols 8 and 9. When imidoaryl biphenols **3** were polymerized with activated difluoro compounds to give poly(aryl ether)s, stringently anhydrous conditions had to be used to avoid the hydrolysis of the imide groups.[16] Biphenols **8** and **9** are much more stable than monomers containing the imidoaryl group under the basic conditions of the reaction. Polymers **10** and **11** were synthesized in NMP and sulfolane, respectively (Schemes 4 and 5). During the polymerization reactions, the reaction mixtures became very viscous and could not be stirred; therefore, additional solvents were added. The high molecular weight polymers **10** and **11** are yellow and orange-red in color, respectively.

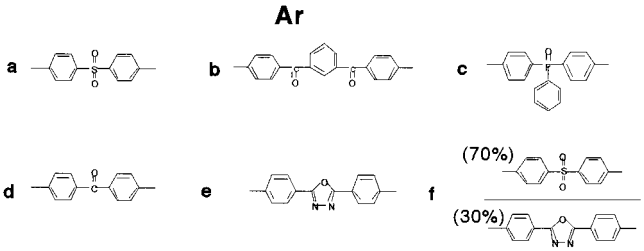
Properties of Poly(arylene ether)s 10 and 11. Poly(arylene ether) homopolymers **10a**−**c** ($m = 0$) were synthesized by reaction of **8** with activated dihalides. In addition a series of copolymers **10a**−**c** were synthesized by replacement of some of **8** with BPA. All of the polymers except **10a** were soluble in NMP, DMSO and hot *s*-tetrachloroethane (TCE). Except for homopolymer **10a** they can be dissolved in NMP and cast into tough, clear, and flexible films with a yellow color that indicates that these polymers have high molecular weights. No GPC data are available due to the poor solubility in chloroform. Only low molecular weight polymer was obtained for polymer **10a1** because the oligomers precipitated out of the reaction mixture during the polymerization.

The thermal properties of **10a**−**c** are listed in Table 1. The T_gs for polymers **10a** increase linearly with increasing biphenol **8** content as expected. The introduction of the very rigid benzimidazolobenzoisoindolinone moiety in the polymeric backbone leads to an increase of molecular rigidity in these polymers. From an energy minimized molecular model of the biphenol **8** (Figure 1), we can see that there is restricted rotation of both aryl linkages which results in rigidity and high T_gs of polymers **10a1**. The homopolysulfone derived from biphenol **8**, i.e., polymer **10a**, has a T_g of 337 °C although its molecular weight is not very high. The thermogravimetric data as shown in Table 1 indicate that the polymers **10a** are extremely thermooxidatively stable. All the $T_{-5\%}$ values are higher than 500 °C except for polymer **10a**. Compared with those for the poly-

Table 1. Properties of Polymers 10a−c

polymer	% **8**	% BPA	T_g °C 1st scan	T_g °C 2nd scan	TGA $T_{-5\%}$, °C
10a	100	0	337	343	410
10a1	60	40	272	280	517
10a2	40	60	248	253	517
10a3	20	80	210	215	516
10b	100	0	264	272	559
10b1	60	40	213	203	525
10b2	40	60	192	192	526
10b3	20	80	144	144	540
10c	100	0	306	307	536
10c1	60	40	281	283	536
10c2	40	20	251	258	533
10c3	20	80	210	215	533

Table 2. Properties[a] and Solubilities of Polymers 11



Ar	T_g, °C	TGA − 5%, °C	M_n	M_w	P_d	solubility
a	352	536	13 700	58 400	4.3	$CHCl_3$, NMP, TCE
b	263	568	19 900	135 300	6.8	$CHCl_3$, NMP, TCE
c	343	581				$CHCl_3$, NMP, TCE
d	317	593	29 800	152 700	5.1	$CHCl_3$, NMP, TCE
e			low MW	low MW		insoluble
f	358	539	17 200	50 100	2.9	$CHCl_3$, NMP, TCE

[a] GPC data are not available for polymer **9c** because phosphorus-containing polymers block the GPC columns.

(arylene ether)s synthesized from imidoaryl-containing biphenol (Table 1),[9] the T_gs and $T_{-5\%}$ of polymers **10a** are much higher.[16]

The thermal properties for the polymers **10b** and **10c** are listed in Table 1. The T_gs for polymers **10b** and **10c** also increase linearly as expected with increasing biphenol **8** content. Compared with the thermal properties of polymers **10a**, polymers **10b** and **10c** have lower T_gs since the difluoro comonomers 1,3-bis(4-fluorobenzoyl)-benzene and bis(4-fluorophenyl)phenylphosphine oxide provide more flexibility in the polymer than bis(4-fluorophenyl)sulfone. The thermogravimetric data as shown in Table 1 indicate that polymers **10b** and **10c** are as thermooxidatively stable as polymers **10a**.

Table 2 gives the thermal properties and solubilities of polymers **11**. The solubilities of the homopolymers **11** are much greater than polymers **10**. Therefore, only homopolymers **11** from biphenol **9** were synthesized. All the polymers **11** except for polymer **11e** remain soluble during polymerization, and therefore, high molecular weight polymers were obtained as shown in Table 2. Only low molecular weight polymer **11e** was produced due to its very rigid molecular chain and insolubility. When a more flexible comonomer bis(4-fluorophenyl)-sulfone (70%) was incorporated, a soluble copolymer **11f** was readily synthesized. No GPC data are available for polymer **9c** because this polymer contains phosphorus moieties thath can block the GPC columns. From Table 1, it is apparent that all the polymers **11** are extremely thermally stable with high T_gs and 5% weight loss temperatures. The highest T_g is 357.6 °C for polymer **11f**, and the highest $T_{-5\%}$ is 592.8 °C for polymer **11d**.

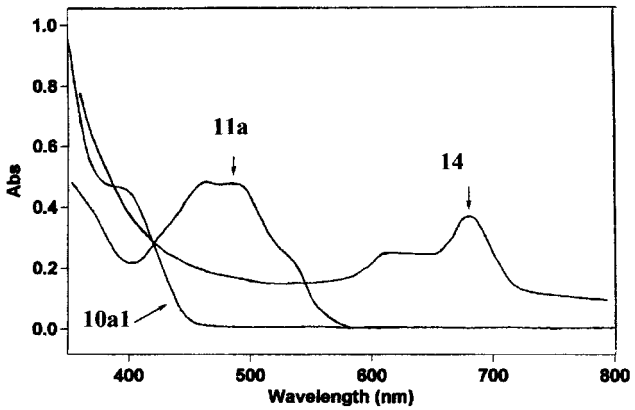


Figure 2. UV−visible spectra of polymers **10a1**, **11a**, and **14**.

Table 3. Physical Properties of Polymers 13−16

polymer	T_g, °C	TGA − 5%, °C	M_n	M_w	P_d	color
13	213	488	20 400	37 100	1.8	white
14	249	476	32 000	65 800	2.1	deep-green to blue
15	278	502	15 300	26 500	1.7	orange-red
16	290	487	23 100	51 000	2.2	black

Because of the bulky pendent group on the biphenol **9**, polymers **11** have much better solubilities than those of polymers **10**. Polymer **10a** is very insoluble and came out of solution during the polymerization reaction. Therefore, it probably has a low molecular weight that can account for the low $T_{-5\%}$. All polymers **11** except for **11e** can be cast into clear, flexible films with an orange-red color.

Synthesis of a Black Poly(arylene ether), 16. We have recently synthesized a new dicyanoarylene biphenol, **12**, from which we have prepared[25] poly(arylene ether) **14**, which has a deep-green to blue color. It was produced according to Scheme 6. The precursor polymer **13** containing a dicyanoarylene moiety was synthesized via the polymerization procedure used for polymers **10** and **11** except that NMP was used as solvent. Polymer **13** was reacted with a large excess of phthalonitrile in the presence of $CuCl_2$ in quinoline. The resulting crude polymer **14** contained large amounts of insoluble copper-(II) phthalocyanine. The crude polymer was dissolved in chloroform followed by filtration to ensure the removal of all the insoluble materials. Polymer **14** is soluble in chloroform and can be cast into a clear, flexible film with a deep-green to blue color. The physical properties of polymers **13** and **14** are listed in Table 3. The glass transition temperature of pendant-capped polymer **14** is higher than that of the corresponding precursor polymer **10**. The apparent molecular weight and molecular weight distribution of polymer **14**, determined by GPC using polystyrene standards, is much higher that of polymer **13**, indicating that a minor amount of cross-linking probably occurred during the phthalocyanine-forming reaction.

Figure 2 shows the UV−visible absorption spectra of polymer **10a1**, polymer **11a**, and polymer **14** in chloroform, respectively. The diluted chloroform solution of polymer **10a1** is yellow in color, and there is no intensive absorption at a wavelength longer than 350 nm. Only a shoulder at 390 nm is observed for polymer **10a1**. The diluted chloroform solution of polymer **11a** is orange-red in color. There are two intensive absorptions (Figure 2) at 463 and 485 nm, respectively. Polymer **14**, pendant-capped with phthalocyanine copper(II) moieties, is deep-

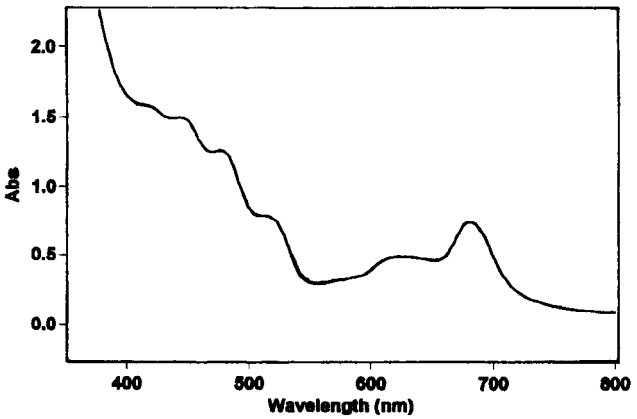


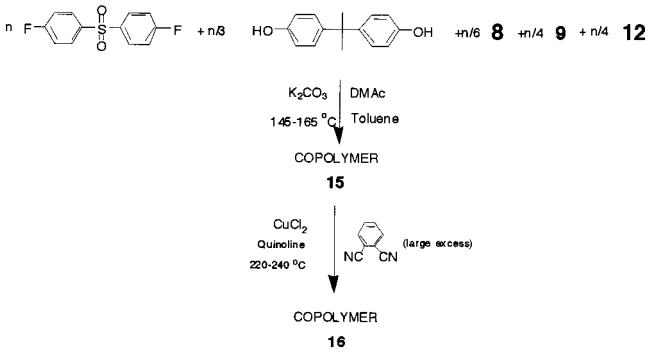
Figure 3. UV−visible spectrum of polymer **16** in chloroform solution.

green to blue in diluted chloroform solution with two intensive absorptions at 620 and 678 nm as shown in Figure 2, The absorption is at a slightly longer wavelength than for the pyrazinoporphyrazine previously synthesized.[24]

To synthesize the black polymer **16**, we first combined polymer **10a1**, polymer **11a**, and polymer **14** in varying molar ratios in solution to determine the optimum concentrations. A black polymeric blend was obtained at a ratio of 20:30:30 for polymer **10a1**:polymer **11a**:polymer **14** (Figure 2). Polymer **15** was synthesized using the ratios as shown in Scheme 7, followed by pendant capping with *o*-phthalonitrile to form phthalocyanine copper(II) moieties. By the same procedure used for synthesis of polymer **14**, polymer **16** was obtained. It is soluble in chloroform and appears black. The glass transition temperature of pendant-capped polymer **16** is higher than that of the corresponding precursor polymer **15**. The T_g of polymer **16** is 290.0 °C, 14 °C higher than that of precursor polymer **15** (276.3 °C). Apparent molecular weights of polymer **15** and **16**, determined by GPC using polystyrene standards, are M_n = 15 300 with a molecular weight distribution of 1.74 and M_n = 23 100 with a molecular weight distribution of 2.21, respectively. Both values of polymer **16** are larger than those of the corresponding precursor polymer **15**. The increase in molecular weight and the widening of the molecular weight distribution as well as the increase in glass transition temperature are due to the formation of the bulky phthalocyanine copper(II) moieties in polymer **16**.

As expected, the polymers synthesized are highly fluorescent materials. The UV−vis spectra of polymers **10a1**, **11a**, **14**, and black polymer **16** are shown in Figures 2 and 3, respectively. The UV−visible absorption data are also listed in Table 3. The absorption of polymer **16** in dilute chloroform solution covers all wavelengths from 350 to 700 nm, and therefore, it is black in color. The emission spectra of these polymers are also given in Figures 4 and 5, respectively, and the excitation wavenumbers and maximum emission wavenumbers for each samples are also tabulated in Table 4. Dilute solutions of polymers **10a1** and **11a** exhibit strong green to yellow and orange to red fluorescence emissions, respectively. When polymer **16** is excited at 353 nm, several fluorescence emissions are produced, as shown in Figure 5 and Table 4, which cover the range from yellow to orange color. However, polymer **14**, which is deep-green to blue in color, gives an emission at 412 nm when excited at 308 nm.

Scheme 7. Synthesis of Polymers 15 and 16



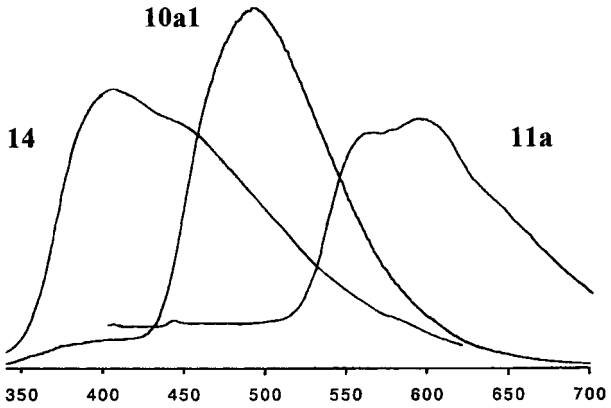


Figure 4. Fluorescent spectra of polymers **10a1**, **11a,** and **14** in chloroform solution.

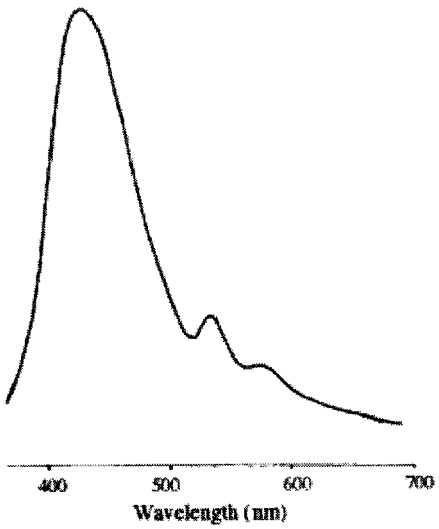


Figure 5. Fluorescent spectrum of polymer **16** in chloroform solution.

Table 4. UV Absorption and Fluorescent Properties of Polymers 10a1, 11a, 14, and 16

polymer	λ_{uv}, nm[a]	λ_{ex}, nm[b]	λ_{em}, nm[c]	color
10a1	402	303	495	yellow
11a	463, 492	350	604	orange-red
14	612, 682	308	412	deep-green to blue
16	300−750	353	424, 532, 581	black

[a] Maximum absorption wavenumber in UV−vis spectra. [b] Excitation wavenumber. [c] Emission wavenumber.

Conclusions

A novel anhydride containing biphenol **7** was synthesized from phenolphthalein. The biphenol can undergo further reactions on the functionalizable anhydride

group. Two biphenols containing a benzoylenebenzimidazole moiety, **8**, and a phthaloperinone moiety, **9**, were prepared from the anhydride biphenol by reaction with aromatic diamines. Two series of poly(arylene ether)s were synthesized from these heterocyclic containing biphenols. The polymers and copolymers synthesized exhibited extremely high glass transition temperatures and excellent thermooxidative stability. The highest T_g and 5% weight loss temperature of these polymers are 358 and 593 °C, respectively. The two series of poly(arylene ether)s, **10** and **11**, are yellow and orange in color, respectively. These poly(arylene ether)s have good solubility and can be cast into tough films from solution. The glass transition temperatures of the copolymers increased with increasing content of the heterocycle-containing moiety, while the solubilities decreased. A terpolymer, **15**, was prepared by copolymerizing the two heterocycle containing biphenols, which are yellow and orange-red, with the monomer containing a dicyanoarylene moiety which was then converted to a phthalocyanine group that has a deep-green to blue color. The resulting polymer **16** absorbs throughout the visible spectrum and is black in color. All of the polymers are highly fluorescent materials with emission wavenumbers ranging from 400 to 750 nm. The polymers are being studied as electron transport and electroluminescent materials in electroluminescent cells.

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