Novel Soluble and Fluorescent Poly(arylene ether)s Containing *p*-Quaterphenyl, 2,5-Bis(4-phenylphenyl)oxadiazole, or 2,5-Bis(4-phenylphenyl)triazole Groups

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ABSTRACT: Three novel conjugated biphenols **3**, **4**, and **8** were synthesized by the $Pd(OAc)_2$-catalyzed regioselective carbon−carbon coupling reaction of 2,6-di-*tert*-butylphenol or 2-phenylphenol with aryl halides. Although poly(arylene ether)s derived from biphenol **3** and arylene difluorides have low solubility in organic solvents, using 4,4′-(9-fluorenylidene)diphenol or 4,4′-(hexafluoroisopropylidene)diphenol as a comonomer gave soluble poly(arylene ether)s **6a**−**c**. High molecular weight poly(arylene ether)s **7a′**−**c′** were also prepared from biphenol **4**. The biscarbamate-masked monomers **5** and **9** improved the polymerization to give higher molecular weight polymers **7a**−**e** and **10a**−**e** in higher yields. Polymers **7** and **10** possess better film-forming capabilities and are still soluble in organic solvents. Polymers **6**, **7**, and **10** are all thermally stable with 5% weight loss temperatures higher than 500 °C under nitrogen. The polymers show strong blue light emission ranging from 387 to 478 nm in solution, depending on the conjugated structure.

Introduction

Conjugated oligomers such as oligophenylenes and oligothiophenes have attracted considerable attention in recent years due to their wide variety of applications such as organic field effect transistors and organic light-emitting diodes (LEDs).[1−3] Although these low molecular weight compounds usually form amorphous thin films after evaporation under high vacuum, they tend to crystallize as a consequence of their low glass transition temperatures and symmetric chemical structures.[4] Therefore, a lot of effort has been consumed to incorporate π-conjugated oligomers into polymers either as polymer backbones or as side chains.[5,6] The major advantages of the polymeric electronic materials over their small molecular counterparts are easy processability for making thin films by spin-coating and improved thermal stability.

Poly(arylene ether)s are well-recognized as a class of high-performance engineering thermoplastics with the characteristics of good thermooxidative stability, high glass transition temperatures (T_g), and excellent mechanical strength.[7] These outstanding physical properties make electroactive moieties containing poly(arylene ether)s potentially useful materials in organic LEDs.[5,8,9] To make rigid conjugated chromophores containing polymers soluble in common organic solvents, flexible substituents have to be introduced.[10] Recently, Maier et al. reported that trifluoromethyl groups make poly(arylene ether)s having quaterphenyl units soluble even in toluene.[11] Poly(arylene ether)s are conventionally synthesized by the polycondensation of biphenols with activated dihalogeno aromatic compounds in aprotic dipolar solvents using K_2CO_3 as a base.[7] Recently, Hay demonstrated that carbamate-masked biphenols are much more reactive in nucleophilic substituted polymerization reactions to give high molecular weight poly(arylene ether)s in a very short period of time.[9,12] The carbamate method is preferable for the preparation of poly(arylene ether)s especially when unstable bisphenols are involved in the polymerization and products with electronic grade purity are required.[9]

In this paper, three novel conjugated biphenols **3**, **4,** and **8** were successfully synthesized by the $Pd(OAc)_2$-catalyzed carbon−carbon coupling reaction. Low molar mass oxadiazole derivatives,[13] such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), and oxadiazole-containing polymers[14] have been used as an electron-transporting material to improve the balance of charge injection and transport and to increase the quantum efficiency in organic LEDs. Since oxadiazole moieties containing biphenols **3** and **8** have a longer conjugation length than widely used PBD, polymers derived from biphenol **3** should be good electron-transporting materials. Biphenol **4** consists of six phenyl groups and has a very strong emission in the UV. Biphenol **3** was easily converted to poly(arylene ether)s by reacting with activated difluoro compounds. Because of its very rigid symmetric structure, homopolymers prepared from biphenol **3** were completely insoluble in common organic solvents. Therefore, other bisphenols, such as hexafluorobisphenol A, have to be used to improve the solubility of the resulting polymers. By using bis(4-fluorophenyl)sulfone as the difluoro monomer and hexafluorobisphenol A as a comonomer, the content of biphenol **3** can reach 44 wt % with the resulting poly(arylene ether) **6a** still showing a good solubility in CH_2Cl_2 and $CHCl_3$. On the contrary, poly(arylene ether) homopolymers prepared from biphenol **4** are quite soluble in common organic solvents, e.g., DMAc, THF, $CHCl_3$, cyclohexanone, and toluene, due to its unsymmetrical structure. The poly(arylene ether)s **7a′**−**c′** directly synthesized from biphenol **4** contained small amounts of cyclic oligomers which can be greatly minimized by using the carbamate method. The yields and the molecular weights of the resulting polymers

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7a−**c** were also increased by using the carbamate method. All poly(arylene ether)s **6a**−**c**, **7a**−**e,** and **10a**−**e** have very high number-average molecular weights and exhibit excellent film-forming capabilities. These poly(arylene ether)s show outstanding thermal stability with 5% weight loss temperatures higher than 500 °C under nitrogen, as determined by thermogravimetric (TGA) analysis. The polymers show UV absorption maxima at 288−320 nm and strong emission maxima at 387−478 nm.

Experimental Section

Materials. Reagent grade solvents and chemicals were used as received. Decafluorobiphenyl, 4-bromobenzoyl chloride, hydrazine monohydrate, *N*-cyclohexyl-2-pyrrolidinone (CHP), *N*,*N*′-dimethylpropyleneurea (DMPU), 2-phenylphenol, 4,4′-diiodobiphenyl, cesium carbonate, 2,6-di-*tert*-butylphenol, phenol, methanesulfonic acid, 4,4′-(9-fluorenylidene)diphenol, 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), bis(4-fluorophenyl)sulfone, and palladium(II) acetate were purchased from Aldrich Co., Inc., while *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were obtained from Fisher Scientific Co., Inc. DMF was dried over magnesium sulfate and distilled under reduced pressure prior to use. 1,2-Bis(4-bromobenzoyl)hydrazide was synthesized from the reaction of 4-bromobenzoyl chloride with hydrazine in DMF in the presence of pyridine as a base at 0 °C and purified by recrystallization from a solvent mixture of DMF and acetic acid. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole was synthesized according to the procedure reported by Hedrick.[15] 3,5-Bis(4-fluorophenyl)-4-phenyl-1,2,4-triazole and 3,5-bis(4-fluorophenyl)-4-(3-trifluoromethylphenyl)-1,2,4-triazole were synthesized as described in the literature.[16]

Characterization. ^{1}H NMR spectra were recorded on a Mercury 400 NMR spectrometer, and ^{13}C NMR spectra were recorded on a JEOL 270 NMR spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF mass spectrometer with the instrument set in the positive reflection mode to get higher resolution. Progress of the organic reactions was monitored by high-performance liquid chromatography (HPLC, Milton Roy, CM4000) with methanol as an eluent and a UV detector set at 254 nm. The molecular weights of polymers were determined by gel permeation chromatography (Waters 510) with a UV detector set at 254 nm, $CHCl_3$ as an eluent, and polystyrenes as the standards. Thermal analyses were conducted on Seiko 220 DSC and 220 TGA/DTA instruments at a heating rate of 20 °C/min under a nitrogen atmosphere. UV−vis absorption spectra were recorded on a CARY 50 spectrophotometer. Photoluminescence (PL) measurements were performed on a SPEX FL-3 fluorescence spectrometer.

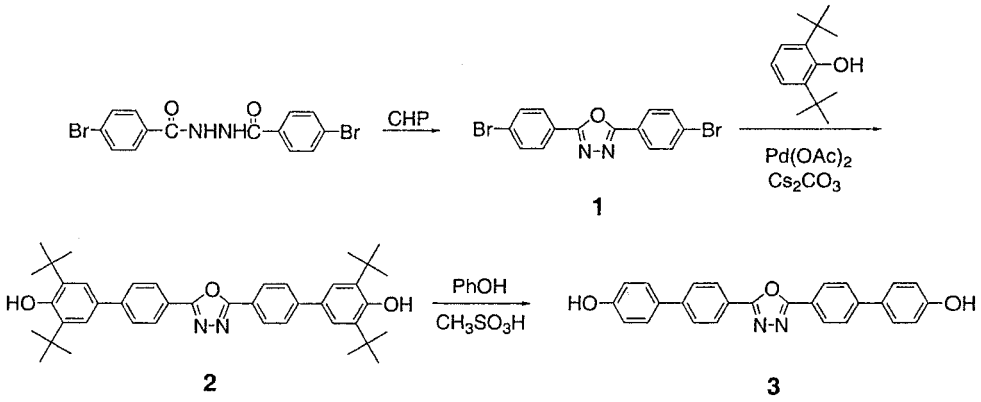
Synthesis of 2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole (1). A 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet was charged with 6.00 g of 1,2-bis(4-bromobenzoyl)hydrazine and 15 mL of CHP. The reaction temperature was gradually increased to 260 °C over a period of 5 h under nitrogen. Upon heating, 1,2-bis(4-bromobenzoyl)hydrazine slowly went into solution and was then reacted at 260 °C for 1 day. After cooling, the reaction mixture was poured into water to precipitate out the product. The crude product was collected by filtration and rinsed with 2-propanol. After recrystallization twice from a toluene/ethyl acetate mixture solvent, 3.96 g (69%) of **1** was obtained as white needles. Mp: 259.0 °C. Purity: 99.7% (by HPLC). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.00 (d, 4H, J = 7.4 Hz), 7.68 (d, 4H, J = 7.4 Hz). ^{13}C NMR NMR ($CDCl_3$): δ (ppm) 164.12, 132.60, 128.41, 126.73, 122.76. MALDI-TOF-MS: 376.2, 378.0, 380.3, 382.4 (calcd: 380.0).

Synthesis of 2,5-Bis(4′-hydroxy-4-biphenylyl)-1,3,4-oxadiazole (3). A 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet was charged with 7.20 g of Cs_2CO_3. The cesium carbonate was dried at 150 °C for 2 h under nitrogen. After cooling, 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (3.80 g, 10.0 mmol), 2,6-di-*tert*-butylphenol (4.95 g, 24.0 mmol), palladium(II) acetate (120 mg, 0.535 mmol), triphenylphosphine (0.530 g, 2.02 mmol), and xylene (70 mL) were added. The resulting mixture was heated to reflux with stirring under nitrogen. The reaction was run at reflux for 4 h until no starting dibromo compound was found by HPLC analysis. The reaction mixture was diluted with 20 mL of xylene, filtered to remove inorganic solids, and decolorized with activated carbon under nitrogen. The filtrate was placed into a 100 mL three-neck flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet. Phenol (11.6 g, 123.4 mmol) and methanesulfonic acid (2.0 mL) were added. The solution was stirred at 125 °C under nitrogen for about 6 h until HPLC analysis showed that all the *tert*-butyl groups of compound **2** were removed. During the reaction, the product precipitated out of the solution. After cooling, the xylene layer was removed, and 10 mL of pyridine was added to neutralize methanesulfonic acid. After stirring for a short time, water was added to precipitate out the product. The crude product was collected by filtration, washed with water, redissolved in a solvent mixture of THF and ethanol, decolorized with activated carbon, and then recovered by evaporation of the solvents. After washing with toluene at reflux under nitrogen, 2.20 g of **3** was obtained in 60% yield. Mp: 303.9 °C (by DSC). Purity: 99.6% (by HPLC). ^{1}H NMR (DMSO-d_6): δ (ppm) 9.74 (s, 2H), 8.13 (d, 4H, J = 8.8 Hz), 7.82 (d, 4H, J = 8.8 Hz), 7.61 (d, 4H, J = 8.4 Hz), 6.88 (d, 4H, J = 8.4 Hz). ^{13}C NMR (DMSO-d_6): δ (ppm) 164.43, 158.55, 143.98, 129.95, 128.62, 127.75, 127.14, 121.68, 116.49. MALDI-TOF-MS: 406.4 (calcd: 406.4).

Synthesis of 2,2‴-Bis(2-hydroxyphenyl)-*p*-quaterphenyl (4). Into a 250 mL three-necked round-bottomed flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet was placed 7.80 g of Cs_2CO_3 which had been dried at 150 °C for 2 h under nitrogen. After cooling, 2-phenylphenol (10.08 g, 59.2 mmol), 4,4′-diiodobiphenyl (4.00 g, 9.85 mmol), molecular sieves (4.0 g), palladium(II) acetate (240 mg, 1.07 mmol), and DMF (80 mL) were added. The reaction mixture was stirred at 105 °C for about 10 h under nitrogen until HPLC analysis showed that all the 4,4′-diiodobiphenyl had disappeared. After cooling, the reaction mixture was filtered to remove the molecular sieves and inorganic solids. The product was precipitated out by pouring the filtrate into 0.02 M HCl aqueous solution (300 mL), then redissolved in toluene at reflux, decolorized with activated carbon, and finally reprecipitated out in hexanes to remove the excess 2-phenylphenol. The crude product was collected by filtration and purified by recrystallization three times from toluene to give 2.65 g of white crystals of **4** in 55% yield. Mp: 156.1 °C (by DSC). T_g: 92.6 °C (by DSC). Purity: 99.0% (by HPLC). ^{1}H NMR (DMSO-d_6): δ (ppm) 9.16 (s, 2H), 7.46 (d, 4H, J = 8.8 Hz), 7.42−7.33 (m, 6H), 7.28 (d, 2H, J = 6.8 Hz), 7.17 (d, 4H, J = 8.8 Hz) 7.02 (t, 2H, J = 7.6 Hz), 6.86 (d, 2H J = 7.6 Hz), 6.73 (d, 2H, J = 7.6 Hz), 6.65 (t, 2H, J = 7.6 Hz). ^{13}C NMR (DMSO-d_6): δ (ppm) 154.93, 141.27, 140.92, 138.00, 137.68, 131.86, 131.79, 130.10, 129.89, 128.88, 128.77, 127.85, 127.44, 126.05, 119.21, 115.89. MALDI-TOF-MS: 489.7 (calcd: 490.6).

Synthesis of Biscarbamate 5 Derived from Biphenol 4. To a 100 mL round-bottomed flask fitted with a magnetic stirrer, a reflux condenser, and a drying tube were added biphenol **4** (1.40 g, 2.85 mmol), *n*-propyl isocyanate (2.1 mL, 22.4 mmol), triethylamine (0.15 mL), and toluene (35 mL). The reaction solution was stirred at about 105 °C for 24 h. After cooling, the product was isolated by distilling the solvents out under reduced pressure. Recrystallization twice from a mixture solvent of toluene and heptane (1:1) yielded 1.35 g (72%) of **5** as a white crystalline powder. Mp: 171.1 °C (by DSC). Purity: 98.4% (by HPLC). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.47 (d, 2H, J = 7.2 Hz), 7.44−7.34 (m, 10H), 7.25−7.20 (m, 6H), 7.10 (d, 2H, J = 8.0 Hz), 7.07−7.02 (m, 4H), 4.70 (t, 2H, J = 5.6 Hz), 3.15−2.95 (m, 4H), 1.49−1.36 (m, 4H), 0.83 (t, 6H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 154.31, 148.47, 140.87, 140.45, 138.67, 136.01, 134.60, 132.06, 131.22, 130.11, 129.71,

Scheme 1. Synthetic Route to 2,5-Bis(4′-hydroxy-4-biphenylyl)-1,3,4-oxadiazole (3)



128.19, 127.90, 127.06, 126.22, 125.25, 122.77, 42.82, 23.07, 11.15. MALDI-TOF-MS: 660.2 (calcd: 660.8).

Synthesis of 2,5-Bis(2-hydroxy-*o*-terphenyl-4′-yl)-1,3,4-oxadiazole (8). The palladium-catalyzed reaction of **1** and 2-phenylphenol was done under the same reaction conditions as for **4** to obtain **8**. Yield: 35%. Mp: 262 °C (by DTA). Purity: 99.0% (by HPLC). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.94 (d, 4H, J = 8.21 Hz), 7.54 (m, 6H), 7.46 (d, 2H, J = 5.40 Hz), 7.32 (d, 4H, J = 7.82 Hz), 7.17 (t, 2H, J = 8.21 Hz), 7.03 (d, 2H, J = 7.82 Hz), 6.85 (t, 2H, J = 7.43 Hz), 6.81 (d, 2H, J = 8.21 Hz), 3.73 (s, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.6, 152.4, 144.3, 140.6, 135.2, 131.4, 131.1, 130.6, 129.8, 129.3, 128.8, 128.7, 127.3, 126.6, 122.3, 120.6, 115.6. MALDI-TOF-MS: 558.6 (calcd: 558.9).

Synthesis of Biscarbamate 9 from Biphenol 8. The reaction of **8** with *n*-propyl isocyanate was done under the same reaction conditions as for **5**. Yield: 85%. Mp: 207 °C (by DTA). Purity: 99.4% (by HPLC). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.95 (d, 4H, J = 8.79 Hz), 7.43 (m, 8H), 7.37 (d, 4H, J = 8.21 Hz), 7.26 (m, 2H), 7.07 (m, 6H), 4.81 (t, 2H, J = 5.28 Hz), 3.07 (m, 4H), 1.41 (m, 4H), 0.84 (t, 6H, J = 7.03 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.4, 154.1, 148.3, 145.0, 139.9, 136.0, 134.1, 131.9, 131.2, 130.0, 129.9, 128.4, 128.0, 127.7, 126.4, 125.3, 122.9, 122.0, 42.7, 23.0, 11.1. MALDI-TOF-MS: 728.9 (calcd: 728.8).

General Procedure for the Synthesis of Poly(arylene ether)s 6a−c and 7a′−c′. Poly(arylene ether)s **6a−c** and **7a′−c′** were synthesized according to the general procedure. The polymerization was carried out initially at 130−140 °C for 3−4 h to azeotrope off the resulting water with toluene and then at 160−175 °C to perform the polymerization. A typical example is given as follows. A 25 mL three-necked round-bottomed flask equipped with an argon inlet, a magnetic stirrer, a Dean−Stark trap, and a condenser was flushed with argon and then charged with biphenol monomer **3** (0.3500 g, 0.861 mmol), 6F-BPA (0.1240 g, 0.369 mmol), K_2CO_3 (0.26 g), DMAc (6 mL), and toluene (8 mL). The reaction mixture was stirred at reflux under argon for 1.5 h to azeotrope off the resulting water with toluene. The toluene was then removed, and the reaction mixture was cooled. After cooling, 0.3127 g (1.23 mmol) of bis(4-fluorophenyl)sulfone was added. The mixture was heated to 170 °C and kept at low reflux until a very viscous solution was obtained. Several drops of benzyl chloride were added to end-cap the resulting polymer. After cooling, the mixture was diluted with 2 mL of DMAc and poured into 150 mL of methanol to precipitate out the polymer. The resulting polymer was redissolved in $CHCl_3$, filtered through a thin layer of Celite to remove inorganic salts, and reverse precipitated out by dropwise adding methanol into the filtrate. The polymer was collected by filtration, redissolved in $CHCl_3$, and reprecipitated in methanol. Finally, the resulting polymer was collected by filtration and dried at 80 °C in a vacuum for 12 h.

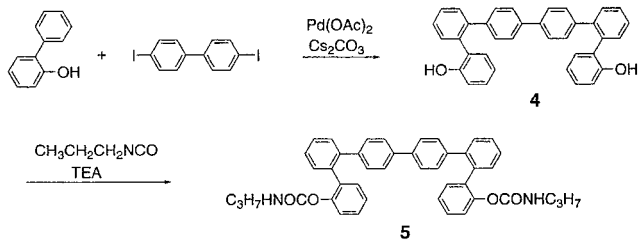
General Procedure for the Synthesis of Poly(arylene ether)s 7a−e and 10a−e from Biscarbamates 5 and 9. A typical example is given as follows. A 25 mL three-necked round-bottomed flask equipped with an argon inlet, a magnetic stirrer, and a condenser was flushed with argon and then charged with biscarbamate **5** (0.4000 g, 0.605 mmol), bis(4-fluorophenyl)sulfone (0.1523 g, 0.599 mmol), K_2CO_3 (0.170 g), and DMAc (4.0 mL). The reaction mixture was heated to reflux under argon. After 4 h, the solution became very viscous, and an additional 1 mL of DMAc was added to make the stirring effective. The polymerization was contimued for 8 h before 0.1 mL of benzyl chloride was added to end-cap the resulting polymer. After cooling, the polymer solution was diluted with 1 mL of DMAc and poured into 150 mL of methanol to precipitate out the polymer. The resulting polymer was purified as described above.

Transformation of 7c to 7d. Into a 25 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a nitrogen gas inlet, and a reflux condenser were placed the polymer **7c** (0.50 g, 0.7 mmol) and 10 mL of CHP. The mixture was heated to 210 °C under a nitrogen atmosphere. After all the polymer was dissolved into the solution, aniline hydrochloride (1.00 g, 7.7 mmol) was added. The mixture was heated at 250 °C for 2 h. After being cooled to room temperature, the mixture was poured into 150 mL of methanol to precipitate out the polymer. The product was purified by precipitation from $CHCl_3$/methanol to obtain the polymer **7d** in 100% yield.

Results and Discussion

Synthesis of 2,5-Bis(4′-hydroxy-4-biphenylyl)-1,3,4-oxadiazole (3). 2,5-Bis(4′-hydroxy-4-biphenylyl)-1,3,4-oxadiazole (**3**) was synthesized from 1,2-bis(4-bromobenzoyl)hydrazine in three steps as shown in Scheme 1. 1,2-Bis(4-bromobenzoyl)hydrazide was converted to 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (**1**) in high yield by cyclodehydration in CHP. Since CHP is not miscible with water at temperatures above 80 °C, it serves as an effective dehydrating agent.[15] During the cyclodehydration, an unknown side product was formed. However, it was effectively removed by crystallization twice from a toluene/ethyl acetate (1/2) solvent mixture. Compound **1** was reacted with 2,6-di-*tert*-butylphenol to give compound **2** by the $Pd(OAc)_2$-catalyzed coupling reaction. In 1998, Miura et al. reported that sterically hindered phenols like 2,6-di-*tert*-butylphenol react with a variety of aryl bromides in the presence of the palladium catalyst and a strong base to afford the corresponding 1,1′-biphenyl-4-ol derivatives.[17] We found that the strong electron-withdrawing oxadiazole group in compound **1** facilitates this carbon−carbon coupling reaction. The reaction was completed within 3 h. Use of very dry Cs_2CO_3 is crucial. The *tert*-butyl groups of compound **2** were removed by a trans-*tert*-butylation reaction with phenol as the *tert*-butyl acceptor and with methanesulfonic acid as catalyst.[18] To obtain **3** in high yield, oxygen susceptible (easily oxidizable) compound

Scheme 2. Synthesis of 2,2‴-Bis(2-hydroxyphenyl)quaterphenyl (4) and Its Biscarbamate Derivative (5)



4 **5**

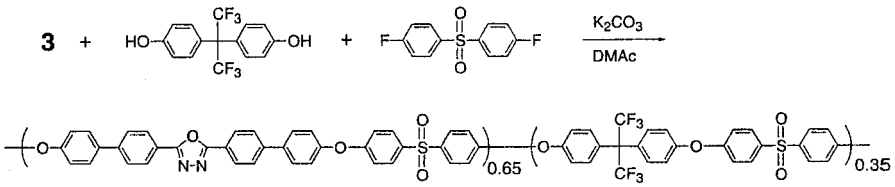
2 should be transferred to the next step, and the reaction should be run under nitrogen. After all the *tert*-butyl groups were removed, the product **3** precipitated out from xylene as a much more stable material than the parent compound **2**.

Synthesis of 2,2‴-Bis(2-hydroxyphenyl)-*p*-quaterphenyl (4) and Its Biscarbamate Derivative 5. An interesting palladium-catalyzed regioselective arylation reaction was reported in 1997.[19] When iodobenzene was reacted with 2-phenyphenol in the presence of $Pd(OAc)_2$ with Cs_2CO_3 as base, 2-hydroxy-2′-phenylbiphenyl was obtained in 63% yield as the single major product. We have prepared the novel biphenol **4** by utilizing this chemistry (Scheme 2). A large excess of 2-phenyphenol was used in order to avoid the formation of oligomeric products arising from the subsequent reaction of **4** with 4,4′-diiodobiphenyl. This reaction is quite sensitive to water; a small amount of water terminates the reaction. The reaction solvent (DMF) and the base (Cs_2CO_3) have to be thoroughly dried prior to use. Molecular sieves (4 Å) were also employed to absorb the water generated during the reaction, and the reaction was run under nitrogen. The progress of this palladium-catalyzed reaction was monitored by HPLC. It was found that one 4,4′-diiodobiphenyl molecule reacts with one 2-phenylphenol to form 2-(2-hydroxyphenyl)-4″-iodoterphenyl first, and then this intermediate continues to react with 2-phenylphenol to give **4**. Although small amounts of side products were formed by the arylation of the 4-position of 2-phenylphenol, they could be removed by crystallization several times from toluene. After the purification, the product showed only one peak in the MALDI-TOF mass spectrum.

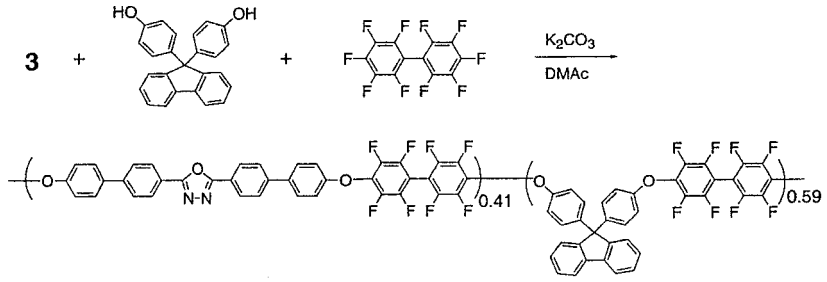
The reaction of isocyanates with alcohols to give *N*-carbamates is a simple addition reaction, and the side reactions can be minimized under optimized conditions.[20] There are various catalysts that promote this reaction, and in this study triethylamine was used. To ensure all the hydroxy groups of biphenol **4** were reacted, a large excess of *n*-propyl isocyanate was employed. Pure biscarbamate **5** was isolated by distilling out the excess *n*-propyl isocyanate and toluene followed by crystallization from toluene and heptane. TGA measurement showed that biscarbamate **5** started to decompose at 150 °C, which is consistent with the decomposition temperature of phenolic urethanes.[21]

Synthesis of Poly(arylene ether)s 6a−c Containing Biphenylyl-Substituted Oxadiazole Moieties. High molecular weight poly(arylene ether) copolymers **6a−c** were easily prepared by the conventional procedure for the preparation of poly(arylene ether)s (Scheme 3, Table 1). Because of the symmetric rigid chemical structure of **3**, poly(arylene ether)s from **3** and arylene difluorides were insoluble in common organic solvents.

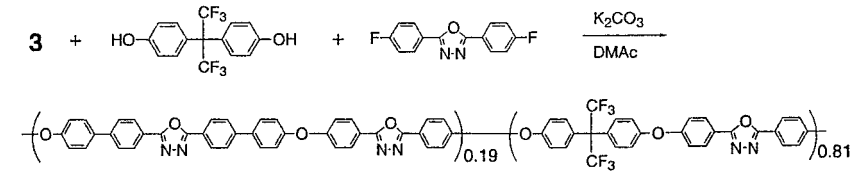
Scheme 3. Synthesis of Poly(arylene ether) Copolymers 6a−c Containing Biphenylyl-Substituted Oxadiazole Moieties



6a



6b



6c

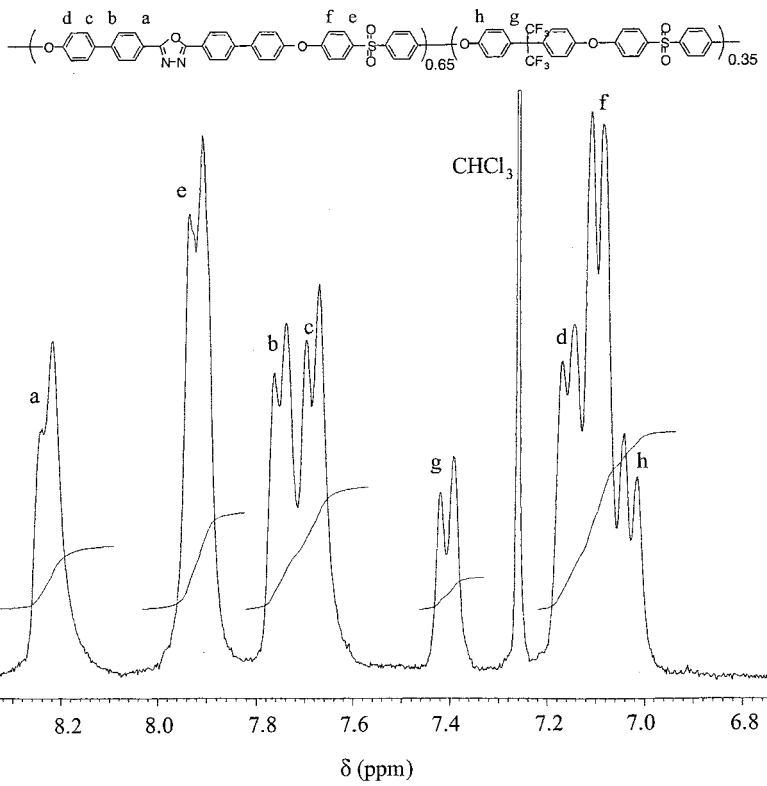


Figure 1. ^{1}H NMR spectrum of copolymer **6a**.

Table 1. Properties of Poly(arylene ether)s 6a−c

		content of **3** (mol %)							
polymer	yield (%)	feed	polymer[a]	M_n[b] ($\times 10^3$)	PD	T_g (°C)	TGA[c] (°C)	λ_{max}[d] (nm)	λ_{em}[e] (nm)
6a	85	70	65	40.7	2.0	245	508	305	478
6b	66	50	41	26.1	3.1	253	546	320	451
6c	66	25	19	49.7	2.1	215	501	308	478

[a] Content of **3** in polymers determined by ^{1}H NMR analysis. [b] Molecular weights determined by GPC in $CHCl_3$ using polystyrene standards. [c] 5% weight loss temperature under nitrogen. [d] Maximum UV absorption wavelength in $CHCl_3$ solution. [e] Maximum emission wavelength excited at the absorption maximum in $CHCl_3$ solution.

Even the polymer from decafluorobiphenyl which usually gives polymers with better solubility[22] suffers from this problem. The products precipitated out of the reaction mixture during the polymerization so that high molecular weight polymers could not be obtained. Incorporation of the polar and branched 4,4′-(hexafluoroisopropylidene)diphenol moiety (6F-BPA) into a polymer backbone is known to be effective for improving the solubility of polymers without losing the thermal stability.[23] The hexafluoroisopropylidene groups increase the glass transition temperature with concomitant decrease of crystallinity.[11] Through several experiments, we found that the content of biphenol **3** in polymer **6a** can reach up to 44 wt % by employing 6F-BPA as the solubilizing moiety. The ^{1}H NMR spectrum of polymer **6a** and its assignments are shown in Figure 1. The integration ratio of the doublet peak at 8.22 ppm to that of the doublet peak at 7.90 ppm suggests that **6a** contains 65 mol % of **3**. 4,4′-(9-Fluorenylidene)-diphenol was also copolymerized with **3** and decafluorobiphenyl to obtain the polymer **6b**. The yield of polymer **6b** is relatively low (66%) because of some materials insoluble in $CHCl_3$, which were removed during the purification process. Despite its lower content of **3**, polymer **6b** showed a T_g 8 °C higher than that of **6a**. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole is a rigid difluoro monomer. As anticipated, the incorporation of biphenol **3** to give a soluble polymer **6c** is low and can only reach 19 mol %.

The three high molecular weight poly(arylene ether)s **6a−c** are colorless and show outstanding thermal stability with 5% weight loss temperatures higher than 500 °C under nitrogen. They are soluble in $CHCl_3$, CH_2Cl_2, and DMAc at room temperature. Polymer **6b** is even soluble in toluene and THF. Polymers **6a−c** form transparent and very tough films by casting from chloroform solution.

Synthesis of Poly(arylene ether)s 7a−c Containing Sexiphenyl Units. A series of five polymers containing sexiphenyl units were synthesized from **4** or **5** and activated arylene difluorides (Scheme 4, Table 2). Polymers **7a−c** were prepared by the carbamate method which gave higher yields, higher molecular weights, and better film-forming capabilities than the direct reaction with the biphenol. Our previous work demonstrated that the carbamate method is quite useful for the synthesis of poly(arylene ether)s, especially when unstable bisphenols are involved in the polymerization and products with electronic-grade purity are required.[9] Furthermore, we have now shown that the carbamate method can significantly suppress the formation of cyclic oligomers. Poly(arylene ether)s **7a′−c′**, prepared from biphenol **4** by the conventional method, required an initial dehydration in the presence of K_2CO_3 followed by the

Scheme 4. Synthesis of Sexiphenyl Moieties Containing Poly(arylene ether)s from Biphenol 4 and Biscarbamate 5

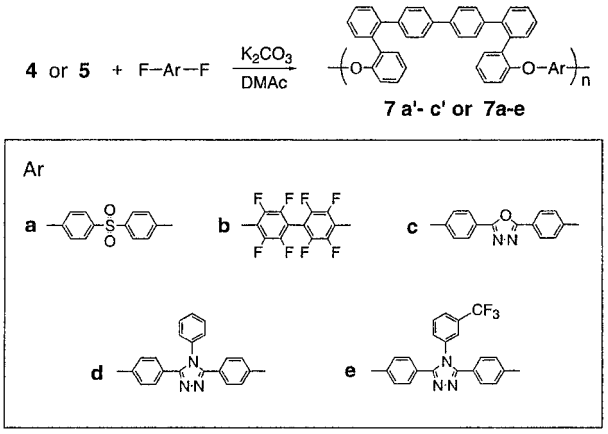


Table 2. Properties of Poly(arylene ether)s 7a′−c′and 7a−e Containing Sexiphenyl Moieties

polymer	yield (%)	M_n[a] ($\times 10^3$)	PD	T_g (°C)	TGA[b] (°C)	λ_{max}[d] (nm)	λ_{em}[e] (nm)
7a	83	53.6	3.1	231	569	288	396
7a′	66	14.3	4.5	226	565		
7b	85	69.6	2.4	210	577	295	442
7b′	60	24.3	2.5	209	581		
7c	85	93.0	6.1	241	515	308	396
7c′	76	35.2	13.4	237	516		
7d[c]	58	61.8	10.5	226	521	289	396
7e[c]	75	90.9	10.3	221	523	288	394

[a] Molecular weights determined by GPC in $CHCl_3$ using polystyrene standards. [b] 5% weight loss temperature under nitrogen. [c] Polymerization run at 180 °C in DMPU. [d] Maximum UV absorption wavelength in $CHCl_3$ solution. [e] Maximum emission wavelength excited at the absorption maximum in $CHCl_3$ solution.

polycondensation with the difluorides. A significant amount of cyclic oligomers was formed perhaps because the chemical structure of biphenol **4** potassium salt favored cyclic formation. In addition, some biphenol **4** might be oxidized at high temperatures with trace amounts of oxygen, which whould change the stoichiometry of the monomers. As a result, the molecular weights of the polymers were not very high and the yields were low. GPC curves of polymer **7a′** and **7c′** indicated that they contained significant amounts of oligomers even after purification. When poly(arylene ether)s **7a**−**c** were synthesized by the carbamate method, the potassium phenoxide groups were generated in situ and reacted as formed. The possibility for the formation of cyclic oligomers was significantly decreased since each carbamate group would react independently. Consequently, high molecular weight polymers **7a**−**c** were obtained in higher yields. A comparison of GPC curves between **7c** and **7c′** is shown in Figure 2, where the minor peaks around 25−30 min of retention time for **7c′** are assigned to the cyclic oligomers. The MALDI-TOF mass spectrum showed the presence of cyclic oligomers in polymer **7c′** (Figure 3a). The poly(arylene ether)s **7a′** and **7c′** have lower T_g's than the corresponding polymers obtained by the carbamate method because they contain low molecular weight cyclic oligomers. The cyclic oligomers in polymer **7b′** were easily removed during purification, so the yield of polymer **7b′** is lower.

It has been reported that triazole-containing difluoro monomers are less reactive in the nucleophilic substitution reactions than oxadiazoles.[16] The polymerization

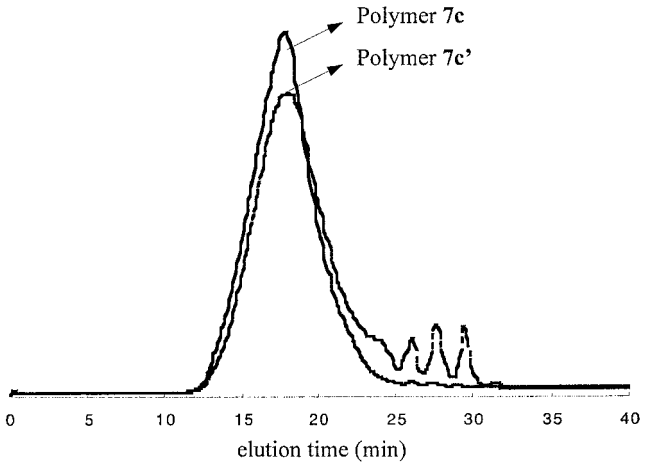


Figure 2. A comparison of GPC curves between **7c** and **7c′**.

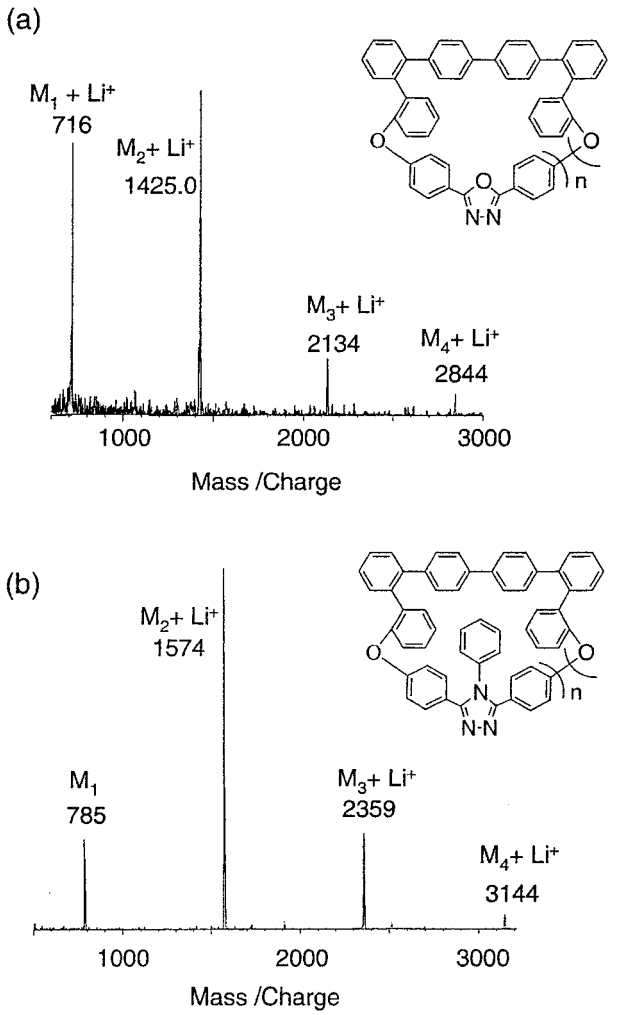
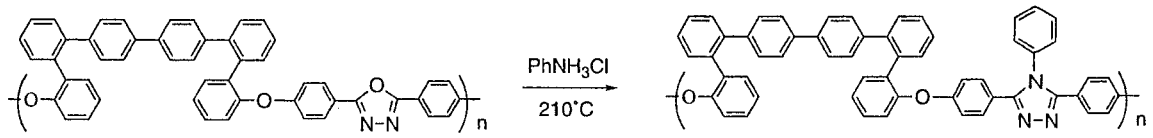


Figure 3. MALDI-TOF mass spectra of cyclic oligomers in polymers **7c′** (a) and **7d′** (b).

of **5** with 3,5-bis(4-fluorophenyl)-4-phenyl-1,2,4-triazole or 3,5-bis(4-fluorophenyl)-4-(3-trifluoromethylphenyl)-1,2,4-triazole did not take place in refluxing DMAc (166 °C). Elevated temperatures were required to produce high molecular weight polymers. Polymers **7d** and **7e** with $M_n > 61.8 \times 10^3$ were obtained by polymerization at 180 °C in DMPU. Although there were no oligomeric and cyclic products indicated by GPC and MALDI-TOF mass spectral analyses, the molecular weight distribution (M_w/M_n) of **7d** and **7e** is very large (ca. 10). The

Scheme 5. Transformation of 7c to 7d



7c **7d**

triazole-containg polymers have more rigid structures because of the restricted rotation resulting from the three phenyl substituents of 1,2,4-triazole ring. A molecular mechanics calculation[24] of 2,5-diphenyl-1,3,4-oxadiazole and 3,4,5-triphenyl-1,2,4-triazole as model compounds shows that there is 17.66 kcal/mol difference in the rotational energy along the C(phenyl)−C(heterocycle) bond between them (5.11 kcal/mol for the oxadiazole and 22.77 kcal/mol for the triazole).

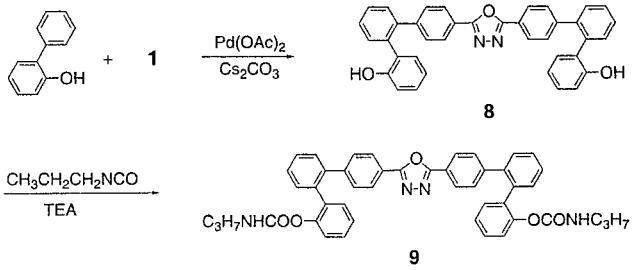
Polymers **7d** and **7d′** were also prepared by treating **7c** or **7c′** with aniline hydrochloride (Scheme 5).[25] The transformation of 1,3,4-oxadiazole to 4-phenyl-1,2,4-triazole groups proceeded quantitatively at 210 °C in CHP with a large excess of aniline hydrochloride. Since cyclic oligomers are characterized easily by MALDI-TOF mass spectroscopy, the acetone soluble parts of the products were extracted and analyzed to compare with that of the parent material. As shown in Figure 3b, the oxadiazole-containing cyclics of monomer, dimer, trimer, and tetramer were completely converted to the corresponding 4-phenyltriazole analogues after the reaction. The polymer obtained showed the same solubility and thermal properties as those of the polymer **7d** synthesized from **5** and 3,5-bis(4-fluorophenyl)-4-phenyl-1,2,4-triazole.

Poly(arylene ether)s **7a**−**e** demonstrated excellent thermal stability. Depending on the chemical structures of difluoro compounds, these polymers exhibited 5% weight loss temperatures between 515 and 580 °C under nitrogen. These values are comparable to those of the aromatic polyimides.[26] Polymers **7a**−**c** possess good film-forming capabilities. Transparent and tough films were easily obtained by casting from chloroform solution. Unlike biphenol **3**, poly(arylene ether) homopolymers made from biphenol **4** are quite soluble in a wide range of organic solvents, e.g., $CHCl_3$, THF, DMAc, and toluene (**7d** and **7e** are not soluble in toluene), due to its bent structures.

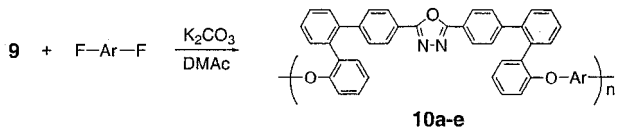
Synthesis and Polymerization of 2,5-Bis(2-hydroxy-*o*-terphenyl-4′-yl)-1,3,4-oxadiazole. The palladium-catalyzed arylation reaction of an aryl iodide with 2-phenylphenol described above in the synthesis of **4** could be applied to aryl bromides (e.g., 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (**1**)). The reaction was done under the same conditions as for the iodide to obtain the novel biphenol **8** (Scheme 6). Although bromides are less reactive than iodides, the pure compound was obtained in 35% yield after crystallization three times from THF and toluene. Compound **8** was characterized by ^1H, ^{13}C NMR, and MALDI-TOF-MS spectra. The biphenol was reacted with *n*-propyl isocyanate in basic toluene solution to prepare propylcarbamoyl-masked compound **9**.

The monomer **9** was polymerized with five different activated arylene difluorides to synthesize polymers **10a**−**e** (Scheme 7, Table 3). The polymers obtained were high molecular weight (M_n: (7.5−22.4) × 10^3) and give flexible and transparent films by casting from solution. Polymers **10** have similar thermal properties as those

Scheme 6. Synthesis of 2,5-Bis(2-hydroxy-*o*-terphenyl-4′-yl)-1,3,4-oxadiazole (8) and Biscarbamate 9



Scheme 7. Synthesis of Polymers 10a−e



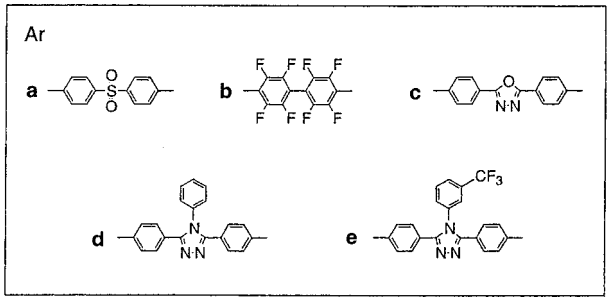


Table 3. Properties of Poly(arylene ether)s 10a−e

polymer	yield (%)	M_n[a] ($\times 10^3$)	PD	T_g (°C)	TGA[b] (°C)	λ_{max}[d] (nm)	λ_{em}[e] (nm)
10a	81	10.9	3.2	225	503	313	413
10b	84	22.4	5.5	238	505	312	436
10c	64	7.5	3.0	228	489	307	382
10d[c]	63	11.8	12.5	237	502	296	392
10e[c]	58	11.5	13.3	221	501	294	387

[a] Molecular weights determined by GPC in $CHCl_3$ using polystyrene standards. [b] 5% weight loss temperature under nitrogen. [c] Polymerization run at 180 °C in DMPU. [d] Maximum UV absorption wavelength in $CHCl_3$ solution. [e] Maximum emission wavelength excited at the absorption maximum in $CHCl_3$ solution.

of **7**, with glass transition temperatures higher than 220 °C and 5% weight loss temperatures about 500 °C. All those polymers show good solubility in organic solvents like $CHCl_3$, DMF, and THF. The extra heterocyclic (oxadiazole) rings in **10**, however, make them less soluble in nonpolar solvents; only two of them (**10a** and **10b**) are soluble in toluene.

UV Absorbance and Photoluminescence Properties. The UV−vis absorption spectra of biphenol monomers **3**, **4,** and **8** were first examined in $CHCl_3$ solution. The biphenol **4** shows an absorption peaked at 286 nm (λ_{max}) tailing to 347 nm (λ_{ed}). The oxadiazole-containing biphenols **3** (λ_{max}: 328 nm; λ_{ed}: 378 nm) and **8** (λ_{max}: 310 nm; λ_{ed}: 368 nm) have absorption batho-

chromically shifted and with small half peak width compared to those of **4**, suggesting that **3** and **8** have a longer conjugated length than **4**. The 18 nm hypsochromic shift of the absorption maximum of **8** compared to that of **3** could be explained by the steric hindrances between the linear arylene groups and the ortho phenyl group, losing the coplanarity and the conjugation in **8**. The polymers **6a**−**c**, **7a**−**e**, and **10a**−**e** derived from those biphenol monomers have similar UV absorptions (Tables 1−3), suggesting that the absorption at the longest wavelength can be ascribed to the biphenol moieties.

The polymers show strong photoluminescence in $CHCl_3$ solution when excited at their absorption maximum. The maximum emission wavelength (λ_{em}) ranges from 394 to 478 nm, depending on the starting biphenol structures. Polymers **6a**−**c** have a pure blue light emission (451−478 nm). Although the sulfone, oxadiazole, or triazole moieties do not have significant differences in their luminescent properties, perfluorobiphenylene containing polymers (**7b** and **10b**) have longer emission maximum (442 and 436 nm, respectively) than the other homologues.

Conclusions

Three novel conjugated biphenols **3**, **4**, and **8** were successfully synthesized by a $Pd(OAc)_2$-catalyzed carbon−carbon coupling reaction. Although poly(arylene ether) homopolymer derived from biphenol **3** is insoluble in organic solvents due to its very rigid structure, the copolymerization with 4,4′-(9-fluorenylidene)diphenol or 4,4′-(hexafluoroisopropylidene)diphenol gave soluble poly(arylene ether)s **6a**−**c**. Polymers **7a**−**c** containing sexiphenyl moieties were synthesized by two different methods. One is the conventional method from biphenol **4**, and the other one is using biscarbamate **5** as a masked biphenol. It was found that the propylcarbamate-masked monomers afford higher molecular weight polymers in higher yield and prevent the formation of cyclic oligomers. The similar polymers **10a**−**e** with extra oxadiazole moieties were also synthesized by the polymerization of **9** with activated arylene difluorides. Colorless polymers **6a**−**c**, **7a**−**e**, and **10a**−**e** possess high T_g's, excellent thermal stability, and good film-forming capabilities. The polymers show strong blue light emission in $CHCl_3$ solution.

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