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Synthesis of Homo- and Copoly(arylene bicarbazole)s via Nucleophilic Substitution Polycondensation Reactions of NH Groups with Activated Dihalides

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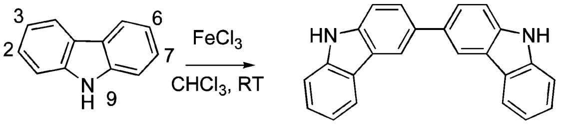
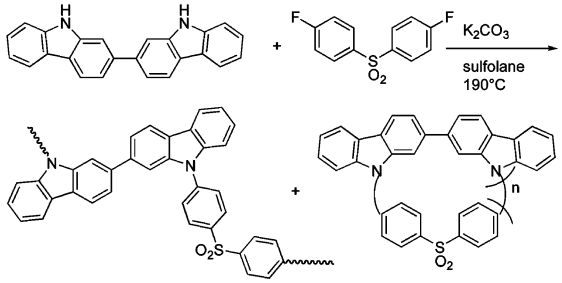
Introduction. Carbazole has become a popular framework for studies in materials chemistry in past decades since oligomers and polymers containing carbazole units display unique electrical, electrochemical, and optical properties.[1] There are three kinds of reactive sites in the carbazole monomer that can lead to chain propagation to give polymers, e.g., the 3,6-positions, 2,7-positions, and 9-hydrogen position (see numbering of carbazole nucleus in Scheme 1). Although different synthetic strategies have been used to prepare a large number of carbazole-based polymers, they can be generally grouped into three types:[2−8] (a) poly(*N*-vinylcarbazole) and analogous side-chain polymers with pendant carbazolyl groups obtained via chain-growth polymerization reactions of vinyl monomers; (b) poly(3,6-carbazole)s or poly(2,7-carbazole)s with various pendant N-substituents as side chains linked by either oxidative coupling polymerization of N-substituted carbazoles or reductive coupling polymerization of 3,6-dihalocarbazoles; (c) polycarbazoles containing C−N bonded main chains containing alkane moieties synthesized via different polymerization reactions. Among the above-mentioned carbazole-based polymers, the least studied are polymers in which C−N bonding is present in the main chain. The C−N bonded polycarbazoles were synthesized by either electrochemical oxidation of a C−N bonded monomer, dehalogenation coupling reaction of dihalogenated carbazole derivatives, or modified Ullmann coupling reactions of 3,3′-bicarbazole with different dihalo compounds such as 3,6-diiodo-9-(2-ethylhexyl)carbazole or 1,6-bis(2-bromophenoxy)hexane.[8] To the best of our knowledge, there have never been attempts to prepare aromatic carbazole-based high-performance polymer materials via nucleophilic substitution polycondensation reactions directly with the NH groups in carbazole units. Herein we report the preparation of bicarbazole-based high-performance polymers by a nucleophilic substitution polycondensation reaction. Both homopolymerization of 3,3′-bicarbazole (BC) with bis(4-fluorophenyl)sulfone (FPS) and copolymerizations with 4,4′-biphenol (BP) or 4,4′-isopropylidenebiphenol (BPA) proceeded smoothly under normal nucleophilic substitution polycondensation reaction conditions and gave high molecular weight polymers. The carbazole-based poly(ether sulfone) analogues have high glass transition temperatures, good thermal stabilities, and reasonable solubilities in organic solvents. The BPA- and BP-based copolymers display similar UV absorption and fluorescence emission properties.

Scheme 1. Synthesis of 3,3′-Bicarbazole



Scheme 2. Reactions between 3,3′-Bicarbazole and Bis(4-fluorophenyl)sulfone



Results and Discussion. 3,3′-Bicarbazole was obtained by chemical oxidation of carbazole in the presence of $FeCl_3$ by the procedure described in the literature,[9] as shown in Scheme 1. Carbazole (5 g, 30 mmol) and anhydrous $FeCl_3$ (20 g, 120 mmol) were suspended in 100 mL of chloroform. After stirring for 30 min, the mixture was poured into a large amount of methyl alcohol. The precipitated green powder was suspended in acetone or ethyl acetate and reduced with zinc powder and acetic acid then purified by sublimation. The product was identified by ^1H NMR which was recorded on a Varian Mercury 300 spectrometer using DMSO as solvent and TMS as standard. ^1H NMR spectrum (DMSO, δ, ppm): 11.27 (s, 2H), 8.52 (s, 2H), 8.25 (d, 2H), 7.82 (d, 2H), 7.65 (d, 2H), 7.55 (d, 2H), 7.40 (t, 2H), 7.18 (t, 2H). TLC and HPLC were used to determine the purity of 3,3′-bicarbazole.

The polymerization reaction of 3,3′-bicarbazole with bis(4-fluorophenyl)sulfone (Scheme 2) was performed in sulfolane at 23 wt % concentration in the presence of 50% excess of K_2CO_3 with toluene or chlorobenzene as azeotropic agent to remove water generated by the condensation reaction. After dehydration at 135−155 °C for 2 h and subsequent removal of toluene or chlorobenzene, the reaction temperature was increased to between 187 and 192 °C. When the solution viscosity had increased significantly, in about 1−2 h, the solution was poured into a large excess of methanol with vigorous stirring. The resulting polymer was insoluble in most common solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N*-methylpyrrolidinone, dimethyl sulfoxide, chloroform, methylene dichloride, 1,1,2,2-tetrachloroethane, concentrated H_2SO_4, acetic acid, trifluoroacetic acid, methanesulfonic acid, and even sulfolane that had been used for the polymerization reaction. Among tested solvents, only *o*-, *m*-, and *p*-cresols dissolved homopoly(arylene bicarbazole) at temperatures $\geq$180 °C. Evaporation of the *o*-, *m*-, or *p*-cresol from a solution of the homopoly(arylene bicarbazole) gave flexible, opaque films. The film-forming ability of the homopoly(arylene bicarbazole) indicates the success in obtaining high molecular weight polymers. In addition to high molecular weight polymers, small amounts of macrocyclic oligomers (repeat unit value *n* from 2 to 9 in Scheme 2) were detected by MALDI-TOF MS. Since the product was insoluble in most common organic and inorganic solvents, it was not possible to calculate the amount of oligomers

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Scheme 3. Synthesis of Homo- and Copoly(arylene carbazole)s

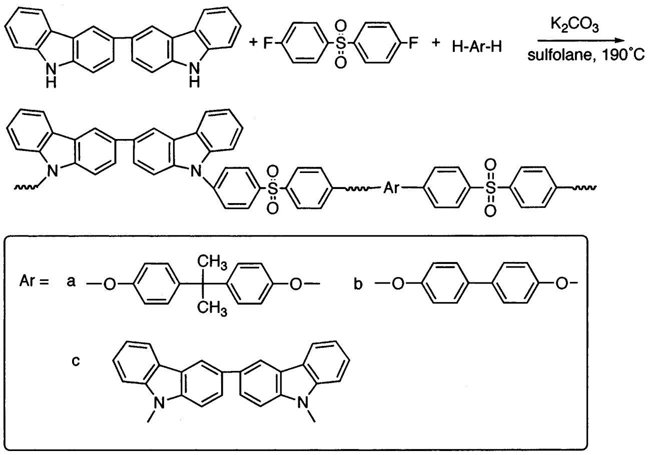

Table 1. Properties of Poly(arylene carbazole)s

polymer	BC:BPA (or BP)	M_n	M_w/M_n	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_d (−5 wt %)[d] (°C)
c	100:0				372[c]	555
a1	75:25				335	496
a2	50:50	13 100	9.35	0.99	295	472
a3	25:75	14 190	7.43	0.98	240	470
b1	50:50			0.77	307	540
b2	40:60			0.93	298	528
b3	25:75			0.95	269	527

[a] Inherent viscosity was measured at a concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane at 30 °C. [b] Heating rate of 20 °C/min under a nitrogen flow rate of 60 mL/min; value from the second scan. [c] Heating rate of 10 °C/min under a nitrogen flow rate of 60 mL/min; value from the second scan. [d] 5% weight loss at a heating rate of 20 °C/min under a nitrogen flow rate of 60 mL/min.

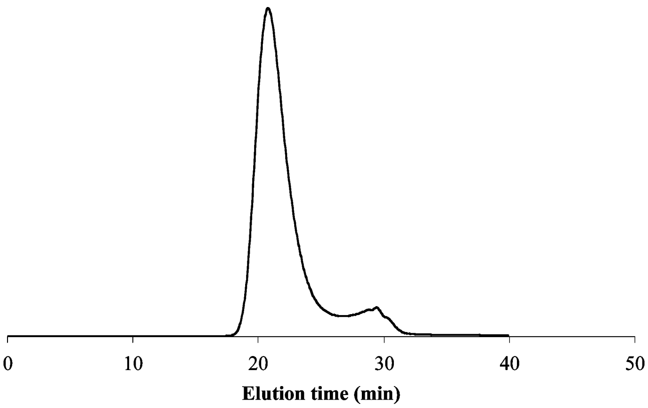

Figure 1. GPC curve of polymer **a2** against polystyrene standard with chloroform as solvent.

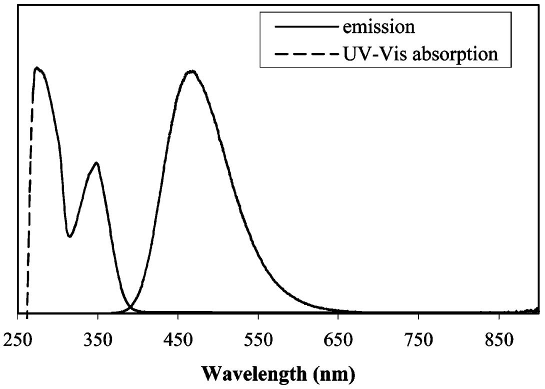

Figure 2. UV−vis absorption and fluorescence spectra of polymer **a2** in 1,1,2,2-tetrachloroethane.

or high molecular weight polymers in the product. The homopoly(arylene bicarbazole) had 5% weight loss, measured by TGA under a nitrogen atmosphere at a heating rate of 20 °C /min, at 555 °C and the glass transition temperature (T_g), measured by DSC under a nitrogen atmosphere at a heating rate of 10 °C /min, at 372 °C in the second scan.

Copolymerizations of 3,3′-bicarbazole with bis(4-fluorophenyl)sulfone and 4,4′-biphenol or 4,4′-isopropylidenebiphenol (Scheme 3) were performed under the same reaction conditions as for the homopolymerization reaction. All copolymerization reactions proceeded smoothly and gave high molecular weights.

As listed in Table 1, the copolymers in 1,1,2,2-tetrachloroethane show inherent viscosities all higher than 0.77 dL/g at 30 °C, indicating high molecular weights. The number-average (M_n) and weight-average (M_w) molecular weights of BPA-based copolymers were determined by GPC against polystyrene standards. The GPC curve of polymer **a2** (Figure 1) demonstrates that the polymerization reaction yielded polymers with high molecular weights and with broad molecular weight distributions as a result of bimodal molecular weight distributions. The larger peak in the GPC curve is attributed to linear high molecular weight molecules, and the smaller peak is attributed to cyclic oligomers. The analysis of the GPC curve of polymer **a2** revealed M_n of around 13 100 with a polydispersity index of 9.35. Copolymers showed improved solubility in organic solvents. For example, polymers **a2, a3, b1, b2**, and **b3** were soluble in chloroform and 1,1,2,2-tetrachloroethane and polymer **a1** swelled in 1,1,2,2-tetrachloroethane at the boiling temperature. Transparent and flexible films were prepared by casting from polymer solutions of **a2, a3, b1, b2**, and **b3** in 1,1,2,2-tetrachloroethane. After an attempt to narrow the molecular weight distribution of polymer **a2** by reverse precipitation with acetone from chloroform solution, the polymer only swelled when trying to redissolve it in chloroform. However, the reprecipitated copolymer was still soluble in 1,1,2,2-tetrachloroethane. The thermal properties of copolymers were examined by DSC and TGA at heating rates of 20 °C/min under a nitrogen atmosphere, and the values of T_g and T_d (−5 wt %) are summarized in Table 1. All reported copolymers were obtained as amorphous substances, and T_gs were observed in the range of 269−372 °C. By addition of 50% of bicarbazole monomer, polymer **a2** shows a remarkable increase in T_g over commercial polysulfone, which was obtained by the nucleophilic substitution polycondensation reaction of BPA and bis(4-fluorophenyl)sulfone and with a T_g of 190 °C.[11] The homopolymer with a very rigid main chain has a very high T_g and, as would be expected, the T_g*s* of copolymers rapidly increase with increasing amount of the bicarbazole moieties. The 5% weight losses are all higher than 470 °C, indicating high thermal stability of all copolymers. BPA-based copolymers are less thermally stable compared with the corresponding BP-based copolymers and homopolymer due to the aliphatic isopropylidene structure in the polymer chains. Thus, thermal properties and solubility can be adjusted by varying the number of bicarbazole units in the feed ratio.

Carbazole-containing polymers are well-known for electro- and photoactive properties that find applications as light-emitting materials.[1,2] UV−vis absorption and fluorescence spectra of dilute solutions of copolymers **a2, a3, b1, b2**, and **b3** in tetrachloroethane were recorded. Figure 2 shows the optical absorption and emission spectra of polymer **a2**. The polymer has two absorption peaks at 285 and 349 nm. The fluorescence curve in Figure 2 shows an emission peak at 465 nm, indicating blue light. The data for the tested polymers are presented in

Table 2. UV Absorption and Emisssion of Copoly(arylene carbazole)s

polymer	UV absorption (nm)	emission (nm)
a2	285, 349	465
a3	282, 347	465
b1	287, 349	470
b2	289, 348	466
b3	299, 344	465

Table 2. All polymers display almost the same electronic absorption energies, and the λ_{max} values are in the range of 282–349 nm. Fluorescence maxima also all appear in a range of wavelengths from 465 to 470 nm. These results indicate that conjugation along the polymer chains is short and limited to bicarbazole units and coincides with the strategy of "isolated chromophores" for blue light emission,[10] which was adopted to prepare polycarbazoles with π-conjugated carbazole or bicarbazole units isolated by aliphatic spacers in the polymer main chain.

In conclusion, we have demonstrated that nucleophilic substitution reactions with the NH group in the bicarbazole molecule as reactive groups under normal polycondensation reaction conditions used to prepare poly(arylene ether)s gave high-molecular-weight homo- and copoly(arylene bicarbazole)s. This provides a simple synthetic pathway that will allow the preparation of a great variety of carbazole-based polymers from commercially available aromatic compounds. High thermal stability, reasonable solubility, and film-forming ability of copoly(arylene carbazole)s make them good candidates for high-performance engineering polymers. UV absorption and blue-light emission characteristics also make these copolymers promising as light emission materials.

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