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Polycarbazole Copolymers from 3-(4-Fluorobenzoyl)carbazole and 4,4′-Biphenol via Combined C-N and C-O Coupling Reactions with Activated Difluorides

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3-(*4*-Fluorobenzoyl)carbazole was synthesized by a Friedel-Crafts reaction of carbazole with *4*-fluorobenzoylchloride. ^{1}H-NMR and MALDI-TOF MS confirmed the structure and the purity. Copolymers of these NH/OH-containing monomers were prepared with 4, 4′-biphenol and bis(4-fluorophenyl)sulfone as comonomers by combined C-O and C-N coupling reactions with activated difluorides. These copolymers were soluble in N-methylpyrrolidinone (NMP), dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and dimethylformamide (DMF). The inherent viscosities of the copolymers in NMP solutions at 30°C were all around 0.8 dL/g. They could be easily cast into tough films from NMP solutions. The copolymers exhibited T_gs ranging from 238°C to 282°C. Thermal stabilities by TGA showed no weight loss below 400°C and the temperatures of 5% weight loss ranged from 535°C to 558°C. The homopolymer of *3*-(*4*-fluorobenzoyl)carbazole was insoluble in common solvents and had a T_g of 332°C, and temperature of 5% weight loss of 560°C. UV-VIS absorption and fluorescence of the polymers are also presented.

Keywords: Carbazole, copolymerization, polycondensation, poly(ether sulfones), UV-Vis absorption, fluorescence

1 Introduction

Carbazole and carbazole-related compounds have attracted much attention in recent years for their photophysical properties (1–4) and are fluorescent in the blue light region (5). Several strategies have been adopted to design macromolecular derivatives with short conjugated segments and wide-band gap (6–8).

Polymers with pendent carbazoyl groups have been studied widely and used in organic photorefractive materials. Compared to polymers with pendent carbazole groups, polymers with carbazole in the main chain are expected to have better mobility of the charge carriers. Poly(3,6-carbazole)s, poly(2,7-carbazole)s and poly(N,N′-bicarbazole)s with carbazole in the main chain have been synthesized.

Our group has successfully synthesized carbazole-containing polymers via a facile nucleophilic polycondensation of 3,3′-biscarbazole with bis(4-fluorophenyl)sulfone (9). The polymers have high T_gs and excellent thermal stabilities (10–12). The polymers showed UV-Vis absorptions at 285 nm and 349 nm and were fluorescent with maxima ranging from 465 to 470 nm. Polycarbazoles containing *p*-phthaloyl biscarbazole (**PPB**) or *m*-phthaloyl biscarbazole (**MPB**) were also synthesized (13). The phthaloyl groups in the main chain increased the solubility and modified the photo properties along with higher T_gs and excellent thermal stability. The UV-Vis absorptions were at 280 nm and 340 nm and the fluorescence maxima ranged from 430 nm to 521 nm.

Based on these results, we designed a new A-B monomer containing a carbazole group. Copolymers with 4,4′-biphenol and bis(4-fluorophenyl) sulfone have been prepared. The viscosities of these copolymers are high and the copolymers can be cast into films from NMP solutions.

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The thermal properties, UV absorption and fluorescence properties of these new carbazole-containing polymers are reported.

2 Experimental

2.1 Materials

Carbazole was purified by recrystallization from alcohol before use. 4-Fluorobenzoyl chloride and iron (III) chloride were purchased from Sigma-Aldrich Chemicals and used without further purification. All common solvents were purchased from Sigma-Aldrich Chemicals and used as received.

2.2 Measurements

^{1}H-NMR spectra were recorded on a Varian Mercury 400 spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the reference. The glass transition temperatures were determined on a Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen atmosphere (flow rate 160 mL/min) and the T_g values reported were from the second heating scan. Thermogravimetric analysis (TGA) data were obtained using a Seiko TG/DTA instrument and the 5% weight loss temperatures were obtained at a heating rate of 20°C/min under nitrogen (flow rate 200 mL/min.). The inherent viscosities (η_{inh}) of the polymers were determined in NMP at 30°C at a concentration of 0.5 dL/g using a calibrated Ubbelohde viscometer. UV absorption spectra were obtained on UV-Vis-NIR Spectrophotometer 5000 of VARIAN. The fluorescent spectra were recorded with a FluoroMax-2 Fluorimeter (S. A. Inc) at ambient temperature.

2.3 Preparation of 3-(4-Fluorobenzoyl)carbazole

To a 100 mL three-necked flask equipped with thermometer, magnetic stirrer and nitrogen inlet was charged carbazole (2 g, 12.00 mmol), iron (III) chloride (0.1 g, 0.60 mmol) and 6 mL of sulfolane. 4-Fluorobenzoyl chloride in 5 mL sulfolane was added dropwise into the reaction mixture over a 2 h period at 170°C. The reaction was continued for a further 3 h. After the reaction mixture was cooled down to room temperature, it was poured into 300 mL of distilled water. The resulting crude product was then washed 3 times with water. Chromatography on a silica gel column was used for separating the product from excess carbazole and other byproducts. The product was then recrystallized with ethyl acetate and hexane. The final product was dried at 80°C under vacuum for 12 h (1.50 g, 86% yield). ^{1}H-NMR (DMSO-$d_{6,}$ δ, ppm): 11.78 (s, 1H); 8.58 (s, 1H); 8.22 (d, 1H); 7.85 (m. 3H); 7.60 (m, 1H); 7.54 (m, 1H); 7.42 (m, 3H); 7.23 (t, 1H). MALDI-TOF MS (*m/s*): 290.63 (M+H$^+$).

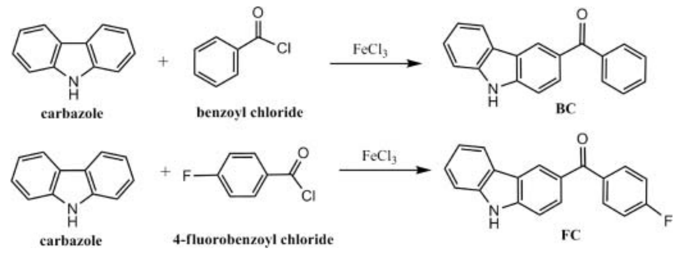
The model reaction of carbazole with benzoyl chloride was carried out in the same way with 90% yield. ^{1}H-NMR (DMSO-$d_{6,}$ δ, ppm): 11.76 (s, 1H); 8.58 (s, 1H); 8.19 (d, 1H); 7.84 (d. 1H); 7.75 (d. 2H); 7.64 (t, 1H); 7.58 (m, 4H); 7.44 (t, 1H); 7.20 (t, 1H). MALDI-TOF MS (*m/s*): 271.70 (M$^+$).

2.4 Preparation of Homopolymer

To a 100 mL three-necked flask equipped with a Dean–Stark trap, water condenser, thermometer, and nitrogen inlet, was charged **FC** (202 mg, 0.70 mmol), K_2CO_3 (116 mg, 0.84 mmol), $CaCO_3$ (74 mg, 0.74 mmol), sulfolane (375 mg) and 2 mL chlorobenzene. The reaction mixture was heated to 170°C under stirring, and then water and chlorobenzene were removed over a 2 h period. The temperature was subsequently brought to 190°C and maintained at this temperature for a further 5 h. The cooled mixture was poured into 80 mL of methanol and the resulting product was collected by filtration. The resulting powder was washed with methanol 3 times and dried at 80°C under vacuum (0.102 g, yield 76%).

2.5 General Procedure for Preparation of Copolymers

A typical synthetic procedure for polymer **3a** that contains 50 mol% of FC is illustrated as follows. To a 100 ml three-necked flask equipped with a Dean–Stark trap, water condenser, thermometer, and nitrogen inlet, was charged **FC** (86.8 mg, 0.30 mmol), bis(4-fluorophenyl) sulfone (76.3 mg, 0.30 mmol), K_2CO_3 (50 mg, 0.36 mmol), $CaCO_3$(32 mg, 0.32 mmol), sulfolane (0.41 g, 35 wt%) and 2 mL chlorobenzene. The reaction mixture was heated to 170°C under stirring, and then water and chlorobenzene were removed over a 2 h period. The temperature was subsequently brought to 190-200°C and maintained at this temperature for a further 3 h. After the mixture was cooled down to room temperature, 4,4′-biphenol (56 mg, 0.3 mmol), K_2CO_3 (100 mg, 0.72 mmol), $CaCO_3$ (64 mg, 0.64 mmol) and 2 mL chlorobenzene were added. After water and chlorobenzene were removed over 1 h, the temperature of the mixture was maintained at 160°C until the viscosity became too high to be stirred. The polymerization was then stopped and 0.5 mL of sulfolane was added into the mixture to dilute the polymer solution. The cooled polymer solution was poured into 80 mL of methanol and the resulting precipitate was collected by filtration. The polymer was then dissolved in NMP, filtered through a thin layer of Celite to remove inorganic salts, and precipitated by the dropwise addition of the solution to methanol. The resulting white polymer was collected by filtration, washed thoroughly with distilled water, and dried at 80°C under vacuum (0.185 g, yield 92%).



Sch. 1. Preparation of 3-Benzoylcarbazole (**BC**) and 3-(4-Fluorobenzoyl) carbazole (**FC**).

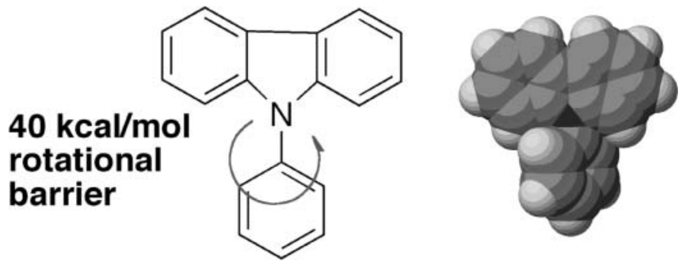


Fig. 1. N-Phenylcarbazole.

3 Results and Discussion

3.1 Synthesis of the Monomer

A model reaction was carried out by reaction of benzoyl chloride with excess carbazole (Sch. 1A). The monosubstituted structure was obtained along with a small amount of the disubstituted byproduct. Column chromatography and recrystallization were used to purify the product. The same method was used for the preparation of 3-(4-fluorobenzoyl)carbazole (Scheme 1B). A high yield of purified product was obtained.

3.2 Polymer Synthesis

In the preparation of homopolymer at 35% reaction concentration, an insoluble material separated from the reaction mixture during the polymerization reaction. This product could not be dissolved in DMSO, NMP or cresol up to their boiling points. A molecular model shows restricted rotations around the C-N bond (rotational barrier 40 kcal/mol) (Fig. 1). The high rotational barrier and resulting rigid structure not surprisingly resulted in the insoluble product.

The NH group in carbazole is less reactive than the OH in 4,4′-biphenol in the nucleophilic substitution condensation reaction. Therefore, 3-(4-fluorobenzoyl)carbazole was first reacted with excess bis(4-fluorophenyl)sulfone to give a carbazole-containing molecule where the N-H groups were completely reacted with the bis-fluorocompound in 3 h, then 4, 4′-biphenol was added to prepare the copolymers (Sch. 2).

3.3 Polymer Characterization

The thermal properties and viscosities of copolymers are listed in Table 1. The values of T_gs ranged from 238.0°C to 282.7°C. The copolymers were stable below 400°C and 5% weight losses ranged from 535.5°C to 558.7°C. Viscosities of the copolymers in NMP solutions were about 0.8 dL/g, and tough polymer films could be cast from NMP solution. The aromatic spacers between carbazole units enhanced the flexibility of the polymer chains and hence increased the solubility compared with the poly(bicarbazole)s previously synthesized. Soluble copolymers with high content of carbazole units were obtained. The 5% weight loss temperatures of the homopolymer were lower, presumably because of low molecular weight.

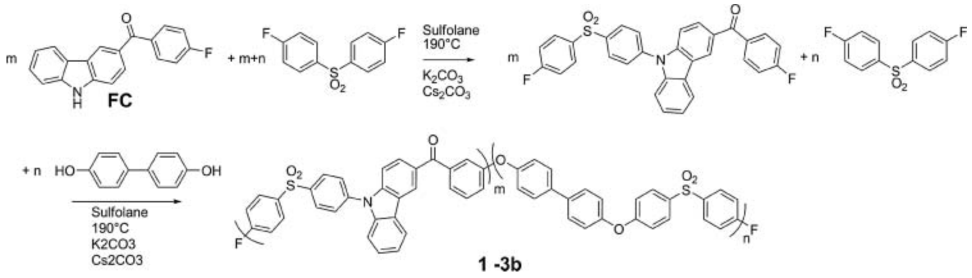
Photo absorption and emission properties of the copolymers are listed in Table 1. The UV absorption showed little change with varying composition, except that the UV absorption around 302 nm was in evidence when the content of monomer went up to 66%. The absorption around 302 nm was similar to that of the monomer FC but slightly "red-shifted".

UV-Vis absorption and photoluminescence spectra are shown in Figure 2. The wavelengths of photoluminescence were lower than the emission wavelengths of poly(bicarbazole)s (11) and other poly(carbazole)s previously prepared (13). As the content of monomer **FC** increased, the wavelength of photoluminescence showed

Table 1. Properties of polymers

Polymer	*[FC]*^{1}	η_{inh} *(dL/g)*^{2}	T_g*(°C)*^{3}	T_d*(-5%wt) (°C)*^{4}	*UV Abs (nm)*	*Emission (nm)*
FC^5	——-	——-	——-	——-	285, 295, 332	447
a	100%	——-	332.0	416.4	insoluble	insoluble
1b	33%	0.80	238.0	535.5	280, 341	445
2b	50%	0.80	244.9	537.4	278, 341	442
3b	66%	0.78	282.7	558.7	278, 302, 341	440

The contents of **FC** were calculated by $mol_{FC}/(mol_{FC}+ mol_{biphenyl})$; measured at a concentration of 0.5 g/dL in NMP at 30°C; determined by DSC at a heating rate of 20°C/min under nitrogen. The reported values are from the second scan; TGA-determined temperature for a 5% weight loss at a heating rate of 20°C/min under nitrogen. Monomer **FC**.



Sch. 2. Synthesis of polymers.

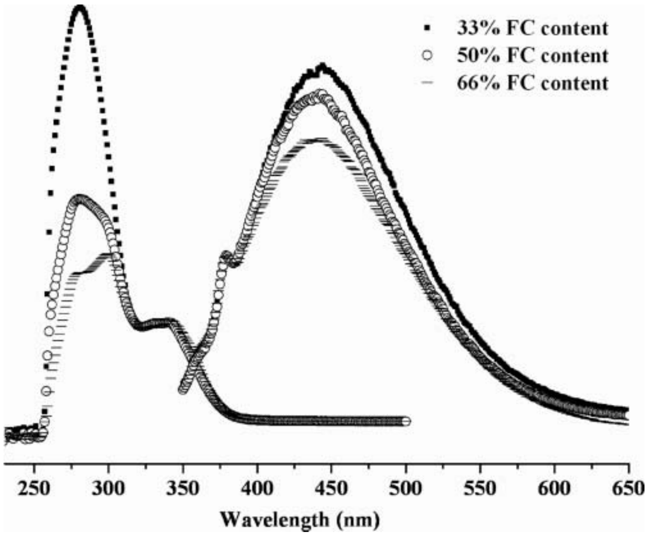


Fig. 2. UV-Vis absorption and photoluminescence of copolymers.

little change and the values were almost the same as the monomer **FC**. This indicated a lack of excimer formation between carbazole-containing units in the polymer chains.

4 Conclusions

The homopolymer prepared from 3-(4-fluorobenzoyl) carbazole was insoluble in all solvents. High molecular weight copolymers were prepared in a nucleophilic substitution polymerization with 4,4′-biphenol and bis (4-fluorophenyl)sulfone as comonomers via combined O-C and N-C coupling reactions. The polymers have high T_gs and excellent thermal stability. The copolymers could be easily cast into tough films from NMP solutions. The copolymers show strong UV absorption with blue light emission.

Acknowledgments

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