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Synthesis and Properties of Carbazole-containing Copolymers from Bis[3-(4-fluorobenzoyl)carbazole] Methane

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A novel difluoride containing carbazole groups was designed. Two series of polycarbazoles based on the novel monomer were synthesized via C-N coupling reactions with either 4,4′-biphenol or bisphenol A. Copolymers were obtained with 4,4′-difluorobenzophenone or bis(4-fluorophenyl) sulfone as comonomer. The solubilities of the poly(carbazole ketones)s were poor, but the poly(carbazaole sulfones)s all dissolved in NMP, DMSO and DMAC. Tough films of poly(carbazole sulfones)s could be easily cast from NMP solutions. The viscosities of poly(carbazole sulfones)s were 0.72 ∼ 0.90 dL/g. The T_gs of polymers ranged from 162.4°C to 258.9°C. The temperatures of 5% wt loss ranged from 460°C to 509°C. UV-Vis absorptions and blue light emissions properties are also presented.

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

1 Introduction

Polycarbazoles have attracted much attention in recent years for their blue light luminescence properties (1,2). The carbazole unit is very interesting for the following reasons: 1) 9H-carbazole is an inexpensive starting material; 2) it is a fully aromatic unit providing a better chemical and environmental stability; 3) the nitrogen atom can be easily substituted with a wide variety of functional groups to help polymer solubility and to tune the optical and electrical properties,; 4) it possesses a bridged biphenyl unit resulting in materials with a lower band gap than traditional poly(p-phenylene)s (3). They have found many applications as photoconductors and charge-transporting materials. Many kinds of polymers with carbazole in the pendent or main chains have been synthesized. Poly(3,6-carbazole), poly(2,7-carbazole) and poly(N,N-carbazole) have been developed with carbazole groups in the main chain of polymers (4,5).

Our group had synthesized several kinds of poly(N,N-carbazole)s as depicted in Figure 1 (6,7). They all have excellent thermal stability and blue light emission, but the solubility and the wavelength scopes need to be optimized.

We have designed a new carbazole-containing bisfluoride for use as a monomer. The introduction of one methylene group between two carbazole groups has expanded the list of wavelengths available and has increased the solubility of the resulting polymers.

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. Anhydrous potassium carbonate (Baker) and anhydrous potassium hydroxide were used without purification. Dibromomethane and all other 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 dimethylsulfoxide-d_6 as the solvent and tetramethylsilane as the reference. The glass transition

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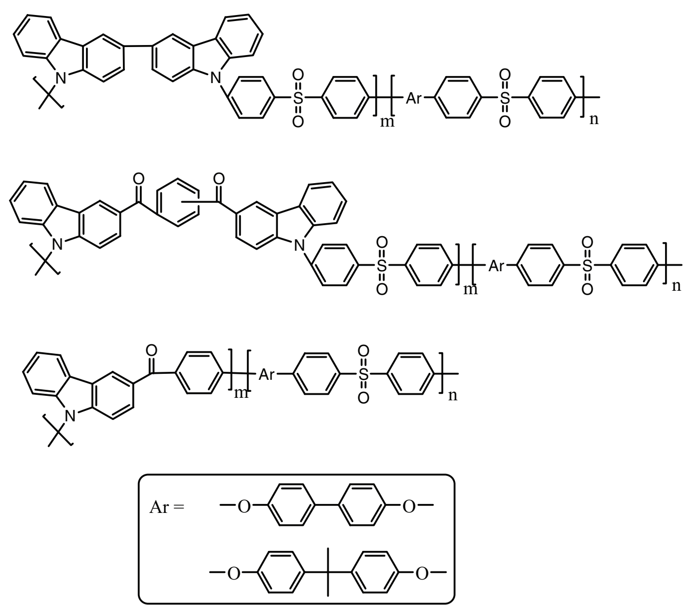
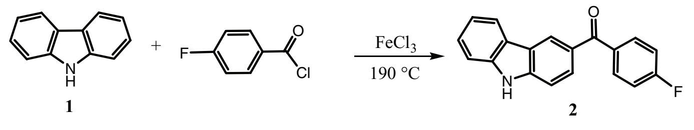


Fig. 1. Poly(carbazole)s.

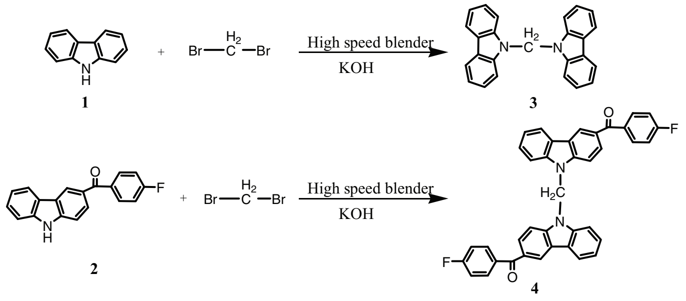
temperatures were determined on a NETZSCH DSC 200PC instrument at a heating rate of 20°C/min under nitrogen atmosphere (flow rate 20 mL/min) and the T_g values were reported from the second heating scan. Thermogravimetric analysis (TGA) data were obtained using a Seiko TG/DTA instrument and the 5% wt loss temperatures were obtained at a heating rate of 20°C/min under nitrogen (flow rate 160 mL/min.). The inherent viscosity (η_{inh}) values of the polymers were determined in NMP at 30°C with a concentration of 0.5 dL/g using a calibrated Ubbelohde viscometer. UV absorptions were obtained on UV-Vis-NIR Spectrophotometer UV-3150 (Shimadzu). The fluorescent spectra were recorded with a Spectrofluorophotometer RF-5301PC (Shimadzu) at ambient temperature.

2.3 Preparation of 3-(4-Fluorobenzoyl)carbazole (Scheme 1)

To a 100 mL three-necked flask equipped with thermometer, magnetic stirrer and nitrogen inlet was charged carbazole (2.0 g, 12.00 mmol), iron (III) chloride (0.1 g, 0.60 mmol) and 6 mL sulfolane. 4-Fluorobenzoyl chloride (0.5 mL, 0.4 mmol) in 5 mL sulfolane was dropped into the reaction mixture over a 2 h period at 170°C. The reaction was continued for a further 3 h. After the mixture was cooled down to room temperature, the reaction mixture was poured into 300 mL distilled water. Then the resulting mixture was 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$^+$).



Sch. 1. Synthesis of 4-fluorobenzoyl carbazole.



Sch. 2. Synthesis routes for biscarbazole methane and bis(4-fluorobenzoylcarbazole) methane.

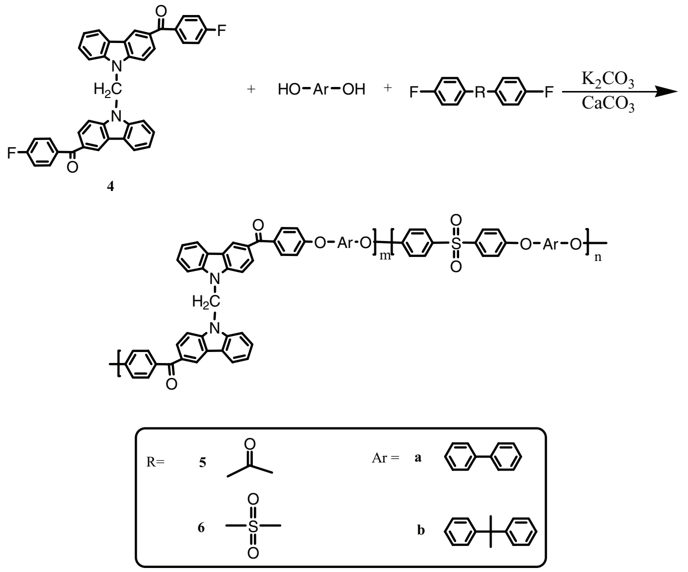
2.4 Preparation of Bis[3-(4-fluorobenzoyl)carbazole] Methane (Scheme 2)

To a 10 mL cuvette in a high-speed blender, and equipped with nitrogen inlet, heater and thermometer, was charged 2.0 g (7.0 mmol) 3-(4-fluorobenzoyl)carbazole, 0.4 g (8.3 mmol) KOH and 3 mL NMP. The mixture was vigorously stirred for 5 min at 70°C. Dibromomethane 0.8 mL (excess) was then added into the mixture under nitrogen. The reaction was continued for a further 8 min at 80°C. The viscosity increased and the stirring was continued with difficulty. The white product was isolated by precipitation in methanol. The product was then dissolved in NMP, and reprecipitated in methanol. The resulting white powder was collected by filtration, washed thoroughly with distilled water, and dried at 80°C under vacuum (0.93 g, yield 91%). Melting point: 292.0°C. ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.55 (s, 2H); 8.32 (d, 2H); 7.84 (m, 8H); 7.68 (d, 2H); 7.47 (t, 2H); 7.38 (t, 4H); 7.29 (t, 4H).

Biscarbazole methane was synthesized in the same way from carbazole and dibromomethane. The yield was 91%. Melting point: 315.0°C. ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.22 (d, 2H); 7.84 (m, 8H); 7.68 (d, 2H); 7.47 (t, 2H); 7.38 (t, 4H); 7.29 (t, 4H).

2.5 General Procedure for Preparation of Copolymers

A typical example for copolymer 6a20 follows. Polymerization reactions were carried out in a dry 25-mL,



Sch. 3. Synthesis of polymers.

three-necked flask equipped with a nitrogen inlet and a Dean–Stark trap fitted with a condenser and magnetic stirrer. **4** (236 mg, 0.4 mmol), 4,4′- biphenol (372 mg, 2 mmol), bis(4-fluorophenyl)sulfone (407 mg, 1.6 mmol), K_2CO_3 (330 mg, 2.4 mmol), 2 mL NMP and 5 mL chlorobenzene was added. The reaction mixture was heated to 170°C under stirring for 2 h, and then water and chlorobenzene were removed. The temperature was subsequently brought to 190 ∼ 200°C and maintained at this temperature until the viscosity became too high for stirring. The reaction was then stopped and 1 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 reprecipitated by the dropwise addition of the solution into methanol. The resulting white polymer was collected by filtration, washed thoroughly with distilled water, and dried at 80°C under vacuum (0.90 g, yield 95%). Syntheses of other copolymers were carried out in the same manner with yields all above 90%.

3 Results and Discussion

3.1 Preparation of Polymers

Poly(carbazole ether ketone)s and poly(carbazole ether sulfone)s can be directly synthesized from the aromatic nucleophilic polycondensation of carbazole derivatives as depicted in Scheme 3. Poly(carbazole ether ketone)s precipitated from the reaction mixtures during polymerization because of poor solubility. High molecular weight poly(carbazole ether ketone)s were therefore difficult to obtain. Poly(carbazole ether sulfone)s were readily obtained with high viscosities as shown in Table 2.

3.2 Polymer Characterization

Thermal properties of polymers are listed in Tables 1 and 2. The T_gs ranged from 162.4°C to 258.9°C. The temperatures of 5% wt loss ranged from 460°C to 509°C. T_gs of poly(carbazole ether sulfone)s were higher than the corresponding ketones, and the polymers were stable up to 400°C by TGA.

UV-Vis absorptions and blue light emission properties were obtained. The polymers all have $\gamma_{\max}$ of 402 nm. The luminescence wavelengths were considerably shorter than those of previously prepared polycarbazoles, and varied from 430 nm to 485 nm (6,7). This indicated that the carbazole units were separated by the aliphatic spacers. The resulting isolated chromophores gave blue light emission. Figure 2 shows the model of the isolated carbazole units.

Table 1. Properties of Poly(carbazole ether ketone)s

Polymer	*Content of 4*	η^1_{inh} *(dL/g)*	Tg^2 *(°C)*	$T_d(-5\%wt)^3$ *(°C)*	*UV-Vis Absorption*^{4} *(nm)*	*Fluorescence (nm)*
5a20	20%	—	198.4	509.1	—	—
5a40	40%	—	200.6	486.4	—	—
5a60	60%	—	213.7	472.2	—	—
a100	100%	—	245.9	—	—	—
5b20	20%	0.74	167.5	455.0	294, 325	402
5b40	40%	0.68	189.7	460.0	294, 325	402
5b60	60%	0.62	208.7	468.8	294, 325	402
b100	100%	—	229.1	—	—	—

[1] Measured at a concentration of 0.5 g/dL in NMP at 30°C.

[2] Determined by DSC at a heating rate of 10°C/min under nitrogen. The reported values are from the second scan.

[3] Onset temperature for 5% weight loss measured by TGA with a heating rate of 20°C/min in nitrogen.

[4] The a series was not soluble.

Table 2. Properties of poly(carbazole ether sulfone)s

Polymer	*Content of 4*	$\eta^{1}_{inh}(dL/g)$	Tg^{2} (°C)	$T_d(-5\%wt)^{3}$ (°C)	*UV-Vis Absorption (nm)*	*Fluorescence (nm)*
6a20	20%	0.82	235.4	510.1	278, 325	403
6a40	40%	0.60	243.5	522.6	278, 325	403
6a60	60%	0.54	258.9	541.4	278, 325	403
a100	100%	—[4]	245.9	—	—	—
6b20	20%	0.89	187.4	443.7	275, 325	402
6b40	40%	0.72	213.6	460.9	275, 325	402
6b60	60%	0.65	233.6	470.8	275, 325	402
b100	100%	—	229.1	—	—	—

[1] Measured at a concentration of 0.5 g/dL in NMP at 30°C.

[2] Determined by DSC at a heating rate of 10°C/min under nitrogen. The reported values are from the second scan.

[3] Onset temperature for 5% wt loss measured by TGA with a heating rate of 20°C/min in nitrogen.

[4] Insoluble.

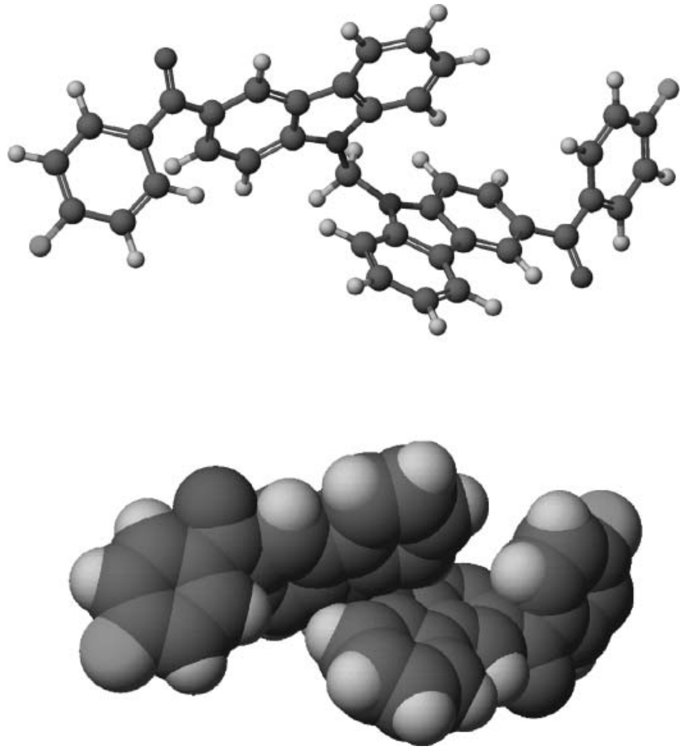


Fig. 2. Minimized energy model of bis[3-(4-fluorobenzoyl) carbazole] methane.

4 Conclusions

A new monomer with a methylene group between two carbazole units in the main chain was designed. Two series of polycarbazoles were synthesized in a nucleophilic substitution polymerization reaction with either bis(4-fluorophenyl)ketone or bis(4-fluorophenyl)sulfone as comonomers. The poly(carbazole ether sulfone)s have higher Tgs than the corresponding ketones and have excellent thermal stability. The solubility of the polycarbazoles was improved and the polymers showed strong UV absorptions and blue light emission.

Acknowledgments

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