Polymer 52 (2011) 1731–1737

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and characterization of polyketones containing pendant carbazoles

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ARTICLE INFO

Article history:
Received 20 January 2011
Received in revised form
14 February 2011
Accepted 18 February 2011
Available online 1 March 2011

Keywords:
Poly(arylene ether ketone)
Carbazole
Fluorescence

ABSTRACT

Condensation of 9-(4-aminobenzene)-carbazole with 4,4′-difluorobenzophenone afforded a carbazole-functionalized poly(aryl amino ketone) (PAK-Cz). Similarly, a series of poly(ether ether ketone)s (PEEK-Cz) and poly(arylene ether ketone)s (PAEK-Cz) containing pendant carbazoles were synthesized from the copolymerization of 9-(4-aminobenzene)-carbazole, 4,4′-difluorobenzophenone and 4,4′-biphenol or 4,4′-isopropylidenebiphenol, respectively. The aforementioned polymers exhibited polystyrene equivalent number average molecular weights of up to 36 kDa, and were found to be thermally stable with high decomposition (T_d) (469–569 °C) and glass transition temperatures (T_g) (155–256 °C). UV–vis absorption and fluorescence spectra revealed that these materials exhibited highly efficient ($\Phi_f = 0.41–0.66$) yellow–green emission ($\lambda_{em} = 500–514$ nm) in solution.

1. Introduction

On account of their unique electronic, electrochemical, and optical properties, polymers containing carbazole moieties in their main or side chains have been widely studied for use in a broad range of applications including photoconduction, electroluminescence, and photorefraction [1–5]. From a synthetic standpoint, there are generally three distinct methods for incorporating carbazole units into a polymeric material: polymerization via the carbazole's 1) 3,6-positions [6–9], 2) 2,7-positions [10], or 3) 9-position (see Fig. 1). The first two approaches are frequently utilized for the preparation of π-conjugated polymers which bear carbazole units in their main chains, often synthesized through a host of transition metal-mediated cross-coupling reactions [6–10]. Polymerization reactions that belong to the third category are generally used to afford polymers with pendant carbazole moieties, and commonly utilize radical, ionic, or ring-opening polymerizations of appropriate N-functionalized monomers, including N-vinylcarbazole [11], carbazole acrylates and methacrylates [12], or carbazole epoxides [13], respectively. Other polymerization methods that afford polymers with pendant carbazoles are less common, but further development of alternative polymerization methods may enable access to a broader range of materials, potentially with tunable physical or electronic properties, or facilitate access to analogous materials in a more efficient manner. Selected examples of such methods include the syntheses of poly(carbazolylacetylene)s from N-alkynylated carbazoles (**A**), the ring opening metathesis polymerization of carbazole-functionalized norbornene derivatives (**B**), and the ring-opening polymerization of oxazole-functionalized carbazoles (**C**) (Scheme 1) [14–16].

Inspired by a report by Hay [17] in which carbazole-based poly(ether sulfone) analogs (**D**; Scheme 1) were prepared via nucleophilic aromatic substitution (S_NAr) condensation of bis(4-fluorophenyl)sulfone with 3,3′-bicarbazole, we developed an interest in the use of S_NAr-type polycondensation chemistry to prepare polymeric materials with pendant carbazoles [12]. In particular, we envisioned using analogous methodology to incorporate the desirable optical properties of carbazoles into industrially relevant thermoplastics such as poly(ether ether ketone)s (PEEKs) and poly(arylene ether ketone)s (PAEKs), polymers which are commonly synthesized via S_NAr-type polycondensation chemistry [18]. Polymers encompassing the useful thermal and mechanical properties of PEEK and PAEK, in combination with the optical properties inherent to carbazole, may find utility in many of the aforementioned applications.

Herein we report the synthesis of a series of copolymers containing carbazoles in their side chains via the condensation of 9-(4-aminobenzene)-carbazole with 4,4′-difluorobenzophenone. To the best of our knowledge, the methods described are the first examples of preparing polymers featuring pendant carbazolyl groups via

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doi:10.1016/j.polymer.2011.02.030

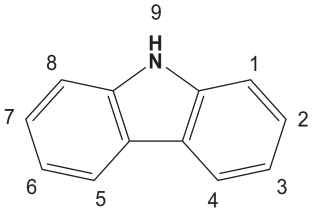


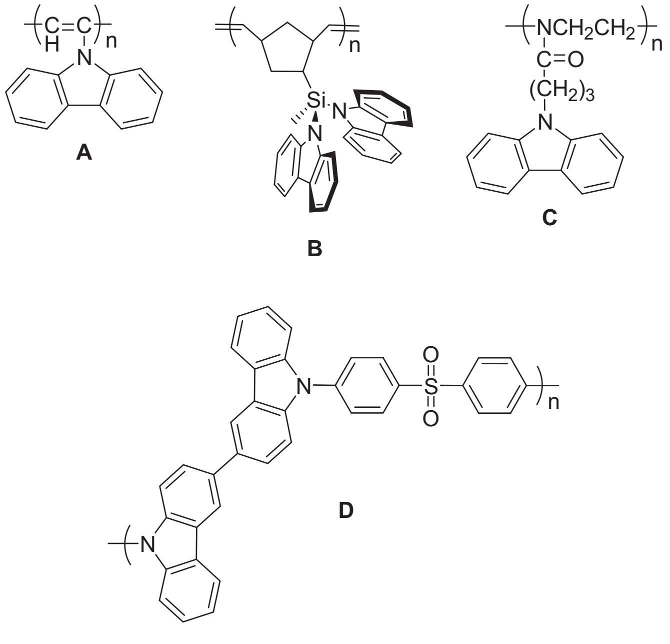
Fig. 1. The structure and numbering system of carbazole.

S_NAr polycondensation chemistry. Likewise, the use of readily accessible primary amines, such as 9-(4-aminobenzene)-carbazole, as a difunctional comonomer in S_NAr polycondensations was hitherto unknown, and represents a new synthetic strategy that may find broad applicability in the preparation of other condensation polymers. The carbazole-based copolymers synthesized were found to have good solubilities in organic solvents, high glass transition temperatures, high thermal stabilities, and high molecular weights, all of which could be modified by varying the carbazole content. The optical properties of the polymers were also examined, and led us to conclude that the desirable emissive characteristics of carbazole were preserved upon polymerization using the methodology described below.

2. Experimental section

2.1. General considerations

All solvents were purchased from Fisher Scientific and used without additional purification unless otherwise noted. Tetramethylene sulfone (TMS) was obtained from the Jinzhou Oil refinery and purified before use. The compounds 9-(4-nitrophenyl)-carbazole (**NO_2–Ar–Cz**) and 9-(4-aminophenyl)-carbazole (**NH_2–Ar–Cz**) were prepared according to literature procedures in comparable purity and yield [19]. All other chemicals were purchased from Aldrich, Alfa Aesar, Acros, or TCI, and were used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker 510 NMR spectrometer (500 MHz). Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent as an internal standard. For ^1H NMR: $CDCl_3$, 7.26 ppm. For ^{13}C NMR: $CDCl_3$, 77.0 ppm. Coupling constants (*J*) are expressed in hertz. Gel permeation chromatography (GPC) was performed at room temperature on a home-built system equipped with a Beckman Coulter System Gold 126 Solvent Module, two fluorinated polystyrene columns (Viscotek IMBHW-3078 and I-MBLMW-3078) arranged in series, and a Beckman Coulter System Gold 168 Diode Array Detector ($\lambda = 254$ nm). Molecular weight and polydispersity data are reported relative to polystyrene standards in tetrahydrofuran (THF). FT-IR spectra were obtained in KBr matrices and were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC823e under an atmosphere of nitrogen at a heating/cooling rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) were performed using a TGA/SDTA851e under an atmosphere of nitrogen at a heating rate of 10 °C min^{-1}. UV–vis absorption spectra were measured using a Perkin Elmer Lambda 35 spectrometer. Emission spectra were recorded using a QuantaMaster Photon Technology International fluorometer.



Scheme 1. Selected examples of polymers which incorporate 9-substituted carbazole units.

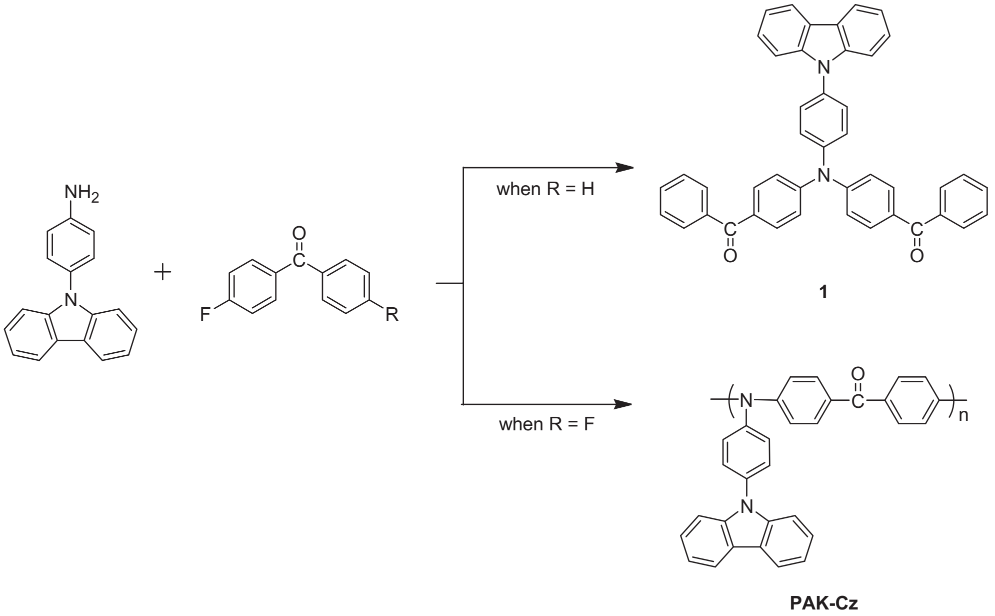
2.2. Synthetic procedures and characterization data

2.2.1. Synthesis of model compound **1**

A three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser was charged with 9-(4-aminophenyl)-carbazole (2.58 g, 10.0 mmol), 4-fluorobenzophenone (4.40 g, 22.0 mmol), and K_2CO_3 (1.52 g, 11.0 mmol). Tetramethylene sulfone (TMS) (30 g) and 10 mL of toluene were then added. After heating the reaction mixture at 140–150 °C for 2 h and subsequent removal of toluene, the reaction temperature was increased to between 198 and 202 °C. After 4–5 h at this temperature, the solution was poured into a large excess of distilled water (300 mL) with vigorous stirring. A green–yellow powder precipitated and was subsequently collected by vacuum filtration, washed with hot deionized water (5 × 300 mL) and ethanol (3 × 300 mL), then dried under vacuum at 80 °C for 10 h to afford the desired product as a yellow powder (5.07 g; 82% yield). m.p. 175 °C (DSC). MALDI-TOF MS calcd for $C_{44}H_{30}N_2O_2$ [M+]: 618.2; found: 618.6. IR (KBr, cm^{-1}): 1450, 1519, 1602 (Ar, C=C), 1662 (Ar–CO–Ar). ^1H NMR (300 MHz, $CDCl_3$): δ 7.36–7.27 (m, 6H), 7.66–7.40 (m, 6H), 7.96–7.75 (m, 16H), 8.16 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR (75 Hz, $CDCl_3$): δ 195.19, 150.49, 144.85, 140.66, 137.87, 134.54, 132.51, 132.32, 132.13, 132.07, 129.75, 128.30, 128.26, 127.33, 125.98, 123.39, 122.69, 120.37, 120.09, 118.56, 109.65. Anal calcd $C_{44}H_{30}N_2O_2$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.22; H, 4.76; N, 4.44.

2.2.2. Synthesis of ***PAK-Cz***

A flask was charged with 9-(4-aminophenyl)-carbazole (2.58 g, 10.0 mmol), 4,4′-difluorobenzophenone (2.18 g, 10.0 mmol), tetramethylene sulfone (30 g), K_2CO_3 (1.52 g, 11.0 mmol) and toluene (10 mL) as an azeotropic agent to remove the water generated during the polycondensation reaction. After heating the reaction mixture to 136–150 °C for 2 h and subsequent removal of toluene, the reaction temperature was increased to 198–202 °C. When the solution viscosity increased significantly (which required approximately 4–5 h), the solution was poured into a large excess of distilled water (300 mL) with vigorous stirring. The precipitated solids were collected and washed repeatedly with hot deionized water (5 × 300 mL) and ethanol (3 × 300 mL), and then dried under reduced pressure at 80 °C for 10 h to afford the desired polymer as a yellow powder (3.49 g; 80% yield). IR (KBr, cm^{-1}): 3040 (Ar–H), 1650 (Ar–CO–Ar), 1592, 1500, 1454 (Ar, C=C), 1309 (NAr_3), 1280



Scheme 2. Preparation of model compound **1** (top) and **PAK-Cz** (bottom). Conditions: K_2CO_3, tetramethylene sulfone, toluene, 200 °C.

(N–C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.12 (br), 7.93–7.62 (br), 8.20–8.95 (br).

*2.2.3. Representative copolymerization procedure (Synthesis of **PAEK-Cz 80%**)*

A flask was charged with 9-(4-aminophenyl)-carbazole (2.58 g, 10.0 mmol), 4,4′-difluorobenzophenone (1.70 g, 8.0 mmol), 4,4′-dihydroxy-2,2-diphenylpropane (BPA) (0.456 g, 2.0 mmol), tetramethylene sulfone (TMS) (30 g), K_2CO_3 (1.52 g, 11.0 mmol) and toluene (10 mL) as an azeotropic agent to remove the water generated during the polycondensation reaction. After heating the reaction mixture to 136–150 °C for 2 h and subsequent removal of toluene, the reaction temperature was increased to between 198 and 202 °C. When the solution viscosity increased significantly (which required approximately 4–5 h), the solution was poured into a large excess of distilled water (300 mL) with vigorous stirring. The precipitated solids were collected and washed repeatedly with hot deionized water (5 × 300 mL) and ethanol (3 × 300 mL), and then dried under reduced pressure at 80 °C for 10 h to afford the desired polymer as a yellow powder (3.57 g; 83% yield). IR (KBr, cm^{-1}): 3040 (Ar–H), 2963 (–CH_3), 1650 (Ar–CO–Ar), 1592, 1500, 1454 (Ar, C=C), 1309 (NAr_3), 1280 (N–C), 1240, 1080 (Ar–O–Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (s), 7.10–7.03 (br), 7.22–7.11(br), 7.34–7.27 (br), 7.50–7.38 (br), 7.61–7.53 (br), 7.90–7.74 (br), 8.18–8.10 (br).

*2.2.3.1. **PAEK-Cz 60%**.* IR (KBr, cm^{-1}): 3040 (Ar–H), 2963 (–CH_3), 1650 (Ar–CO–Ar), 1592, 1500, 1454 (Ar, C=C), 1309 (NAr_3), 1280 (N–C), 1240, 1080 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, Ar–C(CH_3)$_2$–Ar), 7.00–7.06 (m), 7.15–7.19 (q, $J_1 = 9.6$, $J_2 = 19.6$), 7.28 (br), 7.43–7.48 (m), 7.55–7.57 (br), 7.77–7.87 (m), 8.14 (d, $J = 4.4$).

*2.2.3.2. **PAEK-Cz 40%**.* IR (KBr, cm^{-1}): 3040 (Ar–H), 2963 (–CH_3), 1650 (Ar–CO–Ar), 1592, 1500, 1454 (Ar, C=C), 1309 (NAr_3), 1280 (N–C), 1240, 1080 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, Ar–C(CH_3)$_2$–Ar), 6.98–7.06 (m), 7.13–7.17 (t), 7.25–7.31 (m), 7.41–7.48 (q), 7.56 (d), 7.77–7.87 (m), 8.15 (d, $J = 4.4$).

*2.2.3.3. **PAEK-Cz 20%**.* IR (KBr, cm^{-1}): 3040 (Ar–H), 2963 (–CH_3), 1650 (Ar–CO–Ar), 1592, 1500, 1454 (Ar, C=C), 1309 (NAr_3), 1280 (N–C), 1240, 1080 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, Ar–C(CH_3)$_2$–Ar), 6.98–7.06 (m), 7.13–7.17 (t), 7.25–7.31 (m), 7.40–7.47 (q), 7.55 (d), 7.77–7.84 (m), 8.14 (d, $J = 4.4$).

*2.2.4. Representative copolymerization procedure (synthesis of **PEEK-Cz 80%**)*

A flask was charged with 9-(4-aminobenzene)-carbazole (2.58 g, 10.0 mmol), 4,4′-difluorobenzophenone (1.70 g, 8.0 mmol), biphenol (BP) (0.22 g, 2.0 mmol), tetramethylene sulfone (TMS) (30 g), K_2CO_3 (1.52 g, 11.0 mmol) and toluene (10 mL) as an azeotropic agent to remove the water generated during the polycondensation reaction. After heating the reaction mixture to 136–150 °C for 2 h and subsequent removal of toluene, the reaction temperature was increased to between 198 and 202 °C. When the solution viscosity had increased significantly (which required approximately 4–5 h), the reaction mixture was poured into a large excess of distilled water (300 mL) with vigorous stirring. The precipitated solids were collected by vacuum filtration, and washed repeatedly with hot deionized water (5 × 300 mL) and ethanol (3 × 300 mL), and then dried under reduced pressure at 80 °C for 10 h to afford the desired product as a yellow powder (3.17 g; 78% yield). IR (KBr, cm^{-1}): 3040 (Ar–H), 1650 (Ar–CO–Ar), 1593, 1493, 1452 (Ar, C=C), 1313 (NAr_3), 1277 (N–C), 1228, 1110, 1012

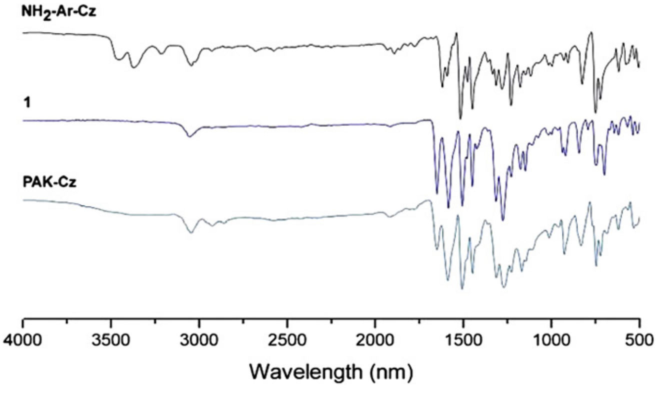


Fig. 2. FT-IR spectra (KBr) of **NH_2–Ar–Cz** (top), **1** (middle), and **PAK-Cz** (bottom).

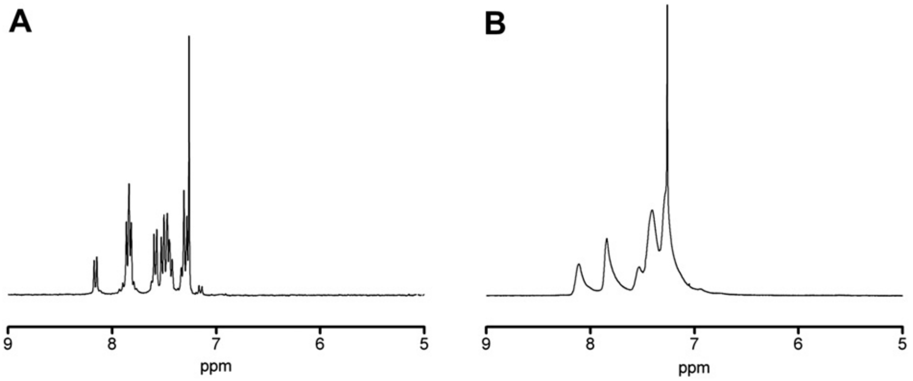


Fig. 3. ^{1}H NMR spectra ($CDCl_3$) of (A) model compound **1** and (B) **PAK-Cz** ($CDCl_3$).

(Ar–O–Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.03 (br), 7.22–7.11 (br), 7.35–7.27 (br), 7.51–7.38 (br), 7.61–7.54 (br), 7.77–7.87 (br), 8.18–8.11 (m).

2.2.4.1. ***PEEK-Cz 60%***. IR (KBr, cm^{-1}): 3040 (Ar–H), 1650 (Ar–CO–Ar), 1593, 1493, 1452 (Ar, C=C), 1313 (NAr_3), 1277 (N–C), 1228, 1110, 1012 (Ar–O–Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (br), 7.13 (s), 7.28 (br), 7.42 (br), 7.55 (br), 7.8–7.86 (br), 8.12 (br).

2.2.4.2. ***PEEK-Cz 40%***. IR (KBr, cm^{-1}): 3040 (Ar–H), 1650 (Ar–CO–Ar), 1593, 1493, 1452 (Ar, C=C), 1313 (NAr_3), 1277 (N–C), 1228, 1110, 1012 (Ar–O–Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, $J = 8$), 7.13 (s), 7.27–7.31 (m), 7.41–7.47 (m), 7.56 (d, $J = 8$), 7.81–7.87 (q, $J_1 = 8$, $J_2 = 17.6$), 8.14 (d, $J = 7.2$).

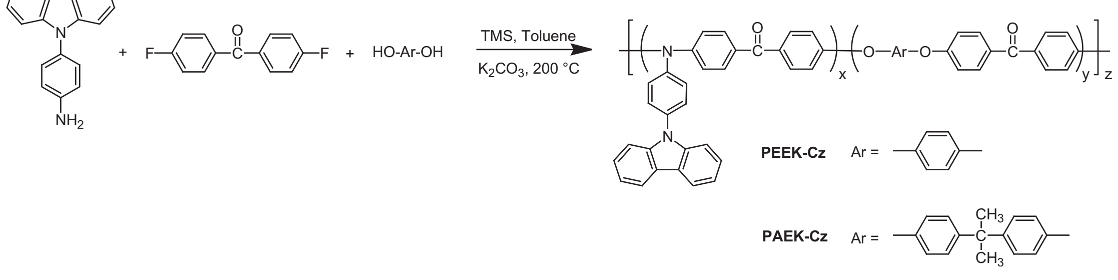
2.2.4.3. ***PEEK-Cz 20%***. IR (KBr, cm^{-1}): 3040 (Ar–H), 1650 (Ar–CO–Ar), 1593, 1493, 1452 (Ar, C=C), 1313 (NAr_3), 1277 (N–C), 1228, 1110, 1012 (Ar–O–Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, $J = 8$), 7.14 (s), 7.25–7.33 (m), 7.42–7.48 (m), 7.55 (d, $J = 8$), 7.80–7.85 (q, $J_1 = 8$, $J_2 = 17.5$), 8.12 (d, $J = 7.1$).

3. Results and discussion

In a preliminary experiment, 9-(4-aminophenyl)-carbazole (**NH_2–Ar–Cz**) [19] was treated with 2 equiv of 4-fluorobenzophenone in tetramethylene sulfone (TMS) in the presence of excess potassium carbonate (Scheme 2). The use of sufficiently elevated reaction temperatures (140–150 °C) and toluene as a co-solvent (30 vol%) facilitated the azeotropic removal of water generated during the condensation reaction. After 4–5 h, the reaction mixture was poured into water, and the precipitated solids were collected by filtration, washed with water and ethanol, and then dried under reduced pressure to afford the desired model compound **1** in 82% isolated yield. As shown in Fig. 2, FT-IR spectroscopy (KBr) confirmed that the characteristic symmetric stretching bands between 3200 cm^{-1} and 3500 cm^{-1} attributed to the Ar–NH_2 groups found in the starting material (**NH_2–Ar–Cz**) were no longer present in the IR spectrum of **1**. In addition, a new, sharp absorption band corresponding to the carbonyl stretching frequency of the aryl ketone appeared at approximately 1650 cm^{-1}. The ^{1}H NMR spectrum of **1** also revealed signals consistent with the assigned structure and the disappearance of the NH_2 signal ($\delta = 5.44$ ppm; DMSO-d_6) of **NH_2–Ar–Cz** (see Fig. 3). Competitive imine formation was not observed by ^{1}H NMR or FT-IR spectroscopy. Collectively, these spectroscopic data suggested to us that **1** was successfully synthesized.

Building on the aforementioned results, we shifted our attention toward the synthesis of polymeric materials. A series of polycondensation reactions were performed using conditions similar to those described above with the exception that an equimolar amount (relative to **NH_2–Ar–Cz**) of ditopic 4,4′-difluorobenzophenone was used in lieu of its mono-fluorinated analog (see Scheme 2). Following 6–7 h of stirring toluene solutions of these monomers at elevated temperatures (2 h at 140–150 °C and then 4–5 h at 200 °C), polymeric materials (i.e., **PAK-Cz**) were isolated in 80% yield by pouring the respective reaction mixtures into an excess of water and ethanol, followed by collection of the precipitated solids via filtration. While this methodology was similar to conventional S_NAr-type polycondensations typically used for the synthesis of polyketones [20], the use of **NH_2–Ar–Cz** as a monomer (instead of a diol) was expected to afford polymers with triarylamine moieties in their main chains.

Limited solubility in common organic solvents precluded molecular weight determination of the materials isolated from the aforementioned polymerization reactions by gel permeation chromatography (GPC) (eluent = THF); however, characterization by FT-IR and ^{1}H NMR spectroscopy ($CDCl_3$) led us to conclude that **PAK-Cz** was successfully formed. For instance, as shown in Fig. 2, the FT-IR spectra of **1** and **PAK-Cz** shared similar features, all of which were consistent with their proposed structures (see Scheme 2). The ^{1}H



Scheme 3. Copolymerization of **NH_2–Ar–Cz** with various diols to form **PEEK-Cz** (Ar = phenyl) or **PAEK-Cz** (Ar = 2, 2-diphenylpropyl). TMS = tetramethylene sulfone.

Table 1
Solubility characteristics of PEEK-Cz, PAEK-Cz, and PAK-Cz in Common Solvents.[a]

	PEEK-Cz					PAK-Cz	PAEK-Cz				
Solvent	0%	20%	40%	60%	80%	100%	80%	60%	40%	20%	0%
NMP	−	−+	++	++	−+	−+	−+	++	++	++	++
DMF	−	−+	+	+	−+	−+	−+	++	++	+	++
DMSO	−	−+	+	+	−+	−+	−+	+	+	+	++
THF	−	−	++	++	−+	−+	−+	++	++	++	++
$CHCl_3$	−	−+	++	++	−+	−+	−+	++	++	++	++
DMAc	−	−	++	++	−+	−+	−+	++	++	+	++

[a] Solubility was determined by studying mixtures of sample to solvent in ratios that were equivalent to 1.0 g L^{-1}. Definitions: ++, Soluble at room temperature; +, soluble upon heating; −+, slightly soluble; −, insoluble even upon heating. The percentages denoted in the table indicate the molar quantity of carbazole in the polymer. NMP = *N*-methyl-2-pyrrolidone. DMF = dimethylformamide. DMSO = dimethylsulfoxide. THF = tetrahydrofuran. DMAc = N-dimethylacetamide.

Table 3
UV–vis absorption and emission data of various polyketones containing carbazole.[a]

Polymer	λ_{max} (nm)	ε (mg^{-1} cm^{-1} mL)	λ_{em} (nm)	Φ_f[b]
PAK-Cz	389	27.01	510	0.55
PAEK-Cz 80%	389	30.00	508	0.49
PAEK-Cz 60%	388	27.01	505	0.59
PAEK-Cz 40%	387	14.20	500	0.41
PAEK-Cz 20%	384	8.46	509	0.66
PAEK-Cz 0%[c]	295	16.82	370	0.08
PEEK-Cz 80%	390	9.66	508	0.59
PEEK-Cz 60%	389	7.67	511	0.59
PEEK-Cz 40%	389	5.67	508	0.48
PEEK-Cz 20%	384	2.33	514	0.59

[a] Absorption and emission spectra were recorded under ambient conditions in $CHCl_3$ at a polymer concentration of 4 mg mL^{-1}.
[b] Fluorescence quantum yields (Φ_f) were determined relative to quinine bisulfate in H_2SO_4.
[c] See Ref. [24].

NMR spectra of the model compound **1** and the isolated polymer **PAK-Cz** are shown in Fig. 3. As was the case in the FT-IR analyses, the disappearance of the signal attributable to the Ar–NH_2 group of **NH_2–Ar–Cz** (5.44 ppm, DMSO-d_6) in the ^1H NMR spectrum of **PAK-Cz** suggested to us that the primary amino groups of the monomer were no longer present in appreciable quantities in the isolated material, presumably having reacted to form triarylamines. Moreover, comparison of the ^1H NMR spectra of **PAK-Cz** and **1** also revealed similar features between the two compounds, and the peak broadening observed in the spectrum of **PAK-Cz** was consistent with the formation of a polymeric material sharing similar molecular connectivity to that of **1**.

From a practical perspective, functional polymers should not only be mechanically and thermally robust but also be readily amenable to common processing conditions. In general, good solubility in organic solvents facilitates polymer processing and enables the use of spin- or dip-coating methodologies to prepare films. With the goal of enhancing the processability of the aforementioned copolymers in mind, we reasoned that integrating PEEK or PAEK with **PAK-Cz** should result in a hybrid material that exhibits both the desirable physical properties and processing advantages of PEEK and/or PAEK [18] while preserving the useful optical properties of carbazole. Thus, subsequent efforts were directed toward copolymerization reactions involving **NH_2–Ar–Cz** and 4,4′-difluorobenzophenone with various bisphenol monomers to form statistical copolymers containing mixtures of amine and ether linkages in the corresponding polymer's backbone.

As depicted in Scheme 3, two series of copolymers were synthesized: the first employed 4,4′-biphenol (BP) to form analogs of PEEK which featured pendant carbazole units (**PEEK-Cz**), and the second employed 4,4′-isopropylidenebiphenol (BPA) to form analogs of PAEK which also featured pendant carbazole units (**PAEK-Cz**). In general, the copolymerization reactions employed similar conditions as the preparation of **PAK-Cz**, albeit with the addition of the comonomer (BP or BPA) in various stoichiometries (see below). The progress of the copolymerization was monitored by GPC; when no further increase in molecular weight was observed, the reaction was purified using a similar procedure as that described for **PAK-Cz** to obtain the statistical copolymers **PEEK-Cz** or **PAEK-Cz**, typically in >80% isolated yield. To prepare polymers with different carbazole contents, the molar feed ratios of **NH_2–Ar–Cz** to BP or BPA were varied. Based on these molar feed ratios, the expected final carbazole contents in the copolymers were 100%, 80%, 60%, 40% and 20%, respectively, where a value of 100% denotes materials that did not contain BP or BPA.

With various **PEEK-Cz** and **PAEK-Cz** copolymers in hand, we next sought to qualitatively measure their solubilities in a variety of solvents. As summarized in Table 1, the solubilities exhibited by the **PAEK-Cz** and **PEEK-Cz** copolymers varied as a function of carbazole

Table 2
Molecular weight and thermal properties of various polyketones containing carbazole.[a]

polymer[b]	M_n (kDa)	M_w (kDa)	M_w/M_n	T_g[d,f] (°C)	T_d[e,f] (°C)
PAK-Cz[b]	–	–	–	256	542
PEEK-Cz 80%	1.3	2.1	1.6	227	534
PEEK-Cz 60%	22	58	2.6	216	569
PEEK-Cz 40%	20	40	2.0	193	560
PEEK-Cz 20%[c]	–	–	–	163	562
PAEK-Cz 80%	3.2	6.3	1.9	184	469
PAEK-Cz 60%	4.4	8.2	1.9	166	511
PAEK-Cz 40%	6.0	12	2.0	155	526
PAEK-Cz 20%	36	90	2.5	163	534

[a] The M_n, M_w, and M_w/M_n values were determined by GPC in THF and are reported relative to polystyrene standards.
[b] The abbreviations PAK, PEEK and PAEK refer to poly(amino aryl ketone), poly(ether ether ketone), and poly(arylene ether ketone), respectively, and the Cz percentages indicate percent composition of **NH_2–Ar–Cz** added to the copolymerization feed.
[c] Molecular weight characteristics could not be determined due to limited solubility in THF.
[d] Determined by DSC.
[e] Defined as the temperature at which 5% mass loss was observed, as determined by TGA.
[f] Heating rate = 10 °C min^{-1}; atmosphere = N_2.

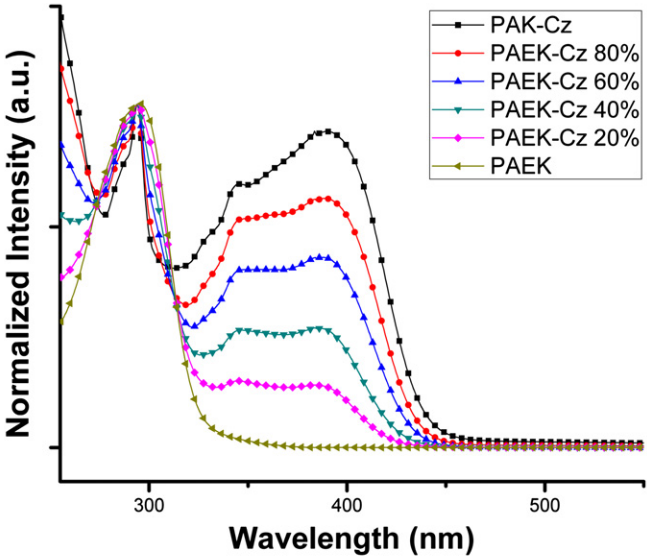


Fig. 4. UV–vis absorption spectra of **PAK-Cz (PAEK-Cz 100%)**, **PAEK-Cz 80–20%** and **PAEK (PAEK-Cz 0%)** in $CHCl_3$.

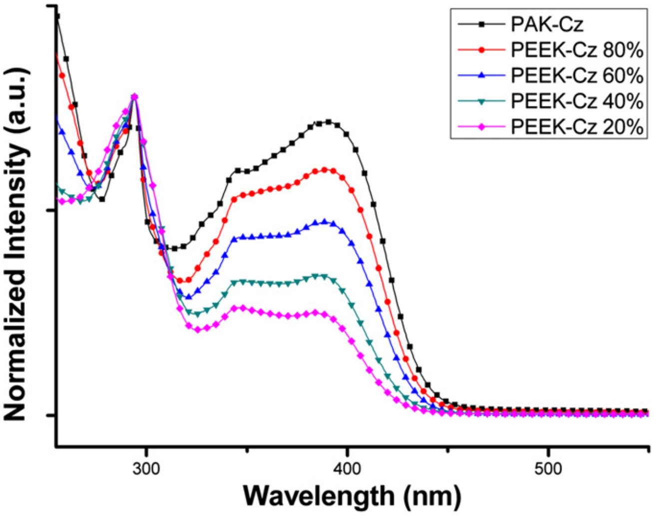


Fig. 5. UV–vis absorption spectra of **PAK-Cz (PEEK-Cz 100%)**, and **PEEK-Cz 80–20%** in $CHCl_3$.

content. While **PAEK-Cz 0%** (zero carbazole content) exhibited good solubility in all of the solvents tested, the solubility of the **PAEK-Cz** copolymers decreased as the percent composition of carbazole increased. **PAEK-Cz 20%**, in particular, displayed good solubility in a range of solvents, including $CHCl_3$, dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and tetrahydroduran (THF), and sturdy, transparent films of this material were obtained via drop casting. In contrast, while **PEEK-Cz 0%** was insoluble in most solvents except sulfuric acid, the solubility of the copolymer increased with carbazole content. Collectively, these results suggested to us that the solubility of the **PAEK-Cz** and **PEEK-Cz** materials could be adjusted by varying the feed ratios of the carbazole and dihydroxylated monomers used in their respective syntheses.

The relatively high solubilities of the **PAEK-Cz** and **PEEK-Cz** copolymers described above enabled analysis of their molecular weights by gel permeation chromatography (GPC). As summarized in Table 2, low molecular weights were measured for copolymers having high carbazole content (i.e., **PAEK-Cz 80–40%**). These data suggested to us that the introduction of bulky and conformationally restrictive triarylamine units into the polymer main chains may challenge the formation of high molecular weight material. Likewise, polymer molecular weight increased as the carbazole content was reduced. As summarized in Tables 1 and 2, the molecular weights of the copolymers qualitatively mirrored their respective solubilities, with the most soluble polymers exhibiting the highest molecular weights. For example, **PEEK-Cz 60%**, **PEEK-Cz 40%**, and **PAEK-Cz 20%**, which were among the copolymers displaying the highest solubilities in the solvents studied, also exhibited the highest number average molecular weights (M_ns). Presumably, precipitation of poorly soluble polymers during the polymerization reactions prevented further growth. In contrast, relatively soluble polymers may remain in solution for longer periods of time, enabling the formation of comparatively high molecular weight polymers.

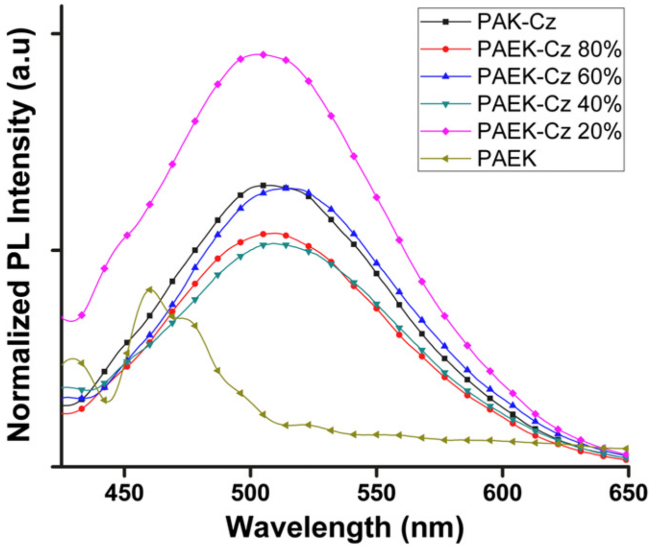


Fig. 6. Fluorescence spectra of **PAK-Cz (PAEK-Cz 100%)**, **PAEK-Cz 80–20%** and **PAEK (PAEK-Cz 0%)** in $CHCl_3$.

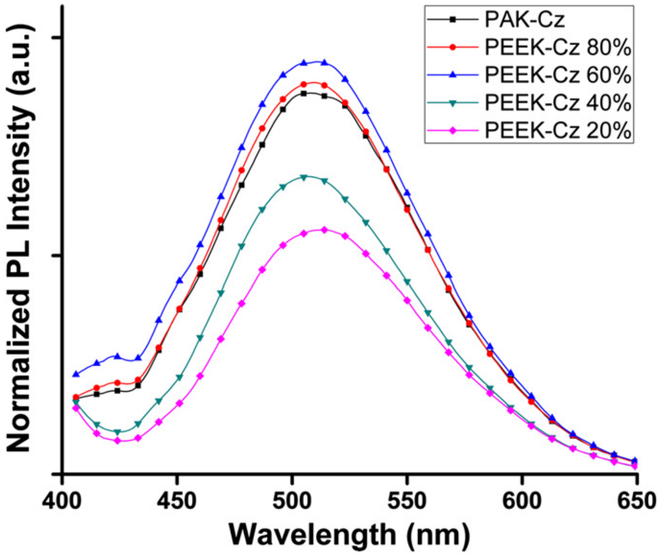


Fig. 7. Fluorescence spectra of **PAK-Cz** (**PEEK-Cz 100%**), and **PEEK-Cz 80–20%** in $CHCl_3$.

With a broad range of copolymers in hand, efforts shifted toward examining the thermal properties of these materials by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As summarized in Table 2, the glass transition temperatures (T_g) of the copolymers were measured in the range of 155–227 °C, and increased with carbazole composition. For example, **PAK-Cz**, which featured the highest carbazole content for any of the copolymers analyzed, exhibited a high T_g (265 °C). The measured T_g values represented a remarkable increase over commercial PEEK or PAEK, which typically exhibit T_gs at 143 and 130 °C, respectively [21]. The decomposition temperatures (T_d), defined as the temperature at which 5% mass loss was observed, were also measured for the aforementioned copolymers and were found to be greater than 469 °C. In general, the **PAEK-Cz** series of copolymers were less thermally stable than their **PEEK-Cz** analogs, presumably due to the instability associated with the former's aliphatic isopropylidene linkages [22]. Overall, however, all of the copolymers showed excellent thermal stabilities, indicating that the thermal properties of these materials were not compromised upon incorporation of the carbazole moieties.

Finally, to determine whether the optical properties inherent to carbazole were retained upon incorporation into various copolymers, the **PAK-Cz** and the series of **PAEK-Cz** and **PEEK-Cz** copolymers were characterized by UV–vis absorption and fluorescence spectroscopies. As shown in Table 3, minimal variability was observed in the UV–vis absorption maxima of the copolymers in chloroform, with all values falling within 5 nm of the optical absorption maximum of **PAK-Cz** ($\lambda_{max} = 389$ nm). As expected, the absorption intensities of the copolymers increased with carbazole composition (see Figs. 4 and 5). Although the copolymers also exhibited a relatively narrow range of emission maxima in the range of $\lambda_{em} = 500–511$ nm (see Table 3), the fluorescence quantum yields ($\Phi_f = 0.41–0.66$) were significantly enhanced when compared to related polymers which also bear the carbazole chromophore as a pendant functionality, such as poly(N-vinylcarbazole) ($\Phi_f = 0.17$) [23]. The nonlinear correlation observed between quantum yield and carbazole content suggested to us to that self-quenching phenomena occurred under the conditions explored [24] (Figs. 6 and 7). Overall, these results suggested to us that the optical properties intrinsic to carbazole were preserved upon incorporation into various copolymers.

4. Conclusion

In conclusion, nucleophilic aromatic substitution of **NH_2–Ar–Cz** with 4,4′-difluorobenzophenone was used to synthesize a series of novel condensation polymers containing pendant carbazole moieties. Remarkably, the reaction of **NH_2–Ar–Cz** with an electron deficient ketone did not yield an imine condensation product; instead, the amine functioned as a ditopic monomer by undergoing successive S_NAr reactions to form a polymer that featured triarylamines in its main chain. The utility of this unique methodology was further demonstrated by adding various commercially available diols to the aforementioned copolymerization reaction to produce a variety of poly(ether ether ketone)s (PEEK)s and poly(arylene ether ketone)s (PAEK) containing pendant carbazole moieties. Ultimately, using the methods described herein, a series of carbazole-containing copolymers featuring improved solubilities in organic solvents and increased molecular weights were successfully synthesized. Moreover, simply adjusting the feed ratio of the **NH_2–Ar–Cz** used in the aforementioned copolymerization reactions enabled tuning of the polymers' photophysical properties. For example, spectroscopic analyses revealed that the optical profiles of the copolymers were dominated by the carbazole chromophore, even at low loadings of **NH_2–Ar–Cz**, ensuring that an optimum in solubility and molecular weight could be reached without sacrificing the material's key photophysical properties. In light of the abovementioned properties as well as their high thermal stabilities, we believe the copolymers describe herein may be used to form mechanically robust fibers or films that also exhibit good optical properties, features which may find utility in the rapidly growing field of flexible electronic applications [1,25].

Acknowledgment

This work was supported by the National Science Foundation of China (50803025) and the Robert A. Welch Foundation (F-1621).

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[24] During our spectroscopic studies, we found that **PAEK-Cz 0%**, which does not contain carbazole moieties, is an excellent blue light emitter with an emission maximum at 459 nm (see also Fig. 6). To the best of our knowledge, this optical property has not been previously reported for PAEK, and given its ease of preparation and scalability, may warrant further exploration.

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