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ORIGINAL PAPER

Synthesis and luminescence properties of long-chain (2,7-carbazolyl)-adamantane copolymers

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Abstract Several long-chain (2,7-carbazolyl) adamantane copolymers, with molecular weight ranging from 4500 to 6000, were synthesized by palladium-catalyzed Suzuki reaction using 1,5-bis (4-bromophenyl) adamantane and N-(2-ethylhexyl)-2,7-carbazole as building molecules. The copolymers were characterized by infrared, ultraviolet, nuclear magnetic resonance (NMR), fluorescence spectroscopies, and thermal analysis. It was found that the introduction of adamantyl group into the backbone of conjugated carbazole polymer significantly improves the thermal stability and spectral stability of the copolymer. These copolymers giving high color purity showed excellent comprehensive performance: the thermal decomposition temperature is up to 409 ~ 432 °C, glass-transition temperature is about 83 ~ 162 °C, fluorescence quantum efficiency is as high as 0.76 ~ 0.85. Hence, the synthesized copolymers have great potential for being used as new blue-light-emitting materials.

Keywords 2,7-carbazole · Adamantane · Blue-light-emitting copolymer · Thermal stability

Introduction

In recent years, long-chain conjugated carbazole polymers are receiving more and more attention for the applications as blue-light-emitting material, for the reason that they have excellent carrier mobility, especially hole mobility, high photochemical stability, strong absorption in UV-light, blue-light-emitting property. Moreover, its band gap is approximately 3.20 eV, and chemical modifications can be easily conducted on the N atom of its structure [1, 2], facilitating to adjust their photoelectric properties. However, glass-transition temperature (T_g) of the most luminescent polycarbazole is relatively low, which alone could limit its applications, because it normally results in unstable luminescence, low stability and short lifetime of the device made from them. Hence, the development of blue-light polycarbazole OLED with high stability has been a hot issue in this field.

Interestingly, copolymers containing adamantane have been reported to show generally high T_g and thermal stability [3–5] due to the unique structure, physical and chemical properties of adamantane groups. Zheng et al. [6] introduced adamantane moiety into the backbone of conjugated poly(phenylenevinylene) PPV, and prepared a blue luminescent material with excellent thermal stability, e.g., decomposition temperature (T_d) up to 411 °C and T_g about 152 °C. They ascribed this improvement of T_d and T_g to the enhancement of PPV polymer chain rigidity thanks to the presence of adamantane. Li et al. [7] reported that bulky adamantane unit can effectively prevent the interaction and aggregation between conjugated fluorene unit; therefore, the fluorene-adamantane copolymers were found to emit more blue color, and to give higher photoluminescence quantum eficiency. From determination of thermogravimetric analysis and

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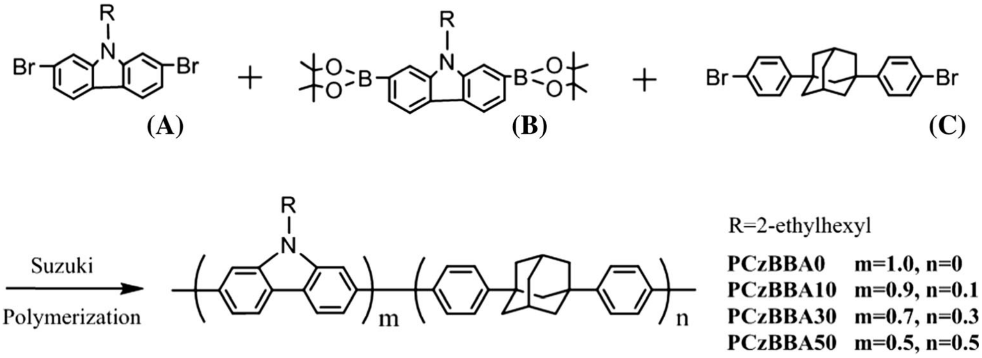

Fig. 1 Synthetic route for carbazole-adamantane copolymers

differential scanning calorimetry, Zhao and Wu [8] revealed that adamantane derivatives modified poly(9,9-dialkylfluorene) s were very thermally stable. After introducing 10, 20, 30 mol% of 1,3-bis(4-bromobenzylideneanimo) adamantane, T_d and T_g of the fluorene-adamantane copolymers were increased from 400 °C and 63 °C (homo-polyfluorene) to 412, 420, 430 °C and 92, 127, 152 °C, respectively. However, it is worth noting that relatively high molecular weight (M_w = 37,000 ~ 210,000) in the polyfluorene polymer system [7, 8] may imply a poor solubility, thus having a negative impact on further fabricating these polymers into useful devices. Long side chains were often deployed to enhance the solubility of the polymer in organic solvents. The PPV-adamantane polymers with molecular weight about 18,000 were soluble in solvent such as THF, chloroform, and 1,2-dichloroethane [6], with the incorporation of side chains such as -OC_6H_{13} and -$OC_{10}H_{21}$. In addition, the large volume of adamantane can reduce the intramolecular interactions of three-dimensional conjugated polymer system [9], and improve their luminescent properties at higher temperatures.

In this work, a long chain low-molecular-weight (M_w = 4500–6000) blue-light-emitting long-chain (2,7-carbazolyl) adamantane copolymers were synthesized through palladium-catalyzed Suzuki reaction with 1,5-bis(4-bromophenyl)adamantane and N-(2-ethylhexyl)-2,7-carbazole. By optimizing adamantane monomer content, the thermal stability (T_g and T_d) and luminescence properties (spectral stability, color purity and fluorescence quantum efficiency) of adamantane-carbazole copolymers were improved remarkably, and high performance blue light emitting materials with good solubility was obtained.

Experimental

Reagents

Bromobenzene, methylbenzene, analytically pure, were purchased from Sinopharm Chemical Reagent Co.,Ltd. Both were treated by non-aqueous processing before use. Trioctyl methyl ammonium chloride, phenylboronic acid, triphenylphosphine palladium catalyst, analytically pure, were purchased from Sinopharm Chemical Reagent Co.,Ltd.; other reagents were sold in the market and used without treatment.

Procedure

The synthetic route of Suzuki coupling reaction was applied to synthesize the copolymers from carbazole compounds (A, B) and1,3-bis(4-bromophenyl) adamantane (C), as indicated in Fig. 1 Building monomers A, B, and C were prepared using the synthetic method reported in previous studies [3, 10–13], but modified to obtain the monomers with higher yields: 88.4% (monomer A), 66.2% (monomer B) and 51.2% (monomer C).

N-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H–carbazole (B, 212.5 mg, 0.4 mmol), N-(2-ethylhexyl)-2,7-dibromo-9H-carbazole (A) and 1,5-bis(4-bromophenyl)adamantane (C) were successively added into an 100 mL three-neck flask. Here, the total amount of substance of the monomer A and C was 0.4 mmol. Then methylbenzene (15 mL), Trioctyl methyl ammonium chloride (2 drops) and potassium carbonate solution (2 $mol \cdot L^{-1}$, 5 mL) was added to the flask. Vacuumize the flask and recharge it with nitrogen three times. Tetrakis(triphenyl phosphine)palladium (12 mg) were added as the catalyst for Suzuki reaction in nitrogen protection. The mixture reacted at 68 °C for 72 h. Then, add 20 mg phenylboronic acid, and keep reacting for 6 h. Add 1 mL bromobenzene, and keep reacting for 6 h. Cool it, and drop the product into absolute methanol. Filter the solution, and wash the obtained solid successively with absolute methanol, distilled water, and absolute methanol. The product was heated with acetone in Soxhlet extractor for 72 h. Celandine green powder can be obtained after a 72 h vacuum drying, with yield of 65% ~ 90%. The ratio of the two monomers (Cz/BBA) was respectively 100/0, 90/10, 70/30 and 50/50, named PCzBBA0, PCzBBA10, PCzBBA30 and PCzBBA50.

Polymer PCzBBA0: FT-IR (KBr, cm^{-1}): 2925, 2856, 1629, 1600, 1556, 1451, 1327, 995, 848, 815, 797. ^{1}HNMR

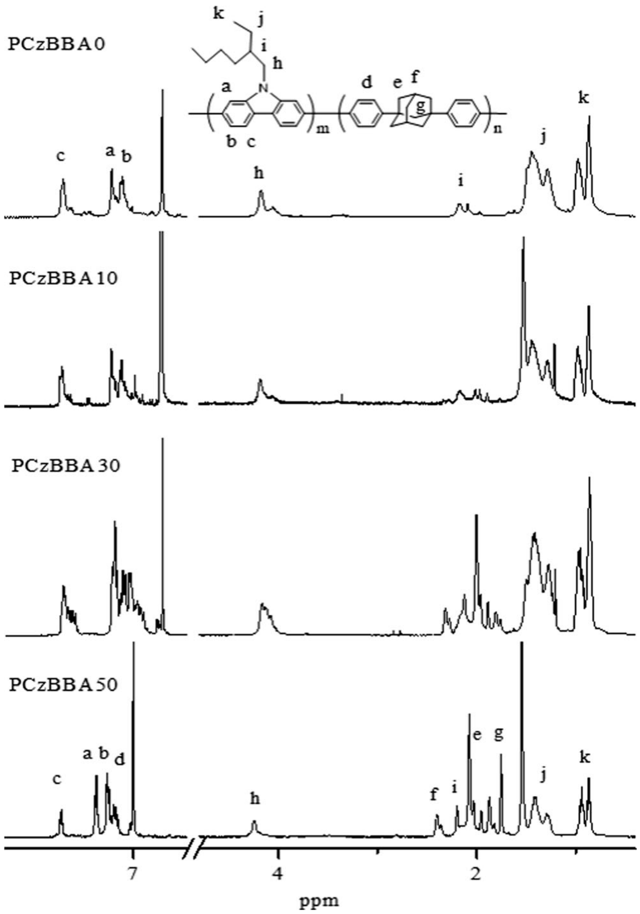

Fig. 2 ^{1}HNMR spectra of the copolymers

(400 MHz, Chloroform-d): δ 8.30–8.11, 7.78–7.53, 4.35, 2.25, 1.64–1.22, 1.08–0.80. ^{13}CNMR (400 MHz, Chloroform-d): 141.17, 121.66, 120.89, 119.53, 118.18, 106.96, 38.57, 30.20, 28.67, 27.92, 23.65, 22.13, 13.03, 10.02. Yield: 89.8%.

Copolymer PCzBBA10: FT-IR (KBr, cm^{-1}): 2955, 2926, 2856, 1630, 1600, 1557, 1452, 1428, 1381, 1328, 1247, 1199, 996, 848, 815, 798. ^{1}HNMR (400 MHz, Chloroform-d): δ 8.24, 8.15, 7.78–7.58, 4.35, 4.23, 2.25, 2.06, 1.42, 1.32, 0.99, 0.89. ^{13}CNMR (400 MHz, Chloroform-d): 148.31, 141.08, 137.88, 126.33, 124.40, 121.61, 120.89, 119.52, 118.18, 106.96, 48.54, 41.47, 38.57, 37.02, 35.56, 30.20, 29.23, 28.66, 27.92, 23.65, 22.13, 13.02, 10.02. Yield: 85.1%.

Copolymer PCzBBA30: FT-IR (KBr, cm^{-1}): 2955, 2925, 2851, 1626, 1602, 1556, 1518, 1453, 1326, 1249, 1216, 1198, 1137, 1013, 997, 848, 800. 1HNMR (400 MHz, Chloroform-d): δ 8.27–8.06, 7.74, 7.74–7.59, 7.61–7.54, 7.58–7.41, 4.34, 4.33–4.22, 2.38, 2.20, 2.08, 2.04, 1.95, 1.45, 1.34–1.21, 1.06–0.92, 0.88. ^{13}CNMR (400 MHz, Chloroform-d): 148.31, 141.02, 137.86, 126.30, 124.39, 121.55, 120.88, 119.51, 118.16, 106.96, 48.51, 41.45, 38.57, 37.01, 35.55, 30.19, 29.22, 28.65, 27.91, 23.65, 22.12, 13.01, 10.01. Yield: 77.6%.

Copolymer PCzBBA50: FT-IR (KBr, cm^{-1}): 2955, 2923, 2849, 1628, 1603, 1518, 1491, 1457, 1324, 1252, 1189, 1139, 1014, 999, 848, 803. ^{1}H NMR (400 MHz, Chloroform-d): δ 8.13, 7.71, 7.51, 4.25, 2.38, 2.20, 2.15, 2.05, 1.96, 1.87, 1.75, 1.54, 1.41, 1.27, 0.91.^{13}CNMR (400 MHz, Chloroform-d): 148.30, 141.03, 137.86, 126.31, 124.38, 121.52, 120.87, 119.50, 118.15, 106.95, 48.53, 41.44, 38.55, 37.02, 35.55, 30.18, 29.21, 28.65, 27.91, 23.64, 22.11, 13.00, 10.01. Yield: 65.2%.

Characterization

^{1}HNMR spectrum was obtained by AVANCEIII 400 MHz Nuclear Magnetic Resonance Spectrometer from Swit Bruker company. FTIR infrared spectrum was obtained by Nieolet380 Fourier infrared spectrometer(KBr tablet). Elemental analysis was carried out with PerkinElmer SeriesIl2400 elemental analyzer from American Perkin Elmer company. The molecular weight of copolymers was investigated by Waters 1525/2414 gel permeation chromatography from American Waters company, with THF as mobile phase and polystyrene as standard sample. Thermogravimetric Analysis was carried out with STA 409 PC comprehensive thermal analyzer from German Netzsch company, with heating rate of 10 °C/min. T_g of copolymers was tested by DSC Q2000 differential scanning calorimeter from American TA company, with heating rate of 10 °C/min. Ultraviolet-visible (UV-Vis) absorption spectrum was obtained by UV2450 ultraviolet-visible spectrophotometer from Shimazu corporation. Fluorescence(PL) spectrum was tested by F7000 fluorescence spectrophotometer from Hitachi, Ltd. UV-Vis and PL spectrum of liquid phase of copolymers was tested by 10^{-5} mol·L^{-1} trichloromethane solution. The films

Table 1 Molecular weight and Adamantane content of copolymers

Copolymer	Mn	Mw	PDI	Theoretical value(%)			Experimental value(%)			Adamantane (mol%) (Elemental analysis)	Adamantane (mol%) (^{1}H NMR spectroscopy)
				C	H	N	C	H	N		
PCzBBA0	3126	4025	1.29	86.59	8.36	5.05	85.99	8.41	4.84	0	0
PCzBBA10	3557	4553	1.28	87.16	8.29	4.54	86.34	8.35	4.52	9.6	9.2
PCzBBA30	4157	5233	1.26	88.29	8.17	3.54	87.68	8.28	3.61	27.9	27.6
PCzBBA50	5074	5474	1.08	89.43	8.05	2.53	88.93	8.17	2.58	48.4	46.1

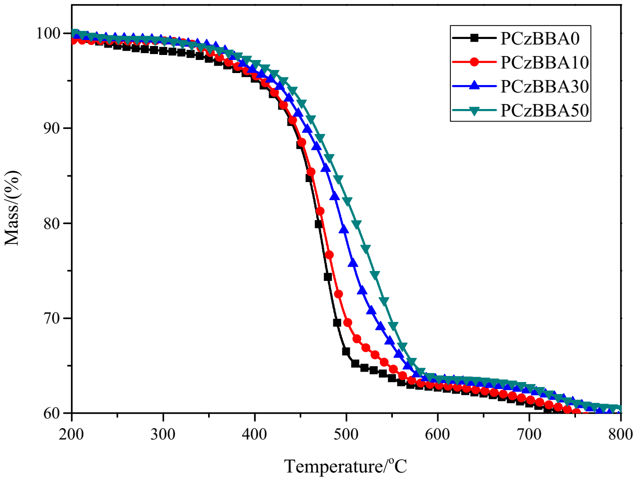

Fig. 3 TGA curves of the copolymers

for UV-Vis and PL spectroscopy were made through spin-coating technique. To calculate the photoluminescence quantum efficiency, the method described in literature [14] was used, taking 9,10-Diphenylanthracene as a reference.

Results and discussion

Synthesis and properties of polymers

Structures and composition of copolymer were characterized by ^{1}HNMR, ^{13}CNMR, FT-IR and element analysis.

We can see from Fig. 2 that the proton peak of the tertiary carbon in adamantane is observed near 2.38 ppm, and that of methyl of long-chain alkyl of carbazole is at 0.91 ppm. According to these two obvious characteristic peaks, the actual mole content of adamantane in the copolymers came out as PCzBBA10 (9.2 mol%), PCzBBA30 (27.6 mol%) and PCzBBA50 (46.1 mol%), respectively. Elemental analysis is used to determine the content of carbon, hydrogen and nitrogen of each copolymer. The results of elemental analysis indicated that the actual mole content of adamantane introduced in the backbone of polycarbazole is close to the calculated value observed in ^{1}HNMR spectrum (as indicated in Table 1). All the actual content of adamantane is lower than the corresponding feed ratio. A possible cause is that in the polymerization reaction, the reactivity of the monomer, 1,5-bis(4-bromophenyl)adamantane is lower than that of N-(2-ethylhexyl)- 2,7-dibromo-9H-carbazole, which is probably caused by the selectivity [7] of the catalyst Tetrakis(triphenylphosphine)palladium.

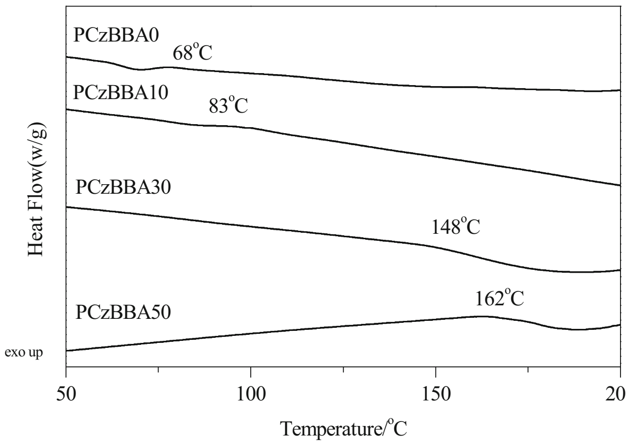

Fig. 4 DSC curves of the copolymers

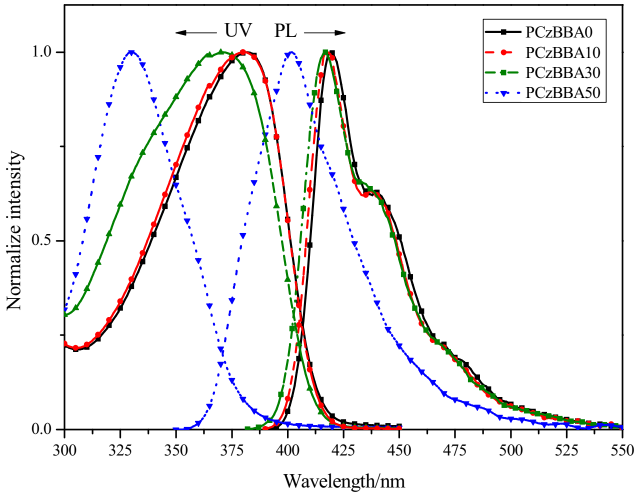

Fig. 5 Ultraviolet-visible absorption spectra and fluorescence emission spectra of copolymers in chloroform solution(1×10^{-5} g·mL^{-1})

Copolymers are tested by gel chromatography. Results showed that the copolymers had low number-average molecular weight(Mn) and weight-average molecular weight(Mw) (3000 ~ 5500), and low polydispersity index (PDI) (1.08 ~ 1.28). Low molecular weight of the copolymers

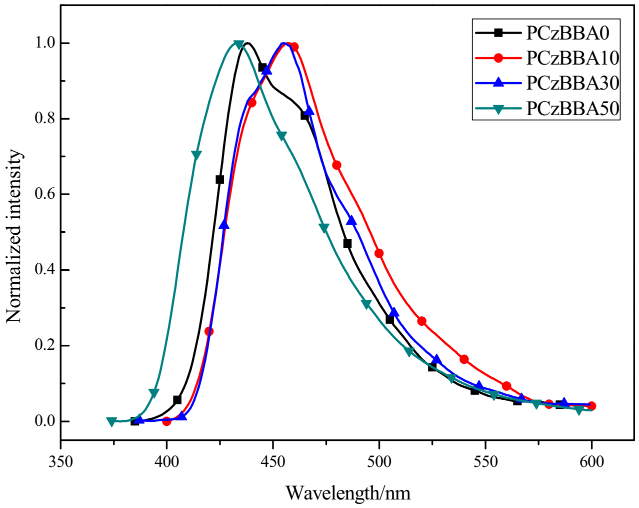

Fig. 6 Fluorescence emission spectra of copolymers in film state

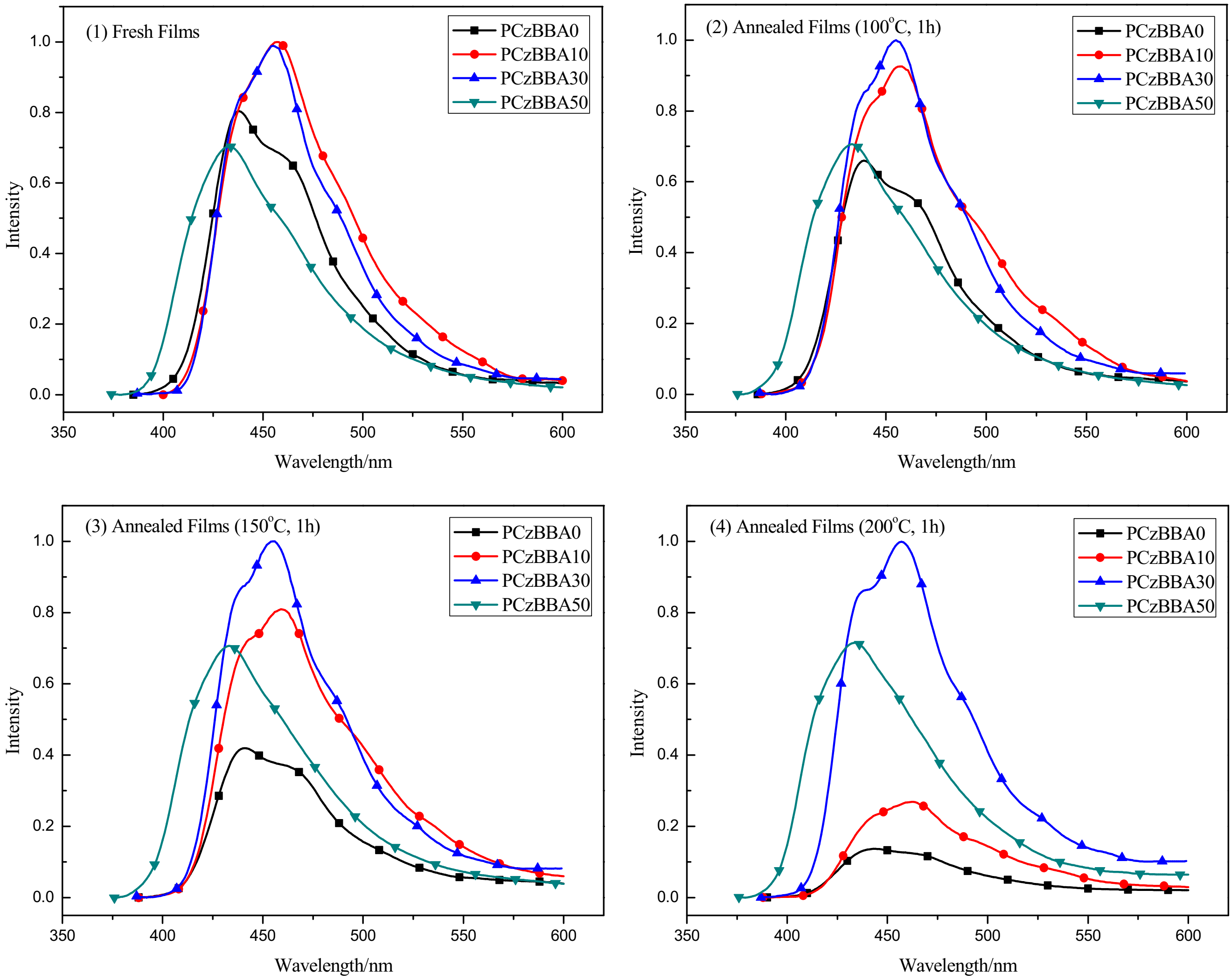

Fig. 7 Fluorescence spectra of the copolymer films (1) untreated and treated at (2) 100 °C (3) 150 °C (4) 200 °C annealing conditions

suggests good solubility in solvents, which ultimately contribute to better processability of fabricating these material into films.

Thermal stability of polymers

It can be seen from the TGA analysis (Fig. 3) that temperature at which copolymers PCzBBA10, PCzBBA30 and PCzBBA50 lose 5% of mass is 409 °C, 420 °C and 432 °C respectively, distinctly higher than that of the polymers without adamantine, PCzBBA0.(402 °C). The same result can be found in the literature. [15, 16] Observed from the DSC images (Fig. 4), the glass-transition temperature of copolymers PCzBBA10, PCzBBA3 and PCzBBA50 with adamantane inside the backbone is 83 °C,148 °C and 162 °C, respectively, which is also largely higher than PCzBBA0 (62 °C). Both TGA and DSC images show that the introduction of adamantane can significantly enhance the thermal stability of the Carbazolyl copolymer, which is crucial to extending the life span of luminescent device.

Photophysical properties of polymers

Fig. 5 shows the UV-Vis absorption spectrum and fluorescence emission spectrum of Cz-BBA copolymer in chloroform solution. In chloroform solution, copolymer PCzBBA10 presents the absorption and emission spectrum similar to Cz, indicating that conjugated length of main chain of Cz copolymers has no significant influence on luminescence properties when adamantane concentration is relatively low. The maximum emission wavelength of PCzBBA30 and PCzBBA50 is 415 nm and 402 nm, respectively. Here blue shift of the copolymers is observed compared to PCzBBA0, possibly because the introduction of adamantane restricted the delocalization of π-electrons of copolymer on the backbone, reducing the effective conjugated length of copolymer.

The intensity of emission peaks of fluorescence spectrum of film was normalized (Fig. 6). In film state, molecules of copolymers are compact, so the possibility of energy transmission between the molecules is high, and thus the effective conjugated length of copolymers increases. As a result, it causes significant red shift of emission peak of copolymers. As the content of adamantane rises, “isolated” structure are formed between long chains of copolymer molecules, impairing the length of conjugated system, thus the degree of red shift decreases, causing progressive blue shift of the maximum emission wavelength. Grell’s research group [17] found that the shoulder peak (460 nm) reflects the order degree within the chains of copolymers, namely the long-range extension of helical conformation of continuous H_{21}in adjacent carbazole rings. In other words, the intensity of the shoulder peaks at 460 nm increases while increasing the order degree in chain or the effective conjugate length. After introducing adamantyl groups, the repulsion between the long chains of alkyl groups was mitigated, and the regularity of long chains of copolymers were enhanced. Therefore the compactly arranged molecules enhanced the effective conjugation length, making the shoulder peak intensity higher. The shoulder peaks of copolymer PCzBBA50 vanished, presenting a different peak pattern from other copolymers. In the process of polymerization, copolymer PCzBBA50 was formed alternately by Cz and Adamantane monomers, attaining the maximum reduction of repulsion between the long chains of alkyl groups in Cz, which presents the highest degree of order among all copolymers. The fluorescence emission wavelength of PCzBBA10, PCzBBA30 PCzBBA50 is 457 nm (444 nm), 455 nm (440 nm) and 432 nm, respectively, so all copolymers are within blue color wavelength (425-480 nm), thus most suitable for blue-light-emitting materials.

Based on the fluorescence emission data (Fig. 6) collected from samples in a thin film state, we calculated the fluorescence quantum yields [14] for PCzBBA0, PCzBBA10, PCzBBA30 and PCzBBA50, and found to be 0.76,0.85,0.83 and 0.27, respectively. Interestingly, when the content of adamantine in the copolymer is lower than 30%, its introduction into the polymer system can increase apparently the quantum efficiency. This phenomenon is due to the enhanced regulation of chain segments along the molecular structure, helping the exciton transfer more smoothly on the conjugated chain, therefore improving energy transmit efficiency. However, there is a limitation for the spatial distance of the exciton transfer. When the adamantane content in the copolymer is too high, this distance will be elongated, leading to a quenching effect for the exciton, thus reducing the number of excitons moving the polymer chain. To this concern, the PCzBBA50 showed the lowest quantum yield, due to the side effect of high fraction of adamantane addition.

Thermal stability of spectrum

To investigate the spectral stability of synthesized copolymers under heating, annealing experiment at different temperatures (100, 150 and 200 °C) was conducted on films of the copolymers. The fluorescence spectra of the films with 1 h annealing treatment are shown in Fig. 7. The transformation of the aggregation structure between chains of copolymer films under heating changed the luminosity, while the luminescent chains of copolymers may also react chemically, affecting their luminosity.

Similar to other luminescent copolymer systems, the pattern of fluorescence emission spectrum of the film mainly depends on the temperature of the heat treatment. Fig. 7 shows that the spectra of copolymers at low temperature present little difference from the ones at room temperature. The introduction of adamantane enhances both thermal stability and spectral stability of the copolymers. Observed from the copolymer PCzBBA50’s fluorescence spectrum images obtained at different temperature, there is no noise peak and the patterns are stable. Affected by the annealing temperature, carbazole molecular chains extend and arrange again, while adamantane can reduce the aggregation effect of the of alkyl groups. When low annealing temperature is used, the full width at half-maximum narrows, meaning a good color purity. When the annealing temperature is high, the conjugation of the molecular chain will be damaged, and red shift of the emission peaks can be observed.

The intensity of emission peaks of the copolymer films at different temperature was shown in Fig. 8. Take PCzBBA30 as an example, the emission peak intensity at different temperature is 100.0, 100.1, 99.4 and 84.9 respectively. The introduction of adamantane has restrained the aggregation of the Carbazole chains, which slightly increased the photon

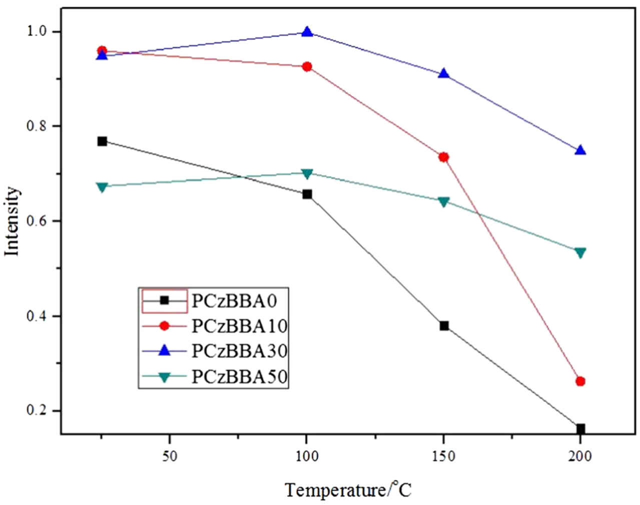

Fig. 8 Intensity of emission wavelength of the polymer films at different temperature

transmission efficiency and emission peak intensity. In the meantime, the intensity within yellow green light wave band are higher than the unmodified copolymers. When the temperature reach the glass transition temperature of PCzBBA30, the intensity of emission peaks decreases. As the film oxidizes and decomposes, the intensity of emission peaks declines distinctly.

In summary, a suitable amount of adamantane in the copolymer system enhances not only their thermal stability, but also their luminescence performance at high temperature.

Conclusions

The long chain (2,7-carbazolyl)adamantane copolymers were synthesized with 1,3-bis(4-bromophenyl) adamantane and N-(2-ethylhexyl)-2,7-carbazole through palladium-catalyzed Suzuki reaction. The copolymer has a number-average molecular weight(Mn) as 3500 ~ 5000, weight-average molecular weight(Mw) as 4500 ~ 5500, and polydispersity index (PDI) as 1.08 ~ 1.28. Both TGA and DSC experiment showed the introduction of adamantane distinctly increased the glass transition temperature (83 ~ 162 °C) and thermal decomposition temperature (409 ~ 432 °C), which is helpful to extending the life span of the luminescent device. The annealing test showed that the copolymer films maintained a high spectral stability at temperature up to 150 °C. Also, the intensity of fluorescence emission is notably higher than the Carbazole homopolymer. The UV-Vis and fluorescence spectroscopy test showed that when the content of adamantane is lower than 30%, the copolymer quantum efficiency reached up to 0.83 ~ 0.85, far beyond the homopolymer. Since the introduction of a certain amount of adamantane enhances not only the thermal stability of carbazole copolymers, but also the blue luminescent properties, the long-chain synthesized (2,7-carbazolyl) adamantane copolymers are suitable for potential applications in blue-light-emitting materials.

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