

# A study of a block copolymer synthesized by RAFT polymerization containing carbazole groups and a europium complex

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A series of block copolymers containing carbazole groups were synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization of styrene monomer. Then the block copolymer containing carbazole groups and europium complex was synthesized by coordination. The block copolymers were characterized by elemental analyses, FT-IR, <sup>1</sup>HNMR, GPC, Uv-vis absorption, fluorescence spectroscopy and cyclic voltammetry. The GPC result shows that the block copolymers have narrow polydispersity and controlled molecular weights (MWs). The fluorescence spectroscopy of the block copolymer containing carbazole groups and europium complex shows red emission assigned to f-f transitions of europium ions in solid state. In addition, the presence of europium complex in the block copolymer was further evidenced by fluorescence characteristic of europium ions. The CV data reveals that in the block copolymer containing carbazole groups and the europium complex a balance can be achieved between electron currents and the electron-hole currents. Thus, the copolymer is a potentially useful candidate for fabricating memory or light emitting devices.

**Keywords:** *reversible addition; fragmentation chain transfer; controlled polymerization; block copolymer; europium complex*

## 1. Introduction

Carbazole based compounds are attractive as photoconductors or charge transporting materials due to their relatively high charge carrier mobilities, hole transporting capability, high thermal and photochemical stability, and electroluminescent properties [1–3]. Rare earth compounds are excellent chromophores exhibiting intense fluorescence with a narrow spectral bandwidth and relatively long lifetime ( $10^{-2}$ – $10^{-6}$  s) [4]. They are the most widely used materials in CRT (cathode ray tube) displays and OLEDs (organic light emitting devices) [5]. Recently, flash (rewritable) and WORM

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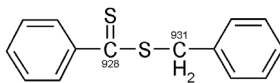
(write once read many times) memories with on carbazole and Eu complex based polymers were demonstrated [6, 7]. In these polymers, the carbazole groups served as electron donors and the hole transporting moieties, and the Eu complex, which was known to exhibit memory effects, was used to hold the charges. Among them, they were synthesized from the corresponding methacrylate or vinyl monomer by free-radical polymerization with 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator. However, it is difficult to control the molecular weights (MWs) and their architectures because most of these polymers with pendant carbazole groups and Eu complexes were synthesized by conventional radical polymerization. The intrinsic wide polydispersity and the difficulty in purifying polymers possibly affect the performance of diode devices. It is desirable to establish new synthetic methods to control MWs, polydispersities, topologies and compositions to manifest their unique properties.

Controlled/living radical polymerization combines the virtues of living polymerization with the versatility and convenience of free radical polymerization. Among all the controlled/living radical polymerizations, RAFT can be considered one of the most promising methods as it allows controlling the homopolymerization of a great variety of monomers such as styrenes, acrylates, methacrylates and vinyl esters [8–12]. RAFT technique has also been successfully applied for controlled polymerization of methacrylate derivatives with carbazole or oxadizole as pendant groups [13].

In this study, the block copolymer containing carbazole groups with controlled MWs and narrow polydispersity were synthesized via RAFT polymerization of styrene monomers. The europium complex which was known to exhibit memory and luminescence properties was synthesized. Then the block copolymer containing carbazole groups and europium complex was synthesized by coordination with europium ion linkage  $\pi$  electron of benzene ring of the block copolymer. By this method, the block copolymer containing carbazole groups and europium complex which had predictable MW and low polydispersity was obtained. Such material has potential use in the fabrication of memories or light emitting devices.

## 2. Experimental

*Material.* All chemicals were obtained commercially and used without further purification unless other-wise noted. Benzene was washed with concentrated sulfuric acid for several times, and then washed with water, aqueous solution of  $\text{Na}_2\text{CO}_3$  (10 wt. %) and water, dried over anhydrous  $\text{CaCl}_2$ , distilled, and preserved over sodium before use. Toluene was refluxed over sodium in the presence of benzophenone until a persistent blue color appeared and then distilled prior to use. 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Chain transfer agent, benzyl dithiobenzoate (BDB) was synthesized according to the procedure reported in the literature [14]. The product was purified by the column chromatography on silica with petroleum ether as the eluent to afford BDB as a purple solid (Scheme 1).



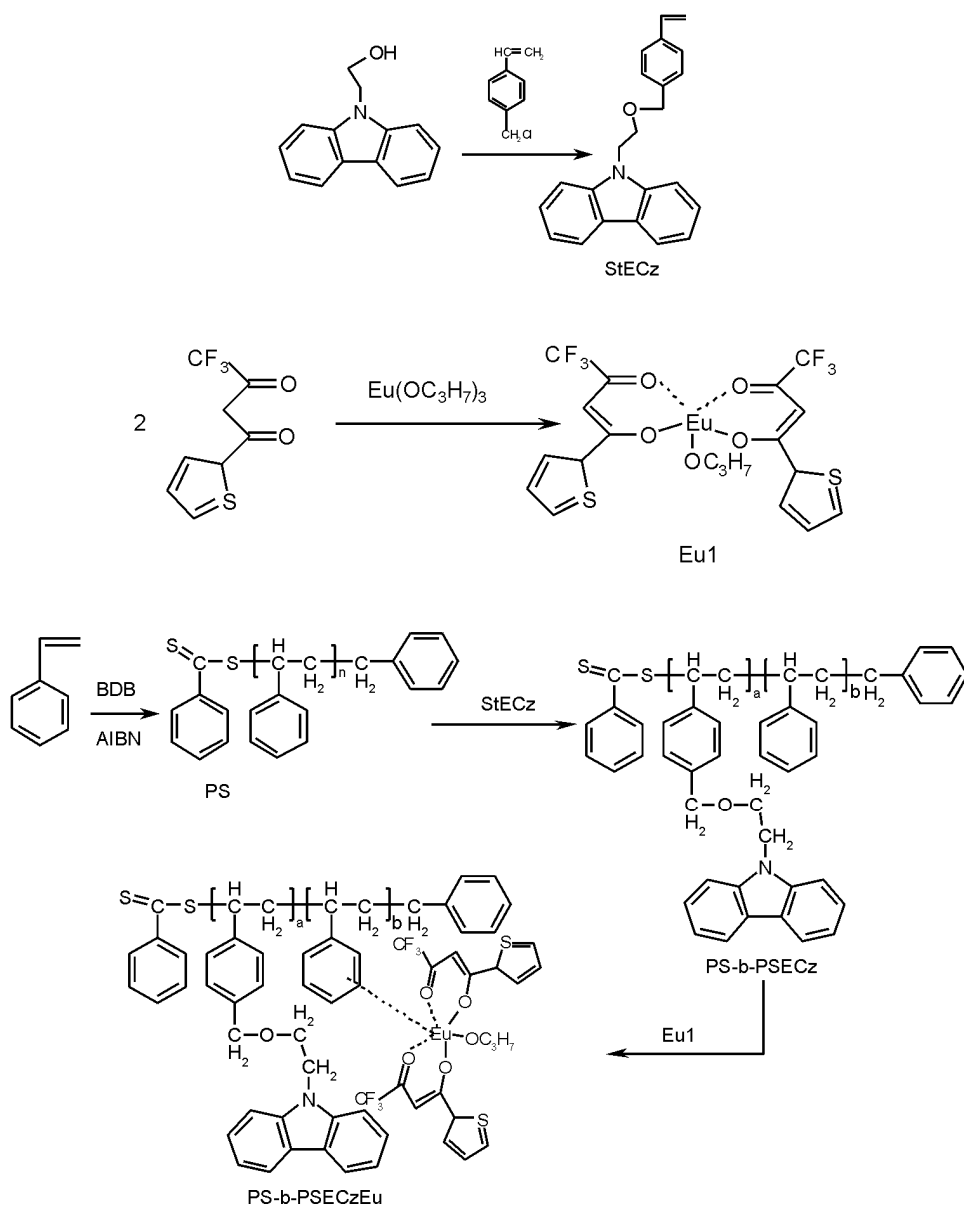
Scheme 1. Chemical structures of the BDB

**Instrumentation.**  $^1\text{H}$ NMR measurements were conducted with a Bruker ACF 300 spectrometer in  $\text{CDCl}_3$  or  $\text{CD}_3\text{OD}$  with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra of the compounds in KBr pellets were recorded on a Nicolet 5700FT-IR spectrophotometer. Gel permeation chromatography (GPC) analyses were conducted with a Shimadzu LC-10AD vp using standard polystyrene samples as the MW references and tetrahydrofuran (THF) as the eluent at the flow rate of  $1.0\text{ cm}^3/\text{min}$ . UV-vis absorption spectra were obtained using a Shimadzu UV 3150 UV-vis spectrometer. Fluorescence spectra were recorded using Edinburgh F900 spectrofluorometer. Elemental microanalyses (for C, H and N) were performed on a Perkin-Elmer 2400 elemental analyser. Eu content was determined by EDTA titration after polymer were decomposed by concentrated  $\text{HNO}_3/\text{HClO}_4$  (1:1, v/v). Cyclic voltammetry (CV) measurements were performed on an Autolab potentiostat/galvanostat system using a three electrode cell under argon atmosphere. The polymer films on a Pt disk electrode (working electrode) were scanned anodically and cathodically in a solution of tetrabutylammonium hexafluorophosphate ( $n\text{-Bu}_4\text{NPF}_6$ ) in acetonitrile (0.1 M) with Ag/AgCl and a platinum wire as the reference and counter electrodes, respectively.

**Synthesis of monomers and the block copolymers.** *Synthesis of the monomer 2-(9H-carbazol-9-yl) methyl styrene (StECz).* A dimethyl sulphoxide solution of NaOH and  $\text{H}_2\text{O}$  was added to the mixture of 2-(9H-carbazol-9-yl) ethanol (2.11 g, 10 mmol), a small quantity of NaI and tetrabutylammonium bromide. The mixture was stirred for 2 h at  $50\text{ }^\circ\text{C}$ , then chloromethyl styrene was added dropwise to the mixture. The reaction mixture was stirred for 4 h at  $50\text{ }^\circ\text{C}$ . The salt was removed by extraction with dichloromethane and water and the solvent was removed by evaporation. The yellow residue was purified by silica gel column chromatography using petroleum and ethyl acetate as an eluent, and further purified by recrystallization in petroleum. Yield: 80% (2.60 g). Anal. Calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}$  (wt. %): C, 84.37; H, 6.46; N, 4.28. Found: C, 84.00; H, 6.70; N, 4.12. IR (KBr,  $\text{cm}^{-1}$ ): 3047.0, 2939.0, 2877.1, 2850.3, 1652.7 ( $\nu_{\text{C}=\text{C}}$ ), 1592.9, 1483.0, 1457.9, 1041.3, 748.2, 719.3 (carbazole ring).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$ (ppm): 3.86(2H, s,  $-\text{CH}_2\text{N}-$ ), 4.00(2H, s,  $-\text{CH}_2-$ ), 4.51(2H, s,  $-\text{OCH}_2-$ ), 5.21 (1H, d, C = C), 5.71(2H, d, C = C), 7.09~8.10 (the H of carbazole and benzene ring) (Scheme 2).

**Synthesis of the europium complex (EuI).** Europium trisopropoxide (3 mmol) was dissolved in  $15\text{ cm}^3$  of anhydrous 2-propanol and toluene (1:1, V/V) by heating in a flask under nitrogen atmosphere. A solution of thenoyltrifluoroacetone (1.44 g, 6 mmol) in  $5\text{ cm}^3$  toluene was added dropwise into the flask. The reaction mixture was

refluxed for 2 h and cooled. The excess solvent was evaporated and a yellow solid was obtained. Yield: 80% (2.0 g). Eu content for  $\text{EuC}_{19}\text{H}_{15}\text{O}_5\text{S}_2\text{F}_6$  (wt. %): 22.6%. Found: 23.3%. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3110, 2921( $\nu_{\text{C-H}}$ ), 1611( $\nu_{\text{C=O}}$ ), 1541( $\nu_{\text{C=C(TTA)}}$ ), 1455, 1412, 1306( $\nu_{\text{C-F}}$ ), 1142, 787, 644( $\nu_{\text{C-CF}_3}$ ), 581, 463( $\nu_{\text{Eu-O}}$ ).  $^1\text{H NMR}$  ( $\text{CD}_3\text{OD}$ , 300 MHz):  $\delta$  (ppm): 1.53(6H, s, 2 $\text{CH}_3$ ), 2.73(H, s, CH), 3.50(2H, s, 2 $\text{COCHCO}$ ), 7.36–8.51(6H, m, 2 $\text{C}_4\text{H}_3\text{S}$ )



Scheme 2. Synthetic routes of the monomer and polymer

**RAFT polymerization of styrene.** All polymerizations were carried out in Schlenk tubes at homogeneous conditions. For a typical polymerization, styrene (8.72 mmol), BDB ( $4.4 \times 10^{-2}$  mmol), AIBN ( $1.4 \times 10^{-2}$  mmol) and dry benzene ( $0.5 \text{ cm}^3$ ) were placed in a dry Schlenk tube equipped with a magnetic stirr bar. Then the solution was thoroughly deoxygenated by three freeze–pump–thaw cycles, backfilled with nitrogen, and the polymerization was conducted at  $70^\circ\text{C}$  for 24 h. The reaction mixture was precipitated in an excess of methanol, collected by filtration, and dried under vacuum to yield (PS) as pink powder. (Scheme 1) The monomer conversion was measured by the gravimetric method. The resulting powder was analyzed by GPC and had number average molar mass  $M_n = 0.6 \times 10^4$ ,  $M_w = 0.7 \times 10^4$  ( $M_w$  is weight average molar mass) and polydispersity index  $PDI = M_w/M_n = 1.13$ .

**The RAFT copolymerization using PS as macro-RAFT agent.** All copolymerizations were carried out in Schlenk tubes at homogeneous conditions. For a typical polymerization, 2-(9H-carbazol-9-yl) methyl styrene (StECz) (0.5 mmol), PS ( $M_n = 0.6 \times 10^4$ ,  $PDI = 1.13$ ) ( $12.5 \times 10^{-2}$  mmol), AIBN ( $3.75 \times 10^{-2}$  mmol) were placed in a dry Schlenk tube equipped with a magnetic stir bar. Then the polymerization was carried out in a similar way as described above. The resulting copolymer PS-*b*-PStECz was analyzed by GPC and had  $M_n = 1.03 \times 10^4$ ,  $M_w = 1.18 \times 10^4$ ,  $PDI (M_w/M_n) = 1.15$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta(\text{ppm})$ : 3.87(2H, s,  $-\text{CH}_2\text{N}-$ ), 4.20(2H, s,  $-\text{CH}_2-$ ), 4.53(2H, s,  $-\text{OCH}_2-$ ), 5.22(1H, d,  $-\text{C}$  (bonded benzene ring)  $\text{H}-\text{C}$ ), 5.73(2H, d,  $-\text{C}-\text{CH}-$ ), 7.08–8.11 (H of carbazole and benzene ring).

**Preparation of the block copolymer containing carbazole groups and Eu complex (PS-*b*-PSECzEu).** PS-*b*-PSECz (0.5 mmol) ( $M_n = 1.03 \times 10^4$ ,  $M_w = 1.18 \times 10^4$ ,  $PDI = 1.15$ ), the europium complex (Eu1) ( $2.5 \times 10^{-2}$  mmol) and dry benzene ( $0.5 \text{ cm}^3$ ) were placed in a dry Schlenk tube equipped with a magnetic stir bar. Then the mixture was heated at  $70^\circ\text{C}$  for 24 h. The reaction mixture was precipitated in an excess of methanol, collected by filtration, and dried under vacuum to yield as yellow powder. The resulting powder was analyzed by GPC and had  $M_n = 1.03 \times 10^4$ ,  $M_w = 1.43 \times 10^4$ ,  $PDI = 1.39$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 Mhz):  $\delta(\text{ppm})$ : 1.56(6H, s,  $2\text{CH}_3$ ), 3.87(2H, s,  $-\text{CH}_2\text{N}-$ ), 4.20(2H, s,  $-\text{CH}_2-$ ), 4.53(2H, s,  $-\text{OCH}_2-$ ), 5.22(1H, d,  $-\text{C}$  (bonded benzene ring)  $\text{H}-\text{C}$ ), 5.73(2H, d,  $-\text{C}-\text{CH}-$ ), 7.08–8.11 (the H of carbazole and benzene ring). The Eu content was 2.57% (wt. %).

### 3. Results and discussion

#### 3.1. Living characters of the polymerization

In the RAFT copolymerization for the St-*b*-StECz system, styrene was the first monomer form the macro-RAFT agent. 2-(9H-carbazol-9-yl) methyl styrene (StECz) served as the second monomer.

A successful RAFT polymerization requires careful selection of a suitable CTA, depending upon the monomer. Benzyl dithiobenzoate (BDB) was selected as the CTA because BDB is an excellent CTA for RAFT polymerization of styrene monomers [15]. The homo-polymerizations of styrene were carried out in benzene at 70 °C using BDB as the chain transfer agent (CTA) and AIBN as an initiator under various conditions. In Table 1, details on syntheses of polystyrenes have been presented.

Table 1. Molecular weights and polydispersity indexes of polystyrene prepared in various conditions

Monomer – St [10 <sup>3</sup> M]	CTA–BDB [10 <sup>5</sup> M]	<i>t</i> [h]	AIBN [10 <sup>5</sup> M]	<i>M<sub>n</sub></i> ×10 <sup>−4</sup>	<i>M<sub>w</sub></i> ×10 <sup>−4</sup>	<i>PDI</i> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> )	<i>M<sub>n, theor.</sub></i> ×10 <sup>−4</sup>	Conv. [%]
8.72	0	24	0.8	6.71	16.9	2.51		77.8
	4.4	24	2.2	0.92	1.16	1.26	0.85	40.9
	4.4	24	1.4	0.63	0.71	1.13	0.69	32.1
	2.2	24	1.1	1.12	1.34	1.20	1.46	35.2
	2.2	24	0.7	1.40	1.74	1.24	1.60	37.8

The theoretical number-average MW (*M<sub>n, theor.</sub>*) was calculated from monomer conversion according to Eq. (1) [16]:

$$M_{n, theor.} = \frac{[\text{monomer}]_0}{[\text{CTA}]_0} M_{\text{monomer}} \times \text{Conv} + M_{\text{CTA}} \quad (1)$$

where *M<sub>monomer</sub>* and *M<sub>CTA</sub>* are the molecular weights (MWs) of monomers and CTA, and [monomer]<sub>0</sub> and [CTA]<sub>0</sub> are the initial concentrations of monomer and CTA, respectively.

The GPC-determined number average MWs are roughly comparable to the theoretical values (*M<sub>n, theor.</sub>*), calculated from the monomer/CTA molar ratio and conversion of the monomer using Eq. (1). The polydispersity index (*PDI*) of the resulting polystyrene was lower than 1.3 which demonstrates that the RAFT polymerization system of styrene was well controlled.

The polystyrene (*M<sub>n</sub>* = 0.6 × 10<sup>4</sup>, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.13) obtained from the RAFT polymerization was chosen as the macro RAFT agent, AIBN as the initiator and 2-(9H-carbazol-9-yl) methyl styrene (StECz) as the second monomer. The block copolymerizations were carried out in benzene at 70 °C under various conditions, respectively. Table 2 shows the summary of the conditions and results.

In an ideal case, the theoretical *M<sub>n, theor.</sub>* of the block copolymer is calculated according to Eq. (2) [17]:

$$M_{n, theor.} = \frac{[\text{monomer}]_0}{[\text{polymer CTA}]_0} M_{\text{monomer}} \text{Conv} + M_{\text{polymer-CTA}} \quad (2)$$

where  $M_{\text{polymer-CTA}}$  is MWs of the first block (polystyrene from the RAFT polymerization),  $M_{\text{monomer}}$  is MWs of the second block (second monomer), Conv is the fractional conversion of the second monomer, and  $[\text{monomer}]_0$  and  $[\text{polymer CTA}]_0$  are the initial concentrations of monomer and polymer CTA, respectively.

Table 2. Molecular weights and polydispersity indexes of PS-*b*-PSECz copolymers in various conditions

Monomer [ $10^{-3}$ mol]	PS [ $10^{-5}$ mol]	<i>t</i> [h]	AIBN [ $10^{-5}$ mol]	$M_n$ $\times 10^4$	$M_w$ $\times 10^4$	<i>PDI</i> $M_w/M_n$	$M_n$ theor. $\times 10^4$	Conv. [%]
0.5	8.33	24	2.50	1.17	1.38	1.18	0.86	19.1
	12.5		3.75	1.03	1.18	1.15	0.93	24.5
	25		7.50	0.72	0.91	1.27	0.84	35.1
	12.5		6.25	0.91	1.11	1.22	0.96	26.8

As shown in Table 2, when the ratio of [monomer]: [polymer CTA]: [AIBN] = 40:1:0.3, the polydispersity index *PDI* of the resulting block copolymer is narrow ( $<1.15$ ) and the MW is close to that calculated from Eq. (2).

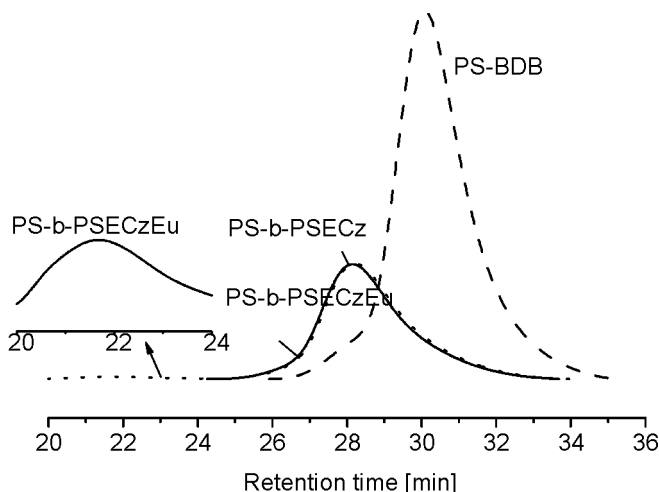


Fig. 1. GPC curves of PS-*b*-PSECz, PS-*b*-PSECzEu and polystyrene; dashed line – PS made from RAFT polymerization ( $M_n = 0.6 \times 10^4$ ,  $PDI = 1.13$ ), dotted line: PS-*b*-PSECz ( $M_n = 1.03 \times 10^4$ ,  $PDI = 1.15$ ), solid line: PS-*b*-PSECzEu ( $M_n = 1.03 \times 10^4$ ,  $PDI = 1.39$ ).

The inset is the the GPC curve of PS-*b*-PSECzEu for higher molecular weights

The GPC curves of the block copolymers and polystyrene made from RAFT polymerization are shown in Fig. 1. There is an obvious peak shift from the macro-RAFT agent (PS-BDB) to the block copolymer (PS-*b*-PSECz). The peak for macro-RAFT agent (PS-BDB) almost disappeared. In addition, the *PDI* values of these two polymers are similar. These demonstrate that the macro-RAFT agent was successfully

extended to block copolymer and PS-*b*-PSECz block copolymer was successfully produced through RAFT polymerization.

In comparison, the curve for PS-*b*-PSECzEu similar to the curve for PS-*b*-PSECz, had a shoulder in the higher molecular weight range (shown in the inset), which resulted in the broader *PDI* range (from 1.15 to 1.39). This indicates introducing europium complex to the block copolymer containing carbazole. The europium complex does not change the molecular weight of the PS-*b*-PSECz due to its low content (ca. 2.57%) and small molecular weight. The coupling of europium and  $\pi$  electrons of the benzene ring results in partial cross-linking in PS-*b*-PSECz-Eu. Thus, a higher molecular weight peak appears, and the *PDI* becomes higher. However, in previous studies, the polymers containing europium complex have higher *PDI* (*PDI* > 1.6) through the conventional radical polymerization [6, 7, 18]. We have successfully obtained a block copolymer containing carbazole groups and europium complex for which the *PDI* is narrow, and it has a controlled molecular weight, through RAFT polymerization.

### 3.2. FT-IR analysis

The FT-IR spectrum of PS-*b*-PSECz shows characteristic absorption bands at 3050–2900  $\text{cm}^{-1}$  (Fig. 2) characteristic of C–H stretching vibrations of carbazole and

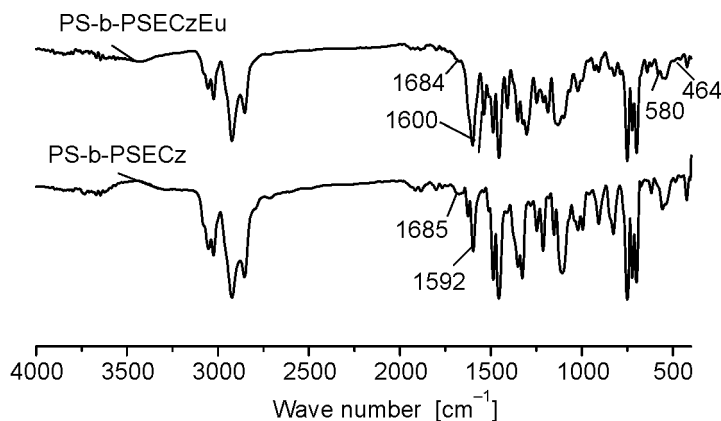


Fig. 2. FT-IR spectra of PS-*b*-PSECz and PS-*b*-PSECzEu

benzene rings. The absorption peaks at 1460  $\text{cm}^{-1}$ , 1489  $\text{cm}^{-1}$  and 1592  $\text{cm}^{-1}$  are assigned to skeleton stretching vibrations of the benzene ring. The peaks at 755 and 724  $\text{cm}^{-1}$  are assigned to vibrations of the carbazole group. However, the peak at 1685  $\text{cm}^{-1}$ , which is assigned to the stretching vibrations of S=C=S, appears in the spectrum of PS-*b*-PSECz indicating that the chain transfer agent was introduced to the end chain of the copolymer by the RAFT polymerization. The spectrum of PS-*b*-PSECzEu is similar to that of PS-*b*-PSECz, the band at 1600–1550  $\text{cm}^{-1}$  becomes



broader and red shifted because the coupling of europium and the  $\pi$  electrons of the benzene ring changes the electron density of the benzene ring. Two absorption peaks at 580 and 464  $\text{cm}^{-1}$ , associated with the Eu–O stretching vibrations [19], are also evident. Due to low content of europium complex in PS-b-PSECzEu, the absorption peaks associated with the ligands are buried under those of other aromatic species.

### 3.3. Optical properties

Optical properties of PS-b-PSECz and PS-b-PSECzEu were examined by UV absorption in dilute THF solutions and photoluminescence in solid state. As shown in Fig. 3, there is no significant difference in the spectrum of PS-b-PSECz and PS-b-PSECzEu. Three peaks at 299, 325 and 344 nm have observed, attributed to  $\pi \rightarrow \pi^*$  transitions of benzene and carbazole ring. The intensity of UV absorption bands in PS-b-PSECzEu is stronger than that in PS-b-PSECz. This indicates that the conjugated intensity of the copolymer containing the europium complex increases with the introduction to the europium.

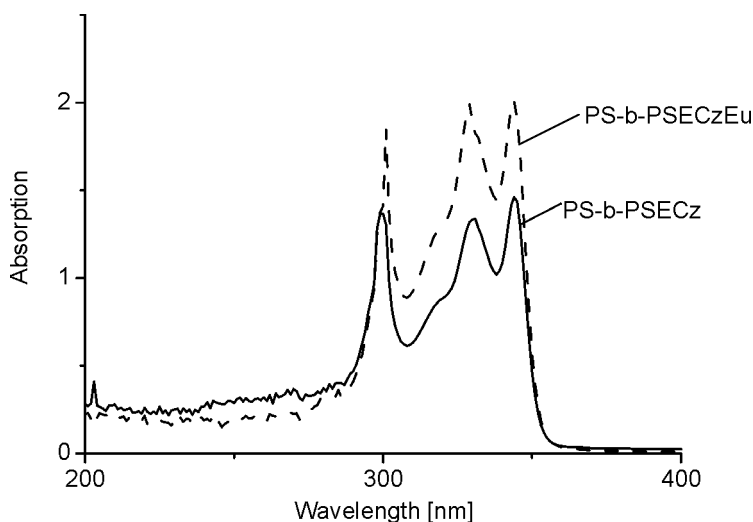


Fig. 3. UV absorption of PS-b-PSECz and PS-b-PSECzEu

Fluorescence spectra of PS-b-PSECz and PS-b-PSECzEu in solid state are shown in Fig. 4. In the excitation spectrum of PS-b-PSECz, excitation peaks appear at 383 nm and 400 nm and are attributed to the  $\pi \rightarrow \pi^*$  transitions of benzene and the carbazole ring, respectively. In the emission spectrum of PS-b-PSECz, two emission peaks at 408 and 433 nm are detected. These emissions can be attributed to the  $\pi \rightarrow \pi^*$  transitions of benzene and the carbazole ring, respectively.

In the excitation spectrum of PS-b-PSECzEu, the strongest excitation band appears at 360–400 nm, which is attributed to the overlap of the  $\pi \rightarrow \pi^*$  transition of ben-

zene, the carbazole ring and the ligand (thenoyltrifluoroacetone). In the emission spectrum, only one group of emission peaks at 577, 592, 614, 650 nm is detected.

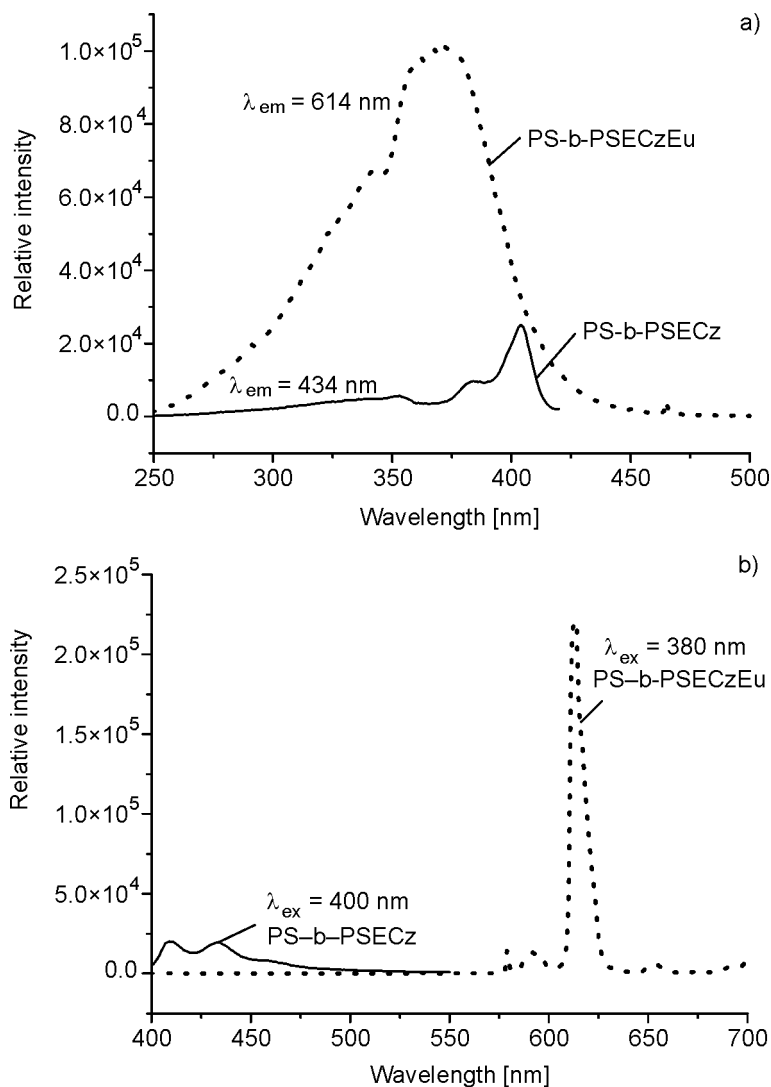


Fig. 4. Fluorescence spectra of PS-b-PSECz and PS-b-PSECzEu: a) the excitation fluorescence spectrum of PS-b-PSECz recorded in the range of 250–430 nm by monitoring the emission at 434 nm; the excitation fluorescence spectrum of PS-b-PSECzEu recorded in the range of 250–500 nm by monitoring the emission at 614 nm; b) the fluorescence spectra recorded in the range of 400–700 nm excited by the peak wavelength in the relative excitation spectra

They are assigned to the f-f transitions of the europium ions [4]. 4f levels of europium ions are protected from environmental perturbations by the occupied  $5s^2$  and  $5p^6$  orbitals, thus the fluorescence peaks of europium ions are expected to be sharp and

narrow. In addition, the presence of europium complex in PS-*b*-PSECzEu is further evidenced by the characteristic fluorescence of europium ions. The emission peaks from benzene and carbazole groups have almost been completely suppressed. This phenomenon can be explained by a long distance (Förster) energy transfer from the benzene and the carbazole groups (donors) to the europium complex (acceptor) in the excited states. Dexter energy transfer from the triplet states (T1) of the ligand (thenoyltrifluoroacetone) to the excited states of  $\text{Eu}^{3+}$  in PS-*b*-PSECzEu by molecular interaction is expected to be similar to the energy transfer mechanism in a low molecular weight europium complex. In addition, the terminal cumyl end group of copolymer by RAFT process has no effect on the luminescence property.

### 3.4. Electrochemical properties

Matching of the valence band (or the highest occupied molecular orbital (HOMO)) and conduction band (or the lowest unoccupied molecular orbital (LUMO)) energy levels of the active material to the work functions of the corresponding cathode and anode is important for the performance of a device. Cyclic voltammetry is an effective method for exploring the relative ionization and reduction potentials. The electrochemical property of PS-*b*-PSECzEu has been investigated using cyclic voltammetry.

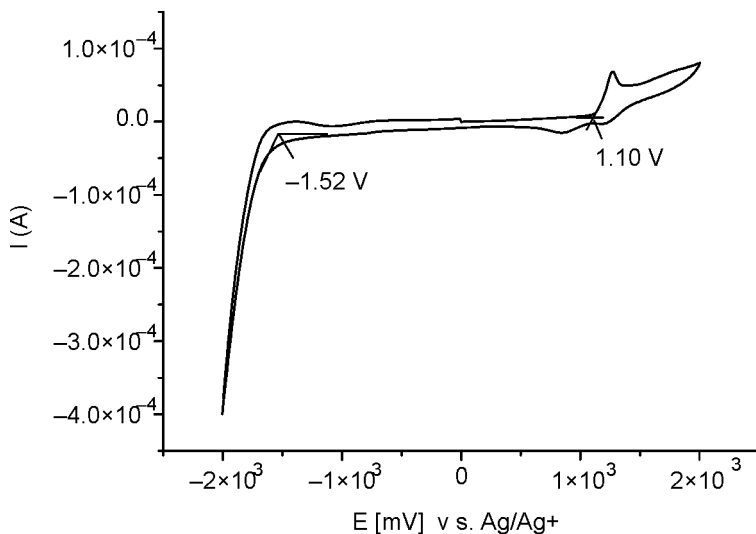


Fig. 5. Cyclic voltammogram of PS-*b*-PSECzEu in 0.1 M  $n\text{-Bu}_4\text{NPF}_6$ /acetonitrile

The reduction and the oxidation onset potential of PS-*b*-PSECzEu is  $-1.52 \text{ V}$  and  $1.10 \text{ V}$ . The HOMO and LUMO energy levels of the polymer materials can be calculated from the  $E_{\text{onset}}(\text{ox})$  and  $E_{\text{onset}}(\text{red})$ , based on the reference energy level of ferrocene (4.8 eV below the vacuum level) [20, 21]:

$$\text{HOMO} = E_{\text{onset}}(\text{ox}) + 4.8 - E_{\text{Foc}} \quad (3)$$

$$\text{LUMO} = E_{\text{onset}}(\text{red}) + 4.8 - E_{\text{Foc}} \quad (4)$$

wherein  $E_{\text{Foc}}$  is the potential of Foc(ferrocene)/Foc<sup>+</sup> vs. Ag/AgCl. The value of  $E_{\text{Foc}}$  is 0.46 V [22]. Based on Eqs. (3) and (4), the HOMO and LUMO energy levels of PS-b-PSECzEu relative to the vacuum level are estimated to be 5.44 eV and 2.82 eV, respectively. The result indicates that the HOMO and LUMO energy levels of PS-b-PSECzEu match well the respective work functions of ITO (4.80 eV) and Ca (2.89 eV) when used as the memory or light emitting material between the two electrodes. With the copolymer PS-b-PSECzEu, a balance can be achieved between the electron currents and the electron–hole currents. Thus, the block copolymer containing carbazole groups and the europium complex is a potentially useful candidate for fabricating memory or light-emitting devices.

## 4. Conclusion

A block copolymer containing carbazole groups and europium with controlled molecular weights (MWs) and narrow polydispersity was synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization and coordination. The elemental analysis shows the europium content is 2.57 wt. %. The fluorescence spectroscopy of the block copolymer containing the carbazole groups and the europium complex exhibits red emission which can be attributed to the f-f transitions of the europium ion in the solid state. The long distance (Förster) energy transfer from benzene and the carbazole groups (donors) to the europium complex (acceptor) in excited states exists in the block copolymer under investigation. In addition, Dexter energy transfer from triplet states (T1) of the ligand (thenoyltrifluoroacetone) to excited states of Eu<sup>3+</sup> also takes place in the copolymer. The cyclic voltammetry data indicate that, in the copolymer, a balance can be achieved between the electron currents and the electron–hole currents. Thus, the copolymer is a potentially useful candidate for fabricating memory or light emitting devices.

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