Synthesis and characterization of novel copolymer containing pyridylazo-2-naphthoxyl group via reversible addition–fragmentation chain transfer (RAFT) polymerization

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A B S T R A C T

A novel monomer containing pyridylazo-2-naphthoxyl group, 1-(1-(4-vinylbenzyloxy)naphthalen-2-yl)-2-(pyridin-2-yl)diazene (VBNPA), was successfully synthesized and copolymerized with styrene (St) in N,N-dimethyl formamide (DMF) via reversible addition–fragmentation chain transfer (RAFT) polymerization using 2-cyanoprop-2-yl-1-dithionaphthalate (CPDN) as RAFT agent. The polymerization behavior exhibited "living"/controlled characters. The obtained copolymer, poly(St-co-VBNPA), with pre-determinable molecular weight and narrow molecular weight distribution can be used as a carrier in metal ion detection and analysis via pre-concentration technique. The copolymer–metal ion (copper (Cu) and europium (Eu)) complexes were prepared and characterized.

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1. Introduction

Trace metal ion detection and determination have received particular attention at present due to their strong environmental impact [1–4]. The direct determination of metal traces in various samples usually requires an efficient pre-concentration step. This pre-concentration step can bring the concentration of the analyte within the dynamic measuring range of the detector and additionally to eliminate mixture effects, interferences, which cannot be manipulated by the measuring device. Conventional separation and pre-concentration techniques, such as coprecipitation, distillation, liquid–liquid extraction, ion exchange, absorptive columns, etc., have been employed for the single- or multi-element extraction of almost every metal from their initial matrices [5–8].

The azo dye 1-(2-pyridylazo)-2-naphthol (Scheme 1, PAN) is a well-known simple, rapid, sensitive, and selective metallochromic indicator for complexometric titration as well as a frequently used colorimetric reagent for the quantitative and qualitative determination of a variety of metal ions [9–13]. PAN acts as a tridentate ligand complexing with metals through the ortho-hydroxyl group, the azonitrogen near the phenolic ring, and the hetrocyclic nitrogen atom, giving two five-membered chelate rings (Scheme 1) [14–18]. Some procedures have been developed for the determination of

metal ions after pre-concentration on PAN loaded silica gel column or PAN coated alumina column [9,13,19,20]. In these methods, PAN was dispersed by mixing with fixed phase. The relatively weak linkage between PAN and carrier may cause unfavorable effects on metal ion determination. Thus, PAN has been supported onto chloromethylated polystyrene through an alkylation reaction [21]. Polymer-supported materials play an important role in the pre-concentration techniques [22–25]. The widely used method of post-modification of polymer may result in uncontrollable concentration of functional groups on the carrier, which limited these materials for practice using.

The fast development of "living"/controlled radical polymerization (LRP) in recent decades offered us a powerful tool for synthesizing polymer material with controlled structures. The most versatile LRP methods have included nitroxide-mediated polymerization [26,27], atom transfer radical polymerization [28–31] and reversible addition–fragmentation chain transfer (RAFT) polymerization [32–35]. RAFT polymerization is probably the most versatile process. It exhibits a high degree of compatibility with a wide range of functional monomers [36–39].

In this work, we first prepared the functional copolymer by the RAFT copolymerization of styrene with 1-(1-(4-vinylbenzyloxy)naphthalen-2-yl)-2-(pyridin-2-yl)diazene (VBNPA, Scheme 2), in N,N-dimethyl formamide (DMF). The main goal of this work is to introduce PAN structure to side chain of the polymer with pre-determined PAN content via LRP techniques, thus, the well-defined
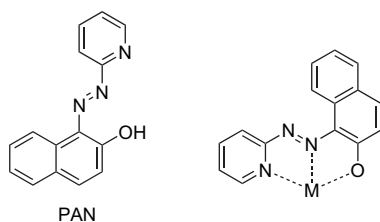
Scheme 1. Chemical structures of PAN and its coordinated complex.
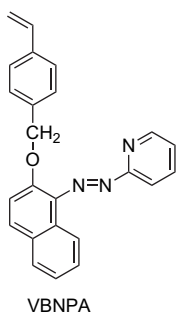
Scheme 2. Chemical structure of monomer VBNPA.

soluble polymeric complexes with controllable polymeric structure were obtained utilizing Cu(II) or Eu(III) complexation chemistry with the PAN unit.

2. Experimental

2.1. Materials

Styrene (St, Shanghai Chemical Reagent Co. Ltd) was washed with an aqueous solution of sodium hydroxide (5 wt%) for three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, styrene was distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Co. Ltd, 99%) was recrystallized twice from ethanol, and then dried at room temperature under vacuum. The RAFT agent, 2-cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized as previously reported [40]. 1-(2-Pyridylazo)-2-naphthol (Scheme 1, PAN, Akfa Aesar, 99%) and *p*-chloromethyl styrene (Acros, 97%) were used as-received. Other reagents (Shanghai Chemical Reagent Co. Ltd, China, analytical grade) were purified with standard methods.

2.2. Synthesis of 1-(1-(4-vinylbenzyloxy)naphthalen-2-yl)-2-(pyridin-2-yl)diazene

A suspension of 15.2 g (0.1 mol) *p*-chloromethyl styrene, 4.0 g sodium hydroxide (0.1 mol), and 24.9 g PAN (0.1 mol) in 200 mL tetrahydrofuran (THF) was prepared and stirred for 24 h at room temperature. The resultant reaction mixture was precipitated in large amount of water. A dull red solid was obtained. Pure VBNPA was obtained after twice recrystallization from ethanol and once silica gel chromatography with petroleum ether:ethyl acetate = 4:1, 10.5 g, 28.8%. ^{1}H NMR (Fig. 1) δ: 8.781–8.809 (d, 1H, pyridine-H), 8.668–8.642 (m, 2H, pyridine-H), 8.369–8.411 (m, 1H, pyridine-H), 7.084–7.897 (m, 10H, naphthalene-H, benzene-H), 6.700–6.744 (t, 1H, =C(Ph)–H), 5.787–5.743 (d, 1H, =CH–H), 5.471 (s, 2H, –CH$_2$–O–), 5.289–5.262 (d, 1H, =CH–H). ^{13}C NMR δ: 181.424, 155.708, 148.834, 143.064, 138.561, 137.940, 137.096, 136.387, 130.801, 129.637, 129.142, 128.667, 127.803, 127.382, 127.281, 126.754,
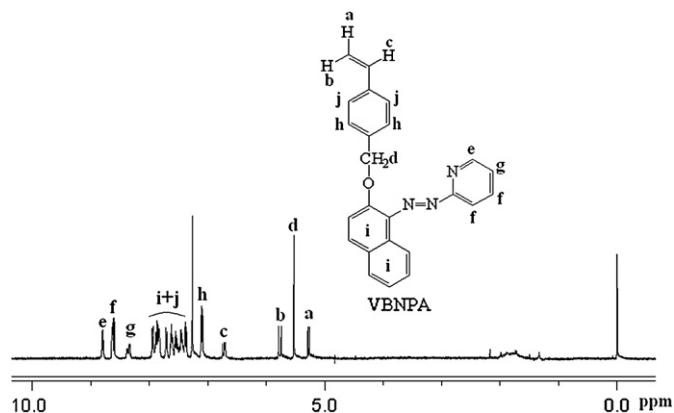
Fig. 1. ^{1}H NMR spectrum of monomer VBNPA.

122.505, 120.521, 114.814 (benzene, naphthalene, and pyridine-C), 133.697 (ethane, –CH–), 110.314 (ethane, CH$_2$=), 69.098 (–CH$_2$–O–). Element. Anal. for C$_{24}$H$_{19}$N$_3$O, calculated: C 78.88 H 5.24 N 11.50; found: C 78.39 H 5.01 N 11.94. The purity was above 99% by HPLC.

2.3. RAFT copolymerization

A stock solution of 2.71 g (26 mmol) St, 9.50 g (26 mmol) VBNPA, 0.0085 g (0.052 mmol) AIBN, 0.0423 g (0.156 mmol) CPDN and 9.45 g DMF was prepared. Then every 3.0526 g solution was placed in 5 mL ampules. The content was purged with argon for approximately 10 min to eliminate oxygen. Then the ampules were flame sealed. The polymerization reaction was performed at appropriate temperature. After the desired reaction time, each ampule was quenched in ice water, and opened. The content was diluted with 2 mL THF, and precipitated in 300 mL methanol. The polymer was obtained by filtration and dried at room temperature under vacuum. Conversion was determined gravimetrically. The block copolymer(PS-*b*-P(St-*co*-VBNPA)) was prepared using obtained poly(St-*co*-VBNPA) as the macro-RAFT agent and styrene as the second monomer with similar procedure.

2.4. Synthesis of copolymer–metal ion complexes

Poly(St-*co*-VBNPA) and 10 mL DMF were added to a 50-mL flask. The mixture was heated slightly to form a homogeneous solution. The molar amount of added Cu(CH$_3$COO)$_2$ or EuCl(PhCOCH$_2$COPh)$_2$ was equal to that of VBNPA unit in copolymer. The mixture was stirred at 80 °C for 24 h. The complex was obtained by precipitation into large amount of methanol followed by filtration. The sample was purified by three cycles of dissolving in DMF and precipitating into the methanol followed by washing with deionized water to remove any unreacted low molecular metal complexes and dried at room temperature under vacuum.

2.5. Characterization

The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 columns. Calibration was performed with polystyrene (molecular weight range 100–500,000) as standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. ^{1}H NMR spectra of the polymers were recorded on an INOVA400 nuclear magnetic resonance (NMR) instrument using CDCl$_3$ as a solvent and tetramethylsilane (TMS) as the internal standard.

Elemental analyses (EA) of C, H and N were measured by the EA1110 CHND-S. The purity of CPDN was determined by Waters 515 HPLC: the mixture of methanol and water ($V_{methanol}$:V_{water} = 80:20) was used as the eluent at a flow rate of 0.8 mL min^{-1} operated at 30 °C using C18 column and using Waters 996 as detector. The UV absorption spectra of the sample were determined on a Shimadzu-RF540 spectrophotometer. The fluorescence intensity was measured by Edinburgh Instruments FLS920. The metal ion concentrations were determined by VISTA-MPX CCD Simultaneous ICP-AES, and the operation conditions are listed: plasma flow rate: 15 L min^{-1}; carrier gas (Ar) flow rate: 1.5 L min^{-1}; incident power (kW): 1.2 kW; vaporization press: 240 kPa.

3. Results and discussion

3.1. The "living"/controlled copolymerization of styrene and VBNPA

The copolymerization of styrene and VBNPA using CPDN as RAFT agent in DMF was carried out. Fig. 2 shows the plots of $\ln([M]_0/[M])$ and conversion vs reaction time for the copolymerization ($[St]_0$:$[VBNPA]_0$:$[AIBN]_0$:$[CPDN]_0$ = 500:500:1:3, 60 °C). In the studied range of conversions, the relationship between $\ln([M]_0/[M])$ and polymerization time was approximately linear, which indicated that the propagating radical concentration was almost constant and the side reactions could be neglected during the polymerization. Fig. 3 shows that the M_n of the obtained copolymer measured by GPC increased linearly with monomer conversion. The value of M_w/M_n was remained in low and decreased with increasing conversion, for example, the M_w/M_n decreased from 1.41 to 1.12 with the conversion increased from 20.7% to 88.6%.

The structure of obtained copolymer was characterized by ^{1}H NMR. A typical ^{1}H NMR spectrum of copolymer (M_n = 13,300, M_w/M_n = 1.16) is shown in Fig. 4, and the peaks were labeled to assign the protons of each unit in it. The number of VBNPA in each polymer chain was calculated according the integral data of peaks d and $e + f$. In this case, d:$(e + f)$ = 2.00:7.10, thus the calculated molar ratio between VBNPA and St (m:n) containing in copolymer was 0.42:0.58. The molar percentage of VBNPA unit was also calculated by the following equation with elemental analysis data according to the different concentration of N in the monomer (St, VBNPA): $m_{VBNPA} = M_{St}/[(3A_N/N\%) - (M_{VBNPA} - M_{St})]$, which was conversion equation according to the following equations: $N\% = 3\,mA_N/(nM_{St} + mM_{VBNPA}) \times 100\%$, $m_{VBNPA} = m/(n + m)$ (M_{VBNPA} was the molecular weight of the VBNPA unit and M_{St} was the molecular weight of St unit; A_N was the atomic

weight of N; $N\%$ was the concentration of N in the copolymer). $N\%$ in the measured copolymer was 7.90%, therefore the value of m_{VBNPA} was 0.39, which was almost equal to the result 0.42 calculated from NMR. Furthermore, chain extension experiment was carried out using the obtained poly(St-co-VBNPA) as the macro-RAFT agent and styrene as the second monomer to validate the activity of the original polymer. Typical GPC plots shown in Fig. 5 explicitly illustrated the changes in M_n and M_w/M_n before (A) and after (B) the chain extension reaction, which was carried out in solution (DMF, 50% v/v) at the ratio of $[St]_0/[poly(St-co-VBNPA)]_0$ = 500:1 at 110 °C. The chain extension resulted in 30.3% conversion after 20 h polymerization. The molecular weight increased from 13,300 to 23,100, which was little lower than the calculated value, 29,100. The molecular weight distribution values increased from 1.16 to 1.21, which may be caused by the bimolecular termination of the propagating free radicals and the dead polymer existing in the original copolymer as reported in the literatures [41,42]. The GPC trace of chain extended polymer showed a side peak in same position with original macro-RAFT agent, which indicated the existence of dead chains in the original copolymer. However, the most of the chains were still living, and the copolymerization of St and VBNPA was well controlled on RAFT polymerization mechanism.

Fig. 3. Evolutions of M_n and M_w/M_n with monomer conversion for the RAFT copolymerization of styrene and VBNPA in DMF with the molar ratio $[St]_0$:$[VBNPA]_0$:$[AIBN]_0$:$[CPDN]_0$ = 500:500:1:3 at 60 °C.
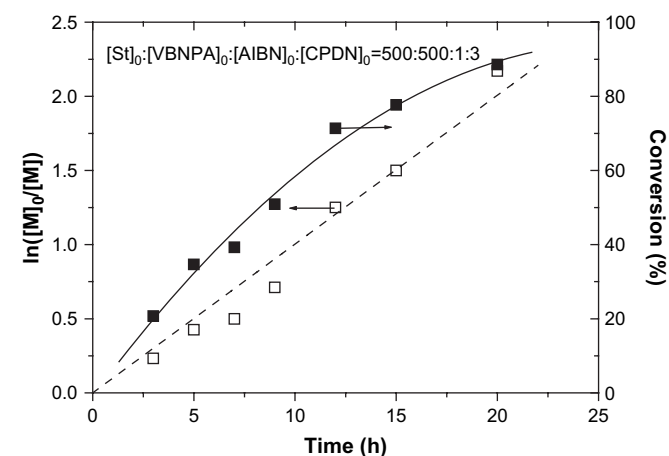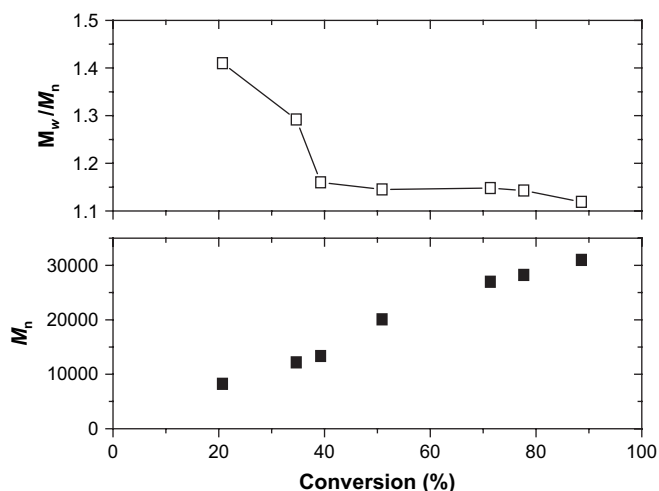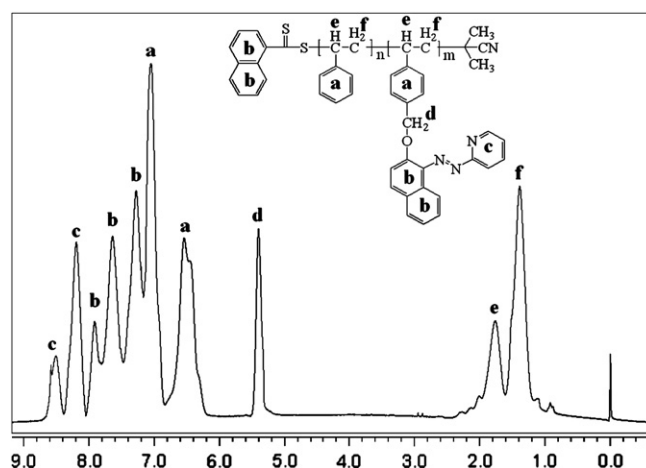

Fig. 2. Kinetic plots of the RAFT copolymerization of styrene and VBNPA in DMF with the molar ratio $[St]_0$:$[VBNPA]_0$:$[AIBN]_0$:$[CPDN]_0$ = 500:500:1:3 at 60 °C.

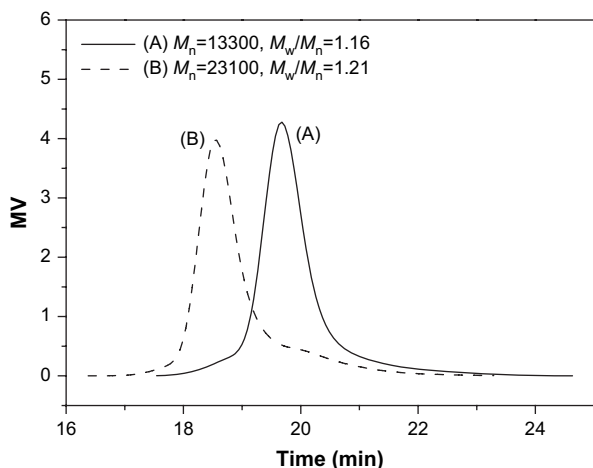Fig. 4. Typical ^{1}H NMR spectrum of copolymer (M_n = 13,300, M_w/M_n = 1.16).

Fig. 5. GPC traces of polymers before (A) and after (B) chain extension reaction (in 50% v/v DMF, $[St]_0/[poly(St-co-VBNPA)]_0 = 500:1$, at 110 °C).

Fig. 6. FT-IR spectra of poly(St-co-VBNPA) (A), poly(St-co-VBNPA)–Cu(II) complex (B) and poly(St-co-VBNPA)–Eu(III) complex (C).

3.2. ICP-AES analysis of copolymer–Cu(II) and copolymer–Eu(III) complexes

ICP-AES was widely used for the determination of metal ions [43–45]. In this work, ICP-AES was also used for the determination of metal ions attached to the copolymer. The amounts of metal ions coordinated with the copolymer were analyzed by ICP-AES as shown in Table 1. The number of metal ion per polymer chain (N) was increased with the molecular weight of copolymer, and N was calculated by the following equation:

$$N \approx C \times M_{copolymer}/M_{metal\ ion}$$

in which $C = C_{metal\ ion}/C_{copolymer}$, $C_{metal\ ion}$ and $C_{copolymer}$ are the concentration of metal ion and copolymer (g/mL), respectively; $M_{copolymer}$ and $M_{metal\ ion}$ are molecular weights of copolymer and metal ion, respectively.

3.3. FT-IR spectroscopic analysis of copolymer–Cu(II) and copolymer–Eu(III) complexes

Fig. 6 shows the FT-IR spectra of poly(St-co-VBNPA) and its copolymer–metal complexes. The copolymer sample was subjected to infrared spectroscopic analysis that showed absorption peaks characteristic for PAN units: the absorption peaks at $1558\ cm^{-1}$ and $1628\ cm^{-1}$ are related to the 2-substituted pyridine ring; the absorptions at $1283\ cm^{-1}$ are corresponding to the aryl–O– bond and the absorptions at $1072\ cm^{-1}$ are corresponding to CH_2–O– bond. The inclusion of the metal ion in a complexed form may be indicated by the absorption peak at about $1599–1655\ cm^{-1}$ as well as by shifting the absorption peaks of the organic functionalities due to the polarizing effect of such metal ions [21,46–48].

Fig. 7. UV–vis spectra of poly(St-co-VBNPA) (a), poly(St-co-VBNPA)–Cu(II) complex (b) and poly(St-co-VBNPA)–Eu(III) complex (c) at the concentration of $1 \times 10^{-5}\ mol\ L^{-1}$ in DMF at room temperature.

3.4. UV–vis spectra of polymer–Cu(II) and polymer–Eu(III) complexes

Fig. 7 reveals the characteristic UV–vis absorbance of poly(St-co-VBNPA) (a), poly(St-co-VBNPA)–Cu(II) complex (b) and poly(St-co-VBNPA)–Eu(III) complex (c). Comparing with curve (a), there was a new absorbance peak at about 555 nm in curve (b), which can be attributed to the red-shift effect of the coordination between Cu(II) and PAN unit in complex. Similar results were reported in the literatures [1,15,25,49–51]. These results showed that Cu(II) had been bonded to PAN unit. When comparing curve (c) with curve (a), the absorbance peak at about 520 nm had no obvious change, which may be due to that the amount of Eu(III) loaded in copolymer was low. But, a new absorbance peak at 350 nm was found in curve (c), which was ascribed to $PhCOCH_2COPh$ unit.

3.5. Fluorescence spectra of copolymer–Cu(II) and copolymer–Eu(III) complexes

Europium (Eu)-based materials are of special interest in optical excitation and emission because of their high luminescent quantum efficiencies. The details of Eu(III) (4f–4f) excitation and emission spectra are particularly sensitive to the structural details of the coordination environment [52–57]. Here, fluorescence spectra of the obtained copolymer–Eu(III) complex and

Table 1
Metal ion concentrations measured by ICP-AES

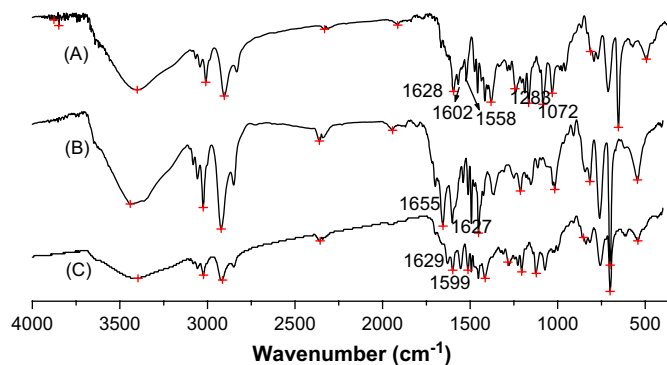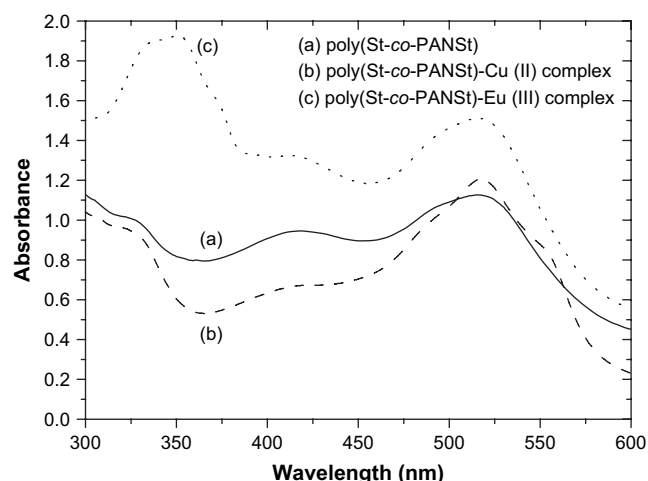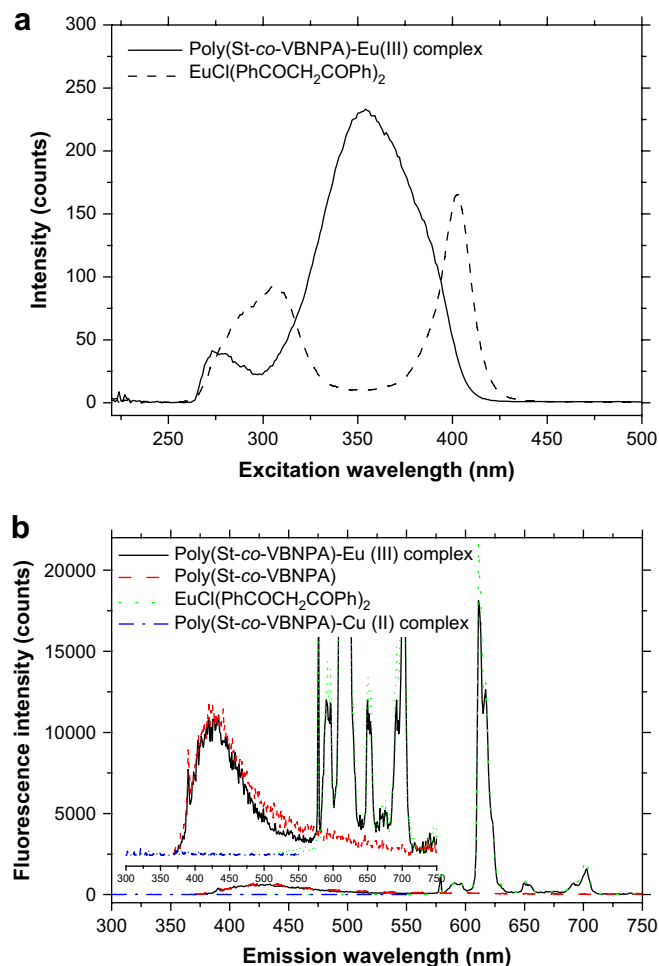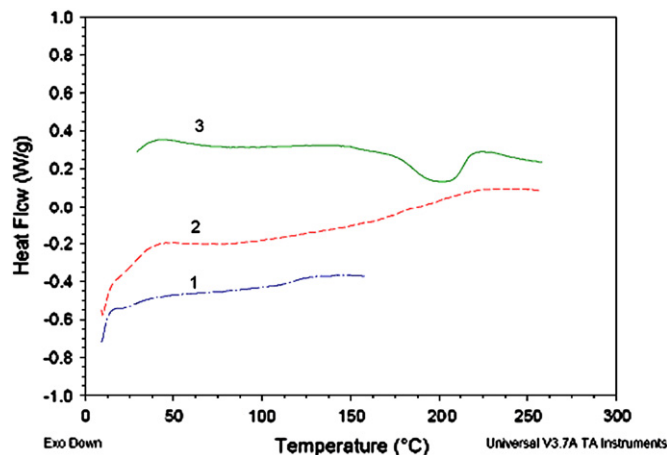| Copolymer	Metal ion	C	N
$M_n = 8200$, $M_w/M_n = 1.41$	Cu(II) complex	3.75	4.81
	Eu(III) complex	6.00	3.24
$M_n = 13,300$, $M_w/M_n = 1.16$	Cu(II) complex	2.45	5.09
	Eu(III) complex	4.16	3.55
$M_n = 31,000$, $M_w/M_n = 1.11$	Cu(II) complex	1.56	7.57
	Eu(III) complex	2.95	6.01

Fig. 8. Excitation spectra and fluorescence spectra of poly(St-*co*-VBNPA) and poly(St-*co*-VBNPA)–Eu(III) complex at the concentration of metal ion 1×10^{-5} mol L^{-1} in DMF at room temperature.

Fig. 9. DSC data of poly(St-*co*-VBNPA) and coordination polymer. (1) Poly(St-*co*-VBNPA), $M_n = 13{,}300$, $M_w/M_n = 1.16$; (2) poly(St-*co*-VBNPA)–Cu(II) complex; (3) poly(St-*co*-VBNPA)–Eu(III) complex.

EuCl(PhCOCH$_2$COPh)$_2$ were investigated. The excitation and emission spectra were measured at room temperature in the solution (DMF). The excitation spectra of poly(St-*co*-VBNPA)–Eu(III) complex and EuCl(PhCOCH$_2$COPh)$_2$, obtained by monitoring the emission of the Eu(III) ions at 611 nm, were quite different (Fig. 8). There were two strong absorptions, 305 nm and 403 nm, appeared in the excitation spectrum of EuCl(PhCOCH$_2$COPh)$_2$. While in the case of poly(St-*co*-VBNPA)–Eu(III) complex, it showed a broad band ranging absorption from 300 nm to 430 nm. This result indicated that the emission of the copolymer–Eu(III) was sensitized by the absorption of the ligand in the UV region rather than directly by the Eu(III) ion absorption and Eu(III) had been bonded to PAN unit. Moreover, as can be seen from Fig. 6, the emission spectra of the copolymer–Eu(III) and the corresponding EuCl(PhCOCH$_2$COPh)$_2$, excited at 359 nm, both showed three major emission bands at 590 nm, 611 nm, and 703 nm, corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2, 4) transitions. Among these transitions, $^5D_0 \rightarrow {}^7F_2$ was the strongest. However, no fluorescence was detected in poly(St-*co*-VBNPA)–Cu(II) complex.

3.6. Thermal analysis of copolymer–Cu(II) and copolymer–Eu(III) complexes

The glass temperature (T_g) values of the copolymer and coordination polymers were measured by differential scanning calorimetry (DSC). Fig. 9 shows that the synthesized copolymer poly(St-*co*-VBNPA) had a single T_g at 116.1 °C (Fig. 9, curve 1), which indicated the formation of random copolymer. A great deviation of T_g between poly(St-*co*-VBNPA) and its Cu(II) complex could be observed. The T_g value of copolymer–Cu(II) complex was 177.9 °C (Fig. 9, curve 2), which was higher than that of poly(St-*co*-VBNPA). Similar results have been reported in the literatures [21,31–33,42]. While in the case of copolymer–Eu(III) complex, the resulting material had an extrapolated thermal decomposition temperature of 170.8 °C (Fig. 9, curve 3).

4. Conclusion

The copolymer bearing PAN unit in side chain was synthesized using the RAFT technique. The obtained polymer showed well-defined structures with controlled molecular weight and narrow molecular weight distribution. Poly(St-*co*-VBNPA)–Cu(II) and poly(St-*co*-VBNPA)–Eu(III) complexes were prepared via the Cu(II)/Eu(III) complexation chemistry. The resultant polymeric complexes were characterized by FT-IR spectra and UV–vis spectra, and the results showed distinct difference between the resultant polymeric complexes and the starting materials. The excitation spectra, fluorescence spectra and thermal analysis of the metal ion coordinated poly(St-*co*-VBNPA) demonstrated the successful incorporation of metal ion with PAN unit.

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