Polymer 51 (2010) 1947–1953

Contents lists available at ScienceDirect

Polymer

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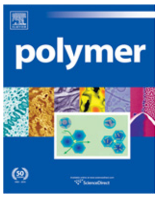

Synthesizing and characterization of comb-shaped carbazole containing copolymer via combination of ring opening polymerization and nitroxide-mediated polymerization

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ARTICLE INFO

Article history:
Received 15 October 2009
Received in revised form
3 February 2010
Accepted 1 March 2010
Available online 10 March 2010

Keywords:
Carbazole
Comb-shaped copolymer
NMP

ABSTRACT

The macro-TEMPO agent (poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl), PGTEMPO) was synthesized by anion ring-opening polymerization (ROP) of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) using potassium *t*-butoxide as the initiator. The comb-shaped copolymer, PGTEMPO-g-PVBK, was prepared via nitroxide-mediated free radical polymerization (NMP) using PGTEMPO as macro-TEMPO agent and 9-(4-vinylbenzyl)-9H-carbazole (VBK) as the monomer. The polymerizations showed characteristics of "living"/controlled behavior. The optical properties, thermal analysis and electrochemical properties of the comb-shaped copolymers were investigated. The fluorescence and ultraviolet intensity and cyclic voltammetries of the comb-shaped copolymers with different molecular weight showed a regular order.

1. Introduction

Polymers containing carbazole structure have attracted much attention because of their characteristic hole transporting and electroluminescence properties [1–3]. These polymers have been used in wide range of functional materials, such as in the electro photographic process and in light-emitting, photorefractive and photovoltaic devices [4]. To fabricate such polymers, carbazole can be easily introduced into chain of the polymer via polymerization of carbazole containing monomers by free radical polymerization, Ziegler–Natta initiators, charge transfer and electrochemical processes, as well as by γ-radiation [5–7]. With the convenience and versatilities of free radical polymerization, a number of polymers with pendant carbazolyl groups have been prepared, including polymethacrylate [5,8,9], polyacrylate [10,11] and polystyrene derivatives [12]. To further control over the structure of the polymers with controlled molecular weights and molecular weight distributions, the "living"/controlled free-radical polymerization (LFRP), such as atom transfer radical polymerization (ATRP) [13,14], reversible addition-fragmentation chain transfer (RAFT) polymerization [15,16] and nitroxide-mediated free-radical polymerization (NMP) [17–24], has been also used. *N*-vinylcarbazole was successfully polymerized under controlled manner via ATRP and xanthate-mediated controlled radical polymerization [25–27]. The RAFT polymerization of *N*-ethyl-3-vinylcarbazole was successfully realized by Endo et al. [28].

Till now, the homopolymerization of *N*-vinylcarbazole via typical nitroxide-mediated free-radical polymerization still showed negative result by Fukuda et al. [29], whereas the copolymerization of *N*-vinylcarbazole with styrene under the same conditions proceeded in a living fashion. Register's group investigated the nitroxide-mediated free-radical polymerization of *N*-ethyl-2-vinylcarbazole. The results showed key characteristics of a living polymerization [30]. Our group previously reported successfully polymerization of 9-(4-vinylbenzyl)-9H-carbazole (VBK) via nitroxide-mediated living free-radical polymerization [31]. The polymerizations were confirmed under typical controlled features by the linear increase in the molecular weight with the monomer conversion while keeping the relative narrow molecular weight distribution, and successful chain extension with styrene. The fluorescence intensity of the polymer was apparently influenced by chromophore concentration, and the maximum value was obtained when the carbazole unit concentration was around 8×10^{-5} mol/L. Moreover, it was shown that the strong fluorescence of PVBK can be quenched by methyl acrylate (MA).

In this work, comb-shaped copolymer (PGTEMPO-*g*-PVBK) with PVBK as the side chain and polyether as the main chain was successfully synthesized via the combination of ring opening

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doi:10.1016/j.polymer.2010.03.001

polymerization and nitroxide-mediated free-radical polymerization techniques. The introduction of polyether chain structure into carbazole containing materials improved its film forming abilities. The fluorescence, ultraviolet absorbance intensity, and the oxidation and reduction potential of the comb-shaped copolymer with different molecular weight exhibited a regular order.

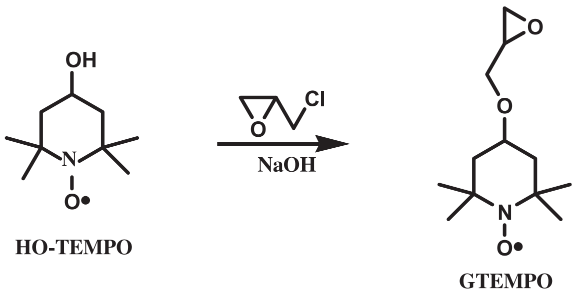
2. Experimental sections

2.1. Materials

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (HO-TEMPO) (98%, from Wuxi Fuan Chemical Plant, China) was recrystallized from *n*-hexane. 4-Vinylbenzyl chloride (Aldrich, 90%) and dibenzoyl peroxide (BPO) (Aldrich) were purified by crystallization from ethanol. Carbazole (analytical reagent), ascorbic acid (VC) (99.7%) and sodium hydroxide (NaOH) (analytical reagent) were all purchased from Shanghai Chemical Reagent Co. Ltd. and used as received. Methanol (commercially available) was used as received. *N*, *N*-Dimethylformamide (DMF) (analytical reagent), chloroform ($CHCl_3$) (analytical reagent), and tetrahydrofuran (THF) (analytical reagent) were all purchased from Shanghai Chemical Reagent Co. Ltd. and purified via standard method before used. All other reagents were used as received unless otherwise noted.

2.2. Preparation of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO)

The monomer 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) was prepared according to reference [32] (Scheme 1). Epichlorohydrin (10 mL, 120 mmol) and tetrabutylammonium hydrosulfate (1.5 g, 4.6 mmol) was added to a sodium hydroxide aqueous solution (16 mL, 50 wt%). The mixture was vigorously stirred for 10 min. A solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy (4.12 g, 24 mmol) in tetrahydrofuran (30 mL) was added as droplets into the mixture. It was vigorously stirred for 12 h at room temperature and then poured into ice water (200 mL). The mixture was extracted with ethyl acetate (50 mL). The organic solution was washed with deionized water (30 mL) and then extracted with ethyl acetate again. After that, the organic solution was dried by anhydrous magnesium sulfate. The crude product was obtained after removing solvent by rotary evaporation under vacuum. It was purified by column chromatography on silica oxide with mixed petroleum ether and ethyl acetate (8:1, v/v) as an eluent. After further recrystallized from hexane, the TEMPO-radical containing epoxy monomer, 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO), was isolated as a red solid (yield 80%). The purity was 98% by HPLC. Element. Anal.: Calcd for $C_{12}H_{22}NO_3$ (%): C, 63.13; H, 9.71; N, 6.14. Found (%): C, 62.52; H, 9.63; N, 5.71.



Scheme 1. The synthesis route of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO).

2.3. Anionic ring-opening polymerization of the epoxy monomer (GTEMPO)

The anionic ring-opening polymerization of GTEMPO was carried out using following procedure: The 25 mL kettle was vacuumed at 100 °C for 24 h and cooled to room temperature and then to −20 °C. GTEMPO (0.456 g, 2 mmol), THF (2 mL) and Potassium *t*-butoxide THF solution (40 μL of 1 M solution, 0.04 mmol) were introduced successively into the kettle under an argon atmosphere. The mixture was stirred for 24 h at 75 °C for polymerization. After that, the content was dissolved in 5 mL tetrahydrofuran and precipitated into 200 mL hexane. The precipitated polymer (PGTEMPO) was collected by filtration. It was further purified by two cycles of dissolution in tetrahydrofuran and precipitation into hexane to yield an orange powder.

2.4. Preparation of 9-(4-vinylbenzyl)-9H-carbazole (VBK)

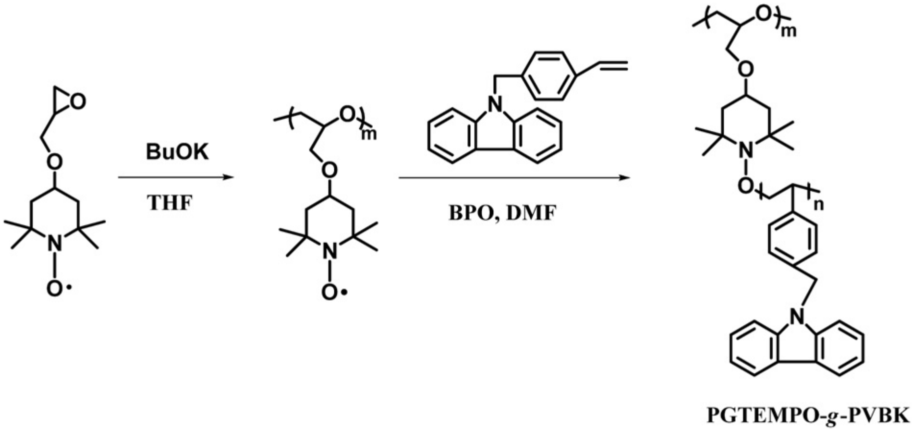
9-(4-Vinylbenzyl)-9H-carbazole (VBK) was synthesized according to reference [31]. Carbazole (8.4 g, 50 mmol) was mixed with NaOH (2 g, 50 mmol) in DMF (100 mL) under vigorous stir. 4-Vinylbenzyl chloride (7.6 g, 50 mmol) was added dropwise at room temperature. The reaction was allowed to stir at room temperature for 24 h. The reaction content was poured into a large amount of deionized water. The product was precipitated and collected by filtration. It was purified by recrystallization from acetone to give white crystal (85%). ^{1}H NMR (DMSO-d_6, tetramethylsilane) (ppm): d 5.71(1H, $CH_2{=}CH$), 5.17(1H, $CH_2{=}CH$), 5.64 (2H, CH_2), 6.64 (1H, $CH_2{=}CH$), 7.34, 7.12, 8.17, 7.42, 7.19, 7.62 (12H, Ar–H). Element. Anal.: Calcd for $C_{21}H_{17}N$ (%): C, 89.01; H, 6.05; N, 4.94. Found (%): C, 88.69; H, 6.11; N, 5.15. HPLC (Waters 515) indicated that the purity of VBK was above 98.5%.

2.5. General procedure for polymerization of VBK

A typical polymerization procedure was as follows (Scheme 2): a mixture of VBK (0.566 g, 2 mmol), BPO (3.7 mg, 0.015 mmol), PGTEMPO (4.6 mg, 0.02 mmol GTEMPO group), and VC (4.6 mg, 0.02 mmol), DMF (3 mL) was added to a dried ampoule ($[VBK]_0/[BPO]_0/[GTEMPO]_0/[VC]_0 = 130/1/1.3/1.3$). The mixture was bubbled with argon for 20 min to eliminate the dissolved oxygen. The ampoule was flame-sealed, and then transferred into an oil bath held by a thermostat at the desired temperature (123 °C) to polymerize. After the desired polymerization time, the ampoule was cooled by immersing it into iced water. Afterwards, it was opened and the contents were dissolved in THF (2 mL), and precipitated into methanol (200 mL). The polymer obtained by filtration was dried under vacuum until constant weight at 50 °C. The monomer conversion was determined gravimetrically.

2.5.1. Characterizations

^{1}H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument, using $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. The molecular weights (M_ns) and polydispersities (PDI) of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. Elemental analysis of C, H, and N were measured with an EA1110 CHNO-S instrument. The purity of products was determined on high-performance liquid chromatography (HPLC, Waters 515 pump with 2996 PAD) using acetonitrile as eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. The UV absorption spectra of the samples in chloroform



Scheme 2. The preparation route of comb-shaped copolymer (PGTEMPO-g-PVBK).

($CHCl_3$) solution were determined on a shimadzu-RF540 spectrophotometer at room temperature. Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) using a TA instruments DSC2010 with a heating/cooling rate of 10 °C min^{-1} under a continuous nitrogen flow. FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Cyclic voltammetries were performed on a CHI631B electrochemical workstation at a constant scan of 0.1 V/s. Measurements were carried out in a conventional three-electrode cell. The working electrode was a Pt electrode and counter electrode was an argentum mesh. The 0.1 mmol polymers were dissolved in 10 mL chloroform containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($(n\text{-Bu})_4NPF_6$) as the supporting electrolyte.

3. Results and discussion

3.1. The polymerization of the epoxy monomer (GTEMPO)

In order to synthesize comb-shaped copolymer via NMP technique, the multiple TEMPO agents should be prepared firstly. Due to the high reactive property of TEMPO with free radical, these kinds of compounds were generally synthesized in the dormant state [33]. Nishide H. et. al. reported the synthesizing of unprotected multi-TEMPO containing polymer, PGTEMPO [32]. Following the reference, the epoxy group was introduced into TEMPO analog by the reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy with epichlorohydrin in the presence of a phase transfer agent in this paper. 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) was obtained in mild yield (80%) after purification. Then, GTEMPO was polymerized by ring opening of epoxy group under the initiating of potassium *t*-butoxide in THF to afford PGTEMPO. Three PGTEMPOs (macro-TEMPO agent) with different molecular weight were obtained (showed in Table 1).

3.2. The preparation of the comb-shaped copolymer (PGTEMPO-g-PVBK)

The PGTEMPO contained TEMPO moieties was used as macro-TEMPO agent to conduct controlled free radical polymerization of 9-(4-vinylbenzyl)-9H-carbazole (VBK) with pendent carbazole group by molar ratios of $[VBK]_0/[BPO]_0/[GTEMPO]_0/[VC]_0 = 130{:}1{:}1.3{:}1.3$ and 65:1:1.3:1.3. A serial of comb-shaped copolymers (PGTEMPO-g-PVBK) with various molecular weights were obtained as shown in Table 1. Fig. 1 showed GPC curves of the polyethers and the corresponding comb-shaped copolymers. As shown in Fig. 2, the corresponding plot of $\ln([M]_0/[M])$ versus the polymerization time was linear, which indicated that the propagating radical concentration was almost constant during the process of the polymerization. However, the extrapolation of the kinetic line does not cross origin point, which should be caused by the slow initiation. The evolution of molecular weights measured by gel permeation chromatograph ($M_{n(GPC)}$s) of the polymers with conversions shown linearly relationship as shown in Fig. 3. These results are similar to the typical living free radical polymerization behavior. However, the PDI of the obtained comb-shaped copolymers is a bit broad, e.g., 1.59–1.87, which may due to the low efficiency termination of propagating free radicals in the multi-TEMPO polymerization.

3.3. Optical properties of PGTEMPO-g-PVBK

Carbazole containing polymers were well known as photoconduct materials. The resulting polymer, PGTEMPO-g-PVBK, was characterized in terms of their optical properties. Fig. 4 depicts the UV–vis absorption spectra of the monomer (VBK) and polymers (PGTEMPO-g-PVBK). Both the monomer and corresponding polymers showed absorption peaks at 294, 331 and 345 nm. The peak at 295 nm should be attributed to the $\pi-\pi^*$ transition of benzene ring. Another two peaks at 330 nm and 345 nm are the characteristic of $\pi-\pi^*$ transition of carbazole molecules [34]. As shown in Fig. 4, the UV absorbance intensity was decreased with the increasing of molecular weights of the polymers, which may due to interaction of neighboring carbazolyl chromophores in the polymers. Additionally, it can be observed that the comb-shaped copolymer exhibited strong fluorescence emission both in solution and film (Fig. 5). The polymer showed the strong monomeric

Table 1
Characterizations of the comb-shaped copolymers, (PGTEMPO-g-PVBK), with different molecular weights.

Macro-TEMPO agent[a]		Molar ratio $[VBK]_0/[BPO]_0/[TEMPO]_0/[VC]_0$	PGTEMPO-*g*-PVBK[b]				
M_n(g/mol)	PDI		Conv. (%)	M_n (g/mol)	PDI	m[c]	n[c]
4080	1.35	130:1:1.3:1.3	81.3	15100	1.74	17	2.3
		65:1:1.3:1.3	81.3	12550	1.70		1.8
4740	1.59	130:1:1.3:1.3	77.7	13700	1.84	20	1.6
		65:1:1.3:1.3	79.5	10580	1.80		1.1
5010	1.59	130:1:1.3:1.3	81.3	16510	1.73	21	1.9
		65:1:1.3:1.3	77.7	10230	1.84		0.9

[a] Where polymerizations were all carried out in 75 °C for 24 h.

[b] Where polymerizations were all carried out in 123 °C for 8 h.

[c] m, n (Scheme 2) value were calculated from $Mn_{(GPC)}$ by assuming equal length of each side chain.

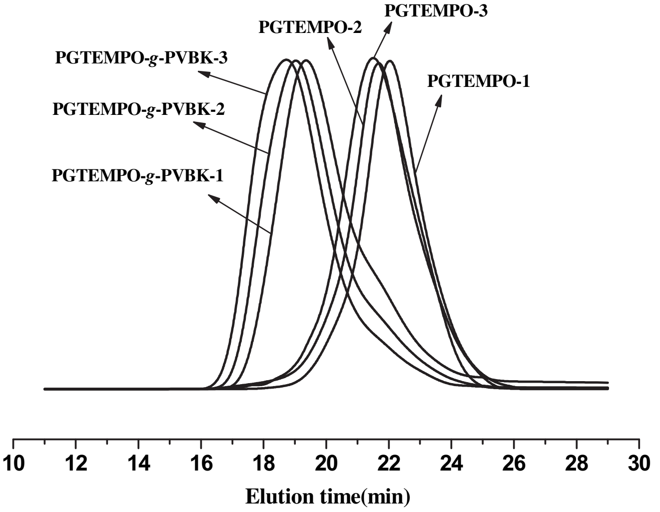


Fig. 1. Evolution of GPC traces of the polyethers (1: $M_{n(GPC)} = 4080$ g/mol, PDI = 1.35; 2: $M_{n(GPC)} = 4740$ g/mol, PDI = 1.59; 3: $M_{n(GPC)} = 5010$ g/mol, PDI = 1.59) and the correspond comb-shaped copolymers (1: $M_{n(GPC)} = 10{,}230$ g/mol, PDI = 1.84; 2: $M_{n(GPC)} = 13{,}700$ g/mol, PDI = 1.84; 3: $M_{n(GPC)} = 17{,}860$ g/mol, PDI = 1.87).

fluorescence at 350 nm and 365 nm together with weak excimer fluorescence at longer wavelength in DMF solution at room temperature (Fig. 5A) [31]. Meanwhile, only the excimer fluorescence at 412 nm and 435 nm was found in film condition (Fig. 5B) [35,36]. Furthermore, the fluorescence intensity of the comb-shaped copolymers in the solution was lower than that of VBK monomer, which may be attributed to the polymerizable double bond in VBK is relatively weakly electron-deficient. Similar results were found in the VBK homopolymer system and *N*-ethyl-3-vinylcarbazole system [31,37]. The results in Fig. 5 also showed that fluorescence intensities of the comb-shaped copolymers had an increase trend with the increasing molecular weights of the polymers at the same concentration of VBK moiety. This should be the increasing of excimer concentration in VBK side chain with the increase of molecular weights of the polymers.

3.4. Thermal properties of the polymers

The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. The results were shown in Fig. 6 and Table 2, respectively. The glass transition temperatures (T_g) of macro-TEMPO agents, PGTEMPO-1∼3, with molecular weights of 4080, 4740 and 5010 were 15.4, 22.7 and 25.3 °C and thermal decomposition temperature (T_d) were 285.9, 294.4 and 306 °C, respectively. After grafted with VBK, the glass transition temperatures and thermal decomposition temperatures of the comb-shaped copolymers were observably improved. The T_g of PGTEMPO-*g*-PVBK-1∼3 was increased to 74.2, 81.5 and 94.1 °C, respectively. Thus, the introduction of VBK would greatly improve the T_g of the polymers, which should be caused by the rigid structure of carbazole in PGTEMPO-*g*-PVBK. The sharp peak in about 175 °C in Fig. 6 should be the melting point of carbazole containing structures [38]. The introduction of carbazole moiety in PGTEMPO-*g*-PVBK also improved the thermal stability of the polymers. There were two decomposition stages in the TGA curves of PGTEMPO-*g*-PVBK polymers (Fig. 6). One should be the decomposition of PGTEMPO main chain, which showed the T_d values at about 218 °C. The other one should be attributed to the decomposition of PVBK chain at the range of 388–397 °C with different molecular weights of PVBK chains. The decomposition temperatures of PGTEMPO chain in comb-shaped copolymers were lower than that of their

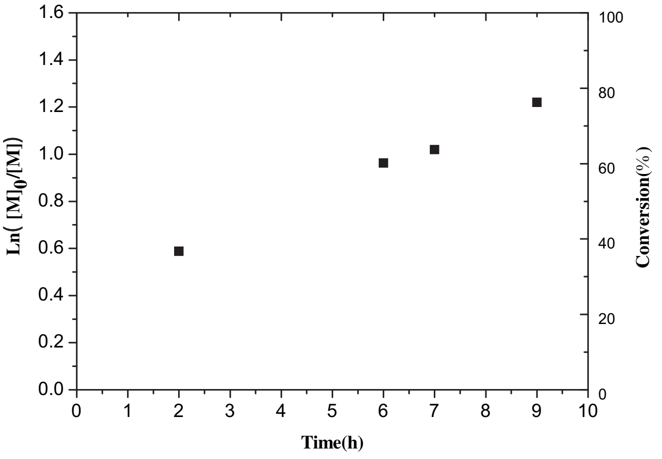


Fig. 2. Relationship of ln([M]$_0$/[M]) and monomer conversion with polymerization time for the NMP of VBK in THF at 123 °C. $[VBK]_0/[BPO]_0/[GTEMPO]_0/[VC]_0 = 130:1:1.3:1.3$ $[VBK]_0 = 0.5$ mol/L. PGTEMPO: $M_n = 4080$, PDI = 1.35.

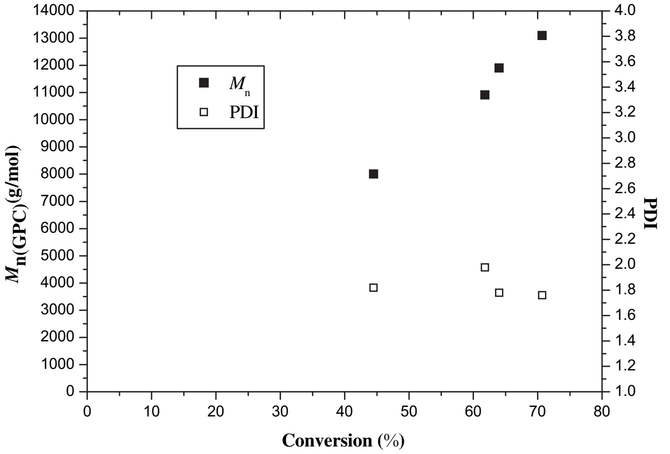


Fig. 3. Evolution of $M_{n(GPC)}$ and PDI with monomer conversion for polymerization of VBK. Polymerization conditions are same as in Fig. 2.

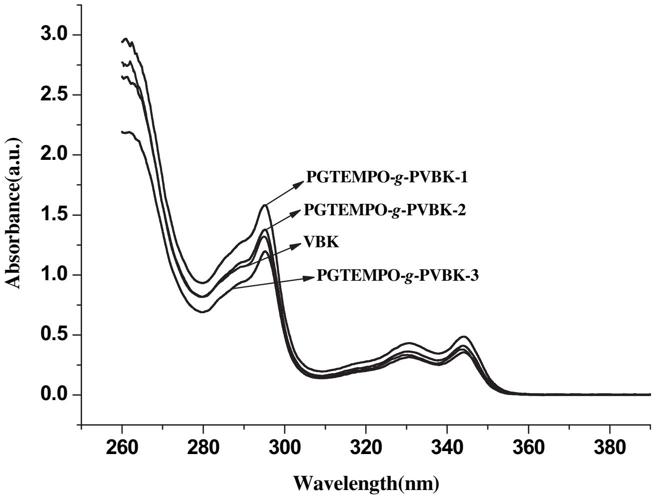


Fig. 4. UV–vis absorption spectra of VBK and PGTEMPO-g-PVBK with different molecular weights (1: $M_{n(GPC)} = 10{,}230$ g/mol, PDI = 1.84; 2: $M_{n(GPC)} = 13{,}700$ g/mol, PDI = 1.84; 3: $M_{n(GPC)} = 17{,}860$ g/mol, PDI = 1.87) in $CHCl_3$ solution at room temperature. The concentration of carbazole moieties was 5×10^{-5} M for all cases.

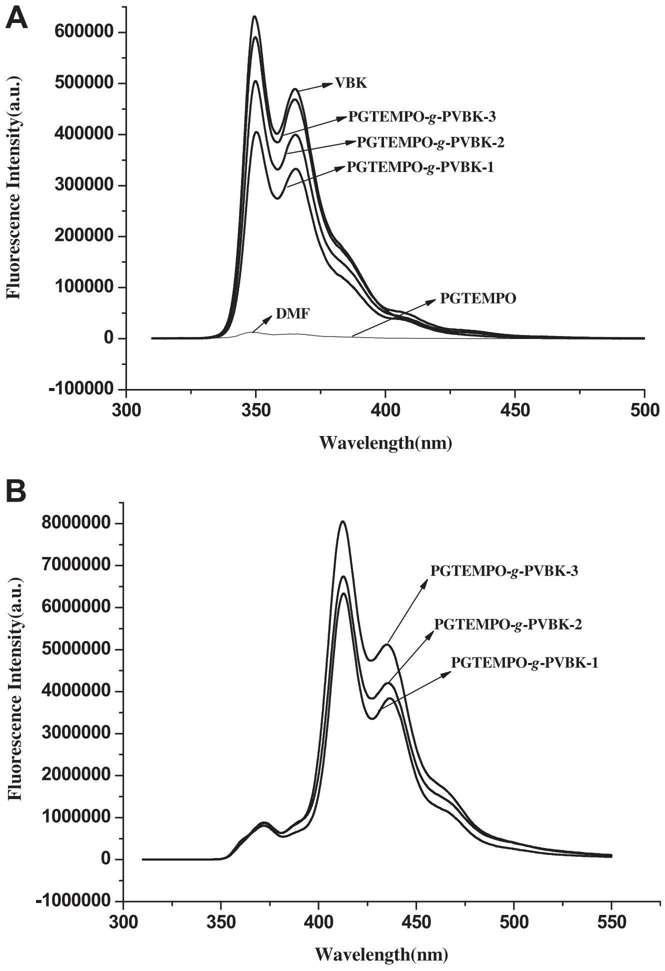


Fig. 5. The fluorescence spectra of PGTEMPO-*g*-PVBK with different molecular weights (1: $M_{n(GPC)} = 10,230$ g/mol, PDI = 1.84; 2: $M_{n(GPC)} = 13,700$ g/mol, PDI = 1.84; 3: $M_{n(GPC)} = 17,860$ g/mol, PDI = 1.87) at room temperature with excitation wavelength of 294 nm. **A**: In DMF solution, the concentration of carbazole moieties is 5×10^{-5} M; **B**: In film.

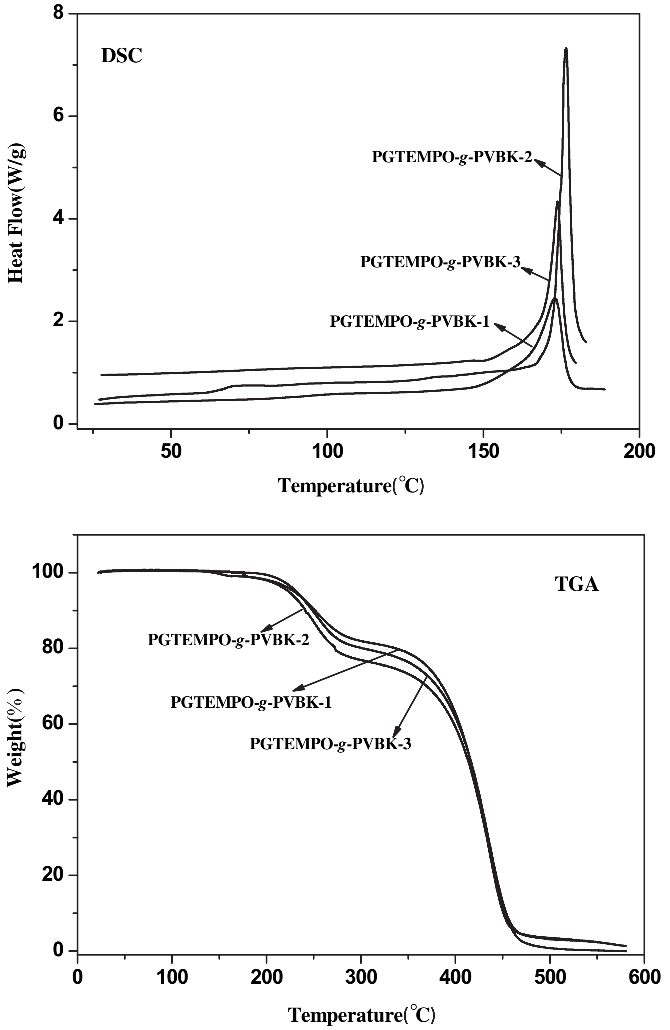


Fig. 6. DSC and TGA of PGTEMPO-*g*-PVBK (1: $M_{n(GPC)} = 10,230$ g/mol, PDI = 1.84; 2: $M_{n(GPC)} = 13,700$ g/mol, PDI = 1.84; 3: $M_{n(GPC)} = 17,860$ g/mol, PDI = 1.87).

homopolymers, which may be attributed to the interaction of neighboring side chain in the polymers.

3.5. Electrochemical properties of the polymers

The redox behavior of the polymers was studied by cyclic voltammetry (CV), using a three-electrode cell in an anhydrous chloroform solution with $(n\text{-Bu})_4NPF_6$ as the support electrolyte. A Pt wire was used as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode. The scans were performed at a scan rate of 50 mV s^{-1} at room temperature. The spectra are shown in Fig. 7 and the results are summarized in Table 3. PGTEMPO ($M_{n(GPC)} = 4740$ g/mol, PDI = 1.59) exhibited chemical reversible oxidation and reduction peaks of 0.62 V and 0.45 V which due to the free radical of the TEMPO. The voltammetries of three comb-shaped copolymers all showed the good reversible oxidation and reduction processes. On anodic sweep, the oxidative peak potentials for PGTEMPO-*g*-PVBK-1, PGTEMPO-*g*-PVBK-2 and PGTEMPO-*g*-PVBK-3 were 0.50, 0.54 and 0.59 V, respectively. The peak values of reductive potentials for these three polymers were 0.46, 0.48 and 0.55 V, respectively. The magnitude of oxidative and reductive potential is considered to reflect the electron-donating and electron-accepting ability of the structure. The results showed that these comb-shaped polymers showed obvious regular changes in their electron-donating and accepting abilities upon the increasing of PVBK chain molecular weight, e.g., easy electron-accepting and hard electron-donating ability with increasing of PVBK chain length. Similar trend was observed in CV curves of 4-vinyl-benzylcarbazole (VBK) homopolymers (the polymers were synthesized according to our previously work [31]), which was shown in the inset figure within Fig. 7. The increasing in molecular weight of polymers should increase the charge carrier's mobility within them [39], which would evidently improve the electron-accepting ability of the

Table 2
The glass transition temperature (T_g)[a] and the thermal decomposition temperature (T_d)[b] of the polymers.

Polymer [c]	$M_{n,GPC}$	PDI	T_g/°C	T_d/°C
PGTEMPO-1	4080	1.35	15.4	285.9
PGTEMPO-2	4740	1.59	22.7	294.4
PGTEMPO-3	5010	1.59	25.3	306.0
PGTEMPO-*g*-PVBK-1[d]	10230	1.84	74.2	218.8, 388.9
PGTEMPO-*g*-PVBK-2[e]	13,700	1.84	81.5	218.5, 397.6
PGTEMPO-*g*-PVBK-3[d]	17,860	1.87	94.1	218.5, 392.7

[a] The glass transition temperature.
[b] The thermal decomposition temperature.
[c] Three polymers were obtained in the same reaction temperature, the same reactant feed molar ratio, and the different reaction time.
[d] Polymers prepared using PGTEMPO-3 as the macro-TEMPO agent.
[e] Polymers prepared using PGETEMO-2 as the macro-TEMPO agent.

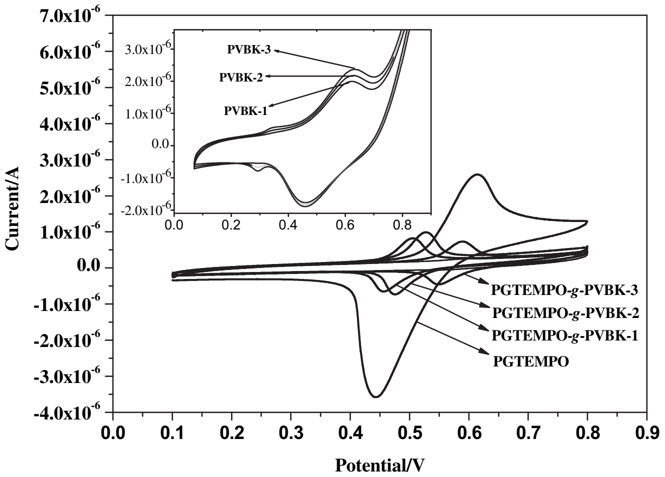


Fig. 7. Cyclic voltammograms of the polyether (PGTEMPO, $M_{n(GPC)} = 4740$ g/mol, PDI = 1.59), PVBK and the comb-shaped copolymer with different molecular weight (PVBK1: $M_{n(GPC)} = 9860$ g/mol, PDI = 1.14; PVBK2: $M_{n(GPC)} = 12530$ g/mol, PDI = 1.21; PVBK3: $M_{n(GPC)} = 14980$ g/mol, PDI = 1.24; PGTEMPO-g-PVBK-1: $M_{n(GPC)} = 10230$ g/mol, PDI = 1.84; PGTEMPO-g-PVBK-2: $M_{n(GPC)} = 13700$ g/mol, PDI = 1.84; PGTEMPO-g-PVBK-3: $M_{n(GPC)} = 17860$ g/mol, PDI = 1.87) in $CHCl_3$ solution. The concentration of repeating units is 5×10^{-4} M in room temperature containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($(n\text{-Bu})_4NPF_6$) as the supporting electrolyte.

typical carbazole functionalized hole transportation materials. However, the difference of electron accepting and donating abilities among different molecular weight polymer was obviously enlarged in comb-shaped PVBK based polymers. The reason should due to the particular assembly behavior of comb-shaped copolymers [40], which may favor for the π–π stacking structure formation in the current comb-shaped copolymers.

The highest occupied molecular orbital (HOMO) energy levels of the polymer materials can be calculated from the onset oxidation potential (E^{ox}_{onset}) based on the reference energy level of ferrocene (4.8 eV below the vacuum level) [41]:

$$\text{HOMO} = E_{\text{onset}}{}^{\text{ox}} + 4.8 - E_{\text{Foc}}$$

where in E_{Foc} was the potential of Foc(ferrocene)/Foc + vs. Ag/AgCl. The value of E_{Foc} was 0.042 V (measure for calibration). The band gaps (E_g) of these polymer materials were estimated by the onset absorption edge of their UV–vis (shown in Fig. 6). Thus, their lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the HOMO and band gap. The HOMO, LUMO and band gap energy levels of the polymers are summarized in Table 3. The HOMO ranged from 5.220 to 5.241, 5.299 eV and the LUMO from 1.694 to 1.711, 1.764 eV for these three polymers. The band gap between the HOMO and LUMO was about 3.53 eV. These polymers have high HOMO levels so that efficient hole injection should occur from indium tin oxide (ITO) anodes (work function about 5.0 eV) making them potentially efficient emissive and/or hole transporting materials for electronic devices. Furthermore, the HOMO, LUMO and band gap increased with the molecular weight of the polymers [39]. Thus, these parameters of the polymers can be adjusted by varying the molecular weights of the polymers. This should be favorable to the application of these polymers in electronic devices.

Table 3
Electrochemical potentials and energy levels of the comb-shaped copolymers.

Polymers	Molecular Weight	$[E^{ox}_{onset}]$[a] (V)	LUMO[b] (eV)	HOMO[c] (eV)	E_g[d] (eV)
PGTEMPO-g-PVBK-1	10230	0.462	1.694	5.220	3.526
PGTEMPO-g-PVBK-2	13700	0.483	1.711	5.241	3.530
PGTEMPO-g-PVBK-3	17860	0.541	1.764	5.299	3.535

[a] Onset oxidation potential measured by cyclic voltammetry.
[b] Lowest unoccupied molecular orbital (LUMO) calculated from the HOMO and band gap.
[c] Highest occupied molecular orbital (HOMO) calculated from the oxidation potentials.
[d] Optical band gap estimated from the UV–vis absorption edge wavelength.

4. Conclusions

The comb-shaped copolymers (PGTEMPO-*g*-PVBK) with polyether main chain and poly(4-vinyl-benzylcarbazole) (PVBK) side chain were synthesized by combination of ring opening polymerization and nitroxide-mediated polymerization. The graft polymerization of VBK from macro-TEMPO showed typical controlled free radical polymerization behaviors. These comb-shaped copolymers had intensity fluorescence emission at 350 nm and 365 nm under the excitation of 294 nm light. The glass transition temperatures and decomposition temperatures of PGTEMPO were improved by grafted of PGTEMPO with VBK to obtain PGTEMPO-g-PVBK. Reversible oxidation and reduction behavior of the polymers was investigated by cyclic voltammetry. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels accompanied with band gaps could be adjustable via molecular weights of the polymers, which should be favorable to the application of these polymers in electronic devices.

Acknowledgments

The financial support from the National Nature Science Foundation of China (No.20874069 and 50803044) and the Specialized Research Fund for the Doctoral Program of Higher Education contract grant (No.200802850005) are gratefully acknowledged. This work was also sponsored by Qing Lan Project and Program of Innovative Research Team of Soochow University.

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