IOP Conf. Series: Materials Science and Engineering **87** (2015) 012058 doi:10.1088/1757-899X/87/1/012058

Synthesis and characterization of well-defined PVBCz-*b*-PDMAEMA multifunctional block copolymer prepared via ATRP

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Abstract. A functional polymer containing carbazole unit, PVBCz, was successfully prepared via atom transfer radical polymerization (ATRP) of 9-(4-vinylbenzyl)-9H-carbazole (VBCz). The controlled features of ATRP were confirmed by the linear increment of the molecular weight with the monomer conversion, while the molecular weight distribution was relatively narrow ($M_w/M_n \leq 1.33$). The block copolymer PVBCz-*b*-PDMAEMA was synthesized via ATRP, using PVBCz-Br as a macro-initiator and DMAEMA as the second monomer. ^{1}H-NMR, GPC and FT-IR characterization confirmed the successful synthesis of PVBCz-*b*-PDMAEMA. The resulting copolymer exhibited both fluorescence from PVBCz segments and thermo-responsiveness from PDMAEMA segments. Moreover, the fluorescent intensity of PVBCz-*b*-PDMAEMA in aqueous solutions increased as the temperature rose, which could be attributed to the coupling of two different functions.

1. Introduction

Atom transfer radical polymerization (ATRP) [1-3], which uses simple organic halides as initiators and transition metal complexes as catalysts, combines the superiority of conventional free-radical polymerization and living polymerization. This method has allowed the preparation of a variety of unique macromolecular architectures, such as block copolymers, graft copolymers, star polymers and hyperbranched polymers with predetermined molecular weights, narrow molecular weight distributions and various functional groups. These unique advantages make the ATRP method a powerful tool to synthesize functional polymers [4].

Carbazole compounds are an important series of nitrogen-containing heterocyclic compounds with a special rigid fused ring structure. The structure has a large conjugated system and a strong intra-molecular electron transfer, and it's susceptible to modification to introduce a variety of functional groups. Polymers containing a carbazole ring in the main or side chains are of considerable scientific and industrial interest due to their unique properties, such as high charge-carrier abilities, hole-transporting and fluorescent and photoconductive features [5-10]. Therefore, carbazole-containing polymers are considered promising organic photoelectric functional materials [11].

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Poly [(dimethylamino) ethyl methacrylate] (PDMAEMA) is a typical so-called ‘‘stimuli-responsive’’ or ‘‘smart’’ polymer, due to its remarkable responsive behavior to environmental stimuli such as temperature, pH and ionic strength etc. [12]. The temperature-sensitive solubility of PDMAEMA in aqueous media also renders it potentially applicable in various fields such as drug delivery systems and sensors [13].

The multifunctional block copolymer can be obtained by copolymerization of carbazole-containing monomer and DMAEMA via ATRP. The carbazole segments exhibit the photoelectric function, and PDMAEMA segments exhibit the stimuli-responsive function. In addition, it’s expected to achieve functional coupling, which can render the copolymer potentially applicable in sensors, smart optoelectronic functional materials. However, to the best of our knowledge, scientific and applied research in this area has rarely been publicly reported before.

In this paper, we report the synthesis of the well-defined homopolymer [(poly (9-(4-vinylbenzyl)-9H-carbazole) (PVBCz)] and the block copolymer PVBCz-*b*-PDMAEMA via ATRP. Meanwhile, the optical properties of polymers and their aqueous solutions were also investigated.

2. Experiment

2.1. Materials

1-(chloromethyl)-4-ethenyl-benzen-was purchased from J&K and passed through a short neutral alumina column to remove inhibitors prior to use, followed by final purification via distillation in vacuum. Copper (I) bromide (CuBr) (J & K, 99%) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol, ether and then dried in vacuum. (Dimethylamino) ethyl methacrylate (DMAEMA) (J & K, 98%) was purified through a neutral alumina column to remove the inhibitor. Cyclohexanone (AR, Sinopharm) was dried with calcium hydride overnight and distilled in vacuum. Ethyl 2-bromoisobutyrate (EBiB), *N, N, N’, N’, N”*-pentamethyldiethylenetriamine (PMDETA) (98%), carbazole (99%) were purchased from J&K and used as received. Tetrahydrofuran (THF) (AR grade) was purchased from Sinopharm. Anhydrous THF was obtained by distillation under argon from sodium benzophenoneketyl. Deuterated chloroform ($CDCl_3$) with 1% v/v tetramethylsilane (TMS) (D, 99.8%) was purchased from Cambridge Isotope Laboratories. All other reagents were supplied as analytic pure and used without further purification.

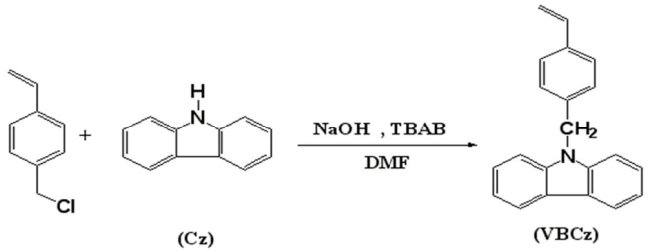
2.2. Instrument

^{1}H-NMR spectra were recorded on an Agilent 400/54 NMR instrument. Monomer conversion was determined by integration of relative peaks in the ^{1}H-NMR spectra. Element analyses were obtained with a PerkinElmer PE-2400-II analyzer. The FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Molecular weight and polydispersity (PDi) were measured using Wyatt gel permeation chromatography (GPC) equipped with a Dawn Heleos-II detector and calibrated using PS standard samples. THF was used as the eluent at a flow rate of 1mL/min, operated at 25°C. Fluorescence (FL) spectra were recorded with a Horiba JY FL-3 spectrometer.

2.3. Synthetic procedures

2.3.1. Synthesis of 9-(4-vinylbenzyl)-9H-carbazole (VBCz). 9-(4-Vinylbenzyl)-9H-carbazole (VBCz) was synthesized according to the reference [14]. A mixture of carbazole (5.00 g, 30.0 mmol), sodium hydroxide (1.20 g, 37.5 mmol) and tetra-n-butylammonium bromide (TBAB) (200 mg, 0.62 mmol) in DMF 100 mL was stirred for 2 h. Then 1-(chloromethyl)-4-ethenyl-benzen (5.50 g, 36.0 mmol) was added dropwise, and the reaction mixture was continually stirred for 20 h at ambient temperature (scheme 1). The resulting mixture was poured into a large excess of deionized water. The resultant white precipitate was filtered and dried in vacuum at 70°C. The crude product was purified by recrystallization from acetone to give 5.40 g (63.5%) of white crystals. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.17-5.22 (d, 1H, C$\boldsymbol{H}_2$=C), 5.51 (s, 2H, N-C$\boldsymbol{H}_2$), 5.65 (d, 1H, C$\boldsymbol{H}_2$=C), 6.65 (m, 1H, CH_2=C$\boldsymbol{H}$),

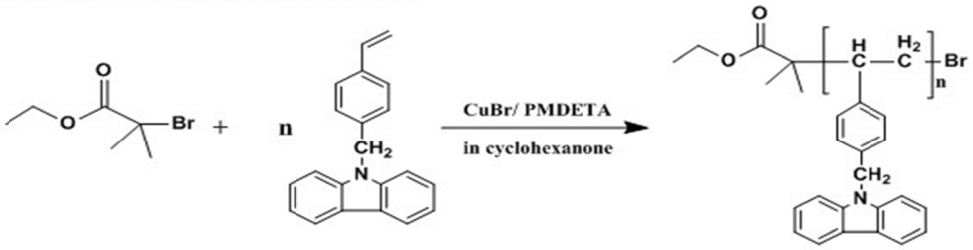
7.05-7.13 (d, 2H, Ar-***H***), 7.20-7.45 (m, 8H, Ar-***H***), 8.10-8.15 (d, 2H, Ar-***H***). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 5.05; % N, 4.94. Found: C, 88.85; H, 5.96; N, 4.92.



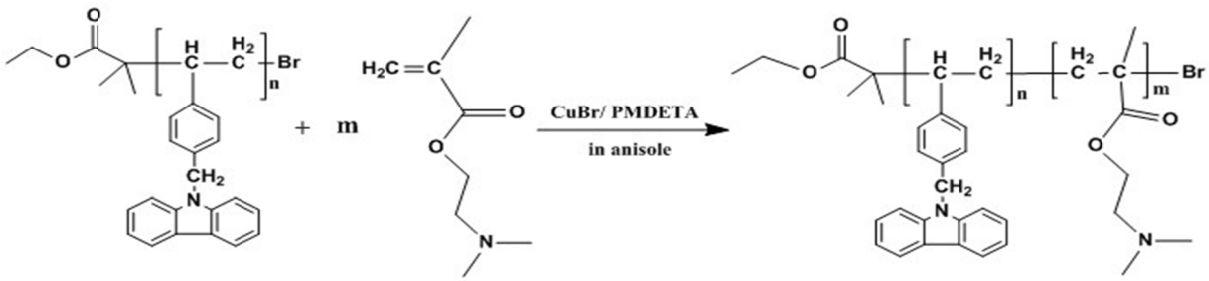
Scheme 1.

2.3.2. Synthesis of PVBCz-Br Macro-initiator (Homogeneous ATRP). A typical ATRP [15] was carried out as follows. VBCz (2.27 g, 8.0 mmol), PMEDTA (16.7 µL, 0.08 mmol) and EBiB (5.9 µL, 0.04 mmol) and anisole (internal NMR standard, 0.5 mL) were charged into a dry Schlenk flask with cyclohexanone (10.0 mL) as solvent. The flask subjected to three freeze-pump-thaw cycles to remove the air inside completely. The solution was then transferred via cannula under nitrogen into another Schlenk flask, previously evacuated and filled with nitrogen, containing Cu(I) Br (0.006 g, 0.04 mmol) and a stir bar. The reaction temperature was adjusted at to 90°C under constant stirring (t = 0). Samples were extracted periodically using a degassed syringe for molecular weight (GPC) and conversion (^{1}H-NMR) analysis. At the end of polymerization, the reaction mixture was diluted with 10 mL of THF, and air was bubbled through for 30 min. The mixture was passed through a short neutral alumina column and subsequently washed with THF to remove the copper complex catalyst. The resulting polymer solution was concentrated by rotary evaporation (ca. 10 mL), followed by being precipitated into methanol (ca. 200 mL). The white precipitate was filtered and dried under vacuum overnight at 50°C. The crude polymers were purified by a Soxhlet extractor with ethanol to further remove the remaining VBCz (scheme 2a).

a. synthesis of PVBCz-Br macroinitiator



b. synthesis of PVBCz-*b*-PDMAEMA copolymer



Scheme 2.

2.3.3. Synthesis of PVBCz-b-PDMAEMA copolymer. A PVBCz-*b*-PDMAEMA copolymer was synthesized using the PVBCz-Br macro-initiator via ATRP. The procedure was the same as discussed in the previous section, except that a macro-initiator (0.89 g, M_n=2.573×10^4, 0.05 mmol) and solvent (anisole, 10.0 mL) were added instead to the flask initially. Once the macro-initiator was dissolved, the second monomer (DMAEMA, 3.57 g, 23.0 mmol) and PMDETA (21.0 μL, 0.10 mmol) were added. The flask was subjected to three freeze-pump-thaw cycles. The solution was then transferred via cannula under nitrogen into another Schlenk flask, previously evacuated and filled with nitrogen, containing Cu (I) Br (0.007 g, 0.05 mmol) and a stir bar. Polymerization was performed at 60°C for 12 h. At the end of polymerization, the reaction mixture was diluted with 10 mL of THF, and air was bubbled through for 30 min. The mixture was passed through a short neutral alumina column and subsequently washed with THF to remove the copper complex. The copolymers were obtained by subsequent concentration, precipitation into *n*-hexane, filtration and finally drying under vacuum overnight at 40°C (scheme 2b).

3. Results and discussion

3.1. Kinetic studies of homogeneous ATRP

Figure 1 shows the kinetic plots of the ATRP of VBCz. The linearity of the semi-logarithmic plot of ln ($[M]_0/[M]_t$) vs time indicates that theATRP was first-order with respect to the monomer and that the concentration of the radicals remains constant during ATRP. Figure 2 shows the number average molecular weights ($M_{n,GPC}$) and the polydispersity indexes (PDi, M_w/M_n) as a function of monomer conversion. $M_{n,th}$ was calculated by the conversion and monomer/initiator ratio.

The reaction time, conversion, number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity indexes (PDi, M_w/M_n) are listed in table 1. The polydispersity indexes (PDi) of PVBCz are relatively narrow (1.12-1.33). All of these results suggest that the ATRP of VBCz using EBiB as an initiator and CuBr/PMDETA as a catalyst is a "living" polymerization process.

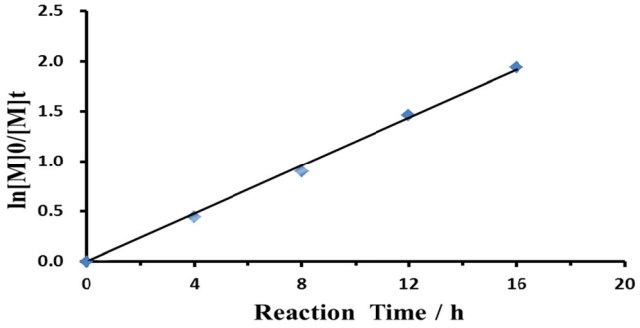


Figure 1. Semi-logarithmic plots of ln ($[M]_0/[M]_t$) *vs.* reaction time for the ATRP of VBCz.

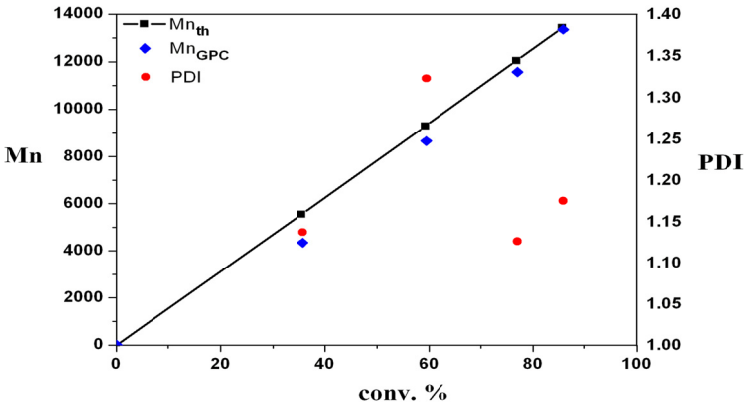


Figure 2. Plots of $M_{n,GPC}$, PDi and $M_{n,th}$ *vs.* monomer conversion for the ATRP of VBCz.

Table 1. Reaction time, M_n, M_w PDi and and monomer conversion of PVBCz made by ATRP.

Reaction time (h)	Conversion (%)	M_n (g/ mol)	M_w(g/ mol)	PDi
4	35.6	4300	4900	1.14
8	59.4	8700	11500	1.32
12	76.9	11600	13000	1.13
16	85.7	13100	15300	1.18

3.2. Structural characterization of PVBCz and PVBCz-b-PDMAEMA

3.2.1. [1]H-NMR Characterization. Figure 3 gives the [1]H-NMR spectra of VBCz and PVBCz. The peaks at δ = 5.18 and 5.65 ppm belonging to the unsaturated C=H in the VBCz monomer disappear. However, the appearance of new peaks at δ = 1-2 ppm is obvious, which is attributed to saturated C-H in PVBCz.

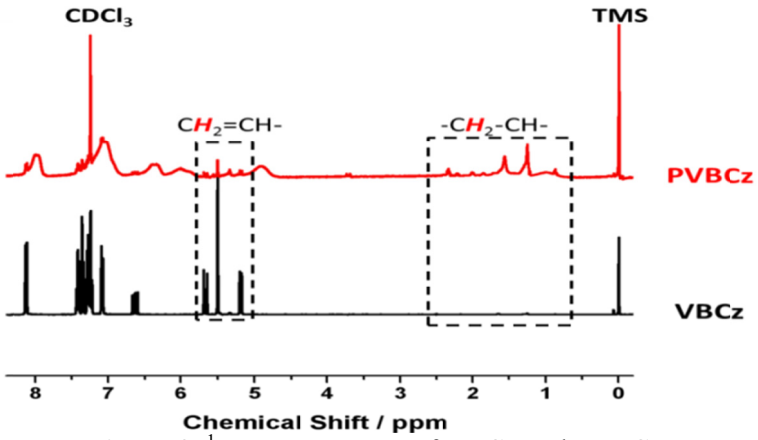


Figure 3. [1]H-NMR spectra of VBCz and PVBCz.

Figure 4 gives the [1]H-NMR spectra of PVBCz, PDMAEMA and PVBCz-*b*-PDMAEMA. In the [1]H-NMR spectrum of PVBCz-*b*-PDMAEMA, proton signals at δ = 2.27, 2.58 and 4.05ppm coming from N-methyl and methylene groups in PDMAEMA are observed [16]. Meanwhile, aromatic signals of PVBCz at 7.0−8.2 ppm can also be observed. These results confirmed the ATRP copolymerization of DMAEMA monomers initiated by the PVBCz-Br macro-initiator.

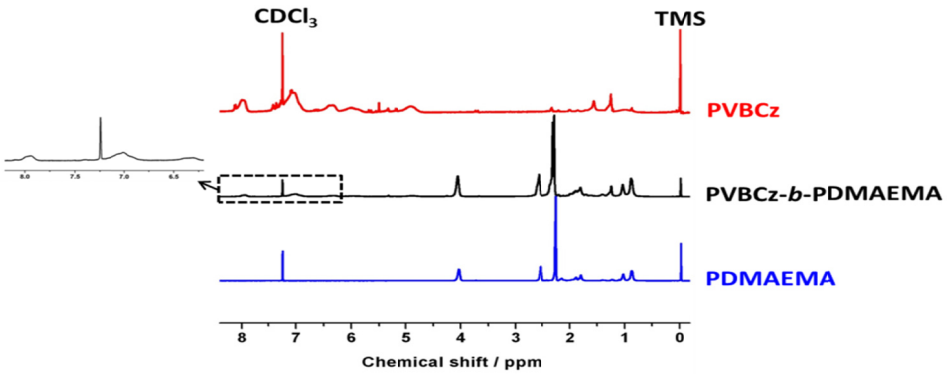


Figure 4. [1]H-NMR spectra of PVBCz, PDMAEMA and PVBCz-*b*-PDMAEMA.

3.2.2. GPC Characterization. The successful chain extension from a preformed polymer chain that acts as the macro-initiator is considered as an important criterion of the controlled/living nature ofATRP [17]. The PVBCz-Br macro-initiator (M_n = 25700 g/mol, PDi = 1.33) prepared via the ATRP of VBCz was employed for the chain extension experiment, using DMAEMA as the second monomer. The results are shown in figure 5 and table 2. M_n increased from 25700 to 68900 g/mol, while the molecular weight distributions still kept relatively narrow (PDi=1.11). This further confirmed the successful synthesis of the block copolymer PVBCz-*b*-PDMAEMA., which also indicated the living properties of ATRP.

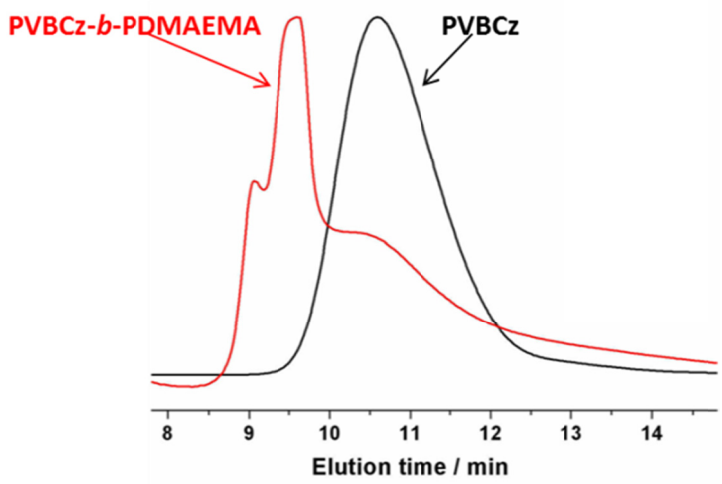


Figure 5. GPC traces of PVBCz and PVBCz-*b*-PDMAEMA.

Table 2. Molecular weight parameters of PVBCz and PVBCz-*b*-PDMAEMA.

Sample	$\overline{DP}$	$M_n(\times 10^4)$	$M_w(\times 10^4)$	PDi
PVBCz	91	2.573	3.427	1.33
PVBCz-*b*-PDMAEMA	(91+274)	6.890	7.670	1.11

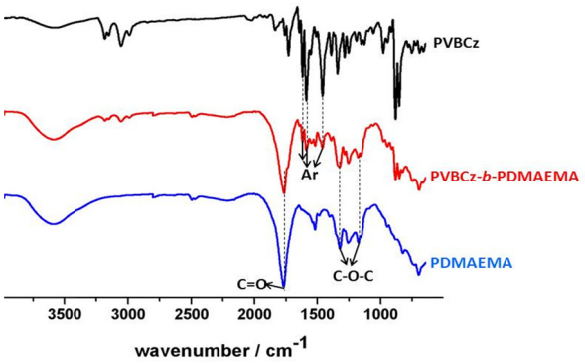


Figure 6. FT-IR spectra of PVBCz, PDMAEMA and PVBCz-*b*-PDMAEMA.

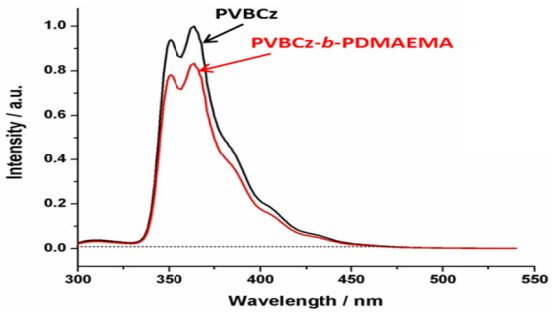


Figure 7. The fluorescence spectra of PVBCz and PVBCz-*b*-PDMAEMA in THF solution at ambient temperature. The concentration of the sample was 1 mg/mL. The excitation wavelength was 280 nm.

3.2.3. FT-IR Characterization. The FT-IR spectra of PVBCz, PDMAEMA and PVBCz-*b*-PDMAEMA are given in figure 6. As shown in the FT-IR spectra, the characteristic absorption bands at 1600, 1580 and 1450 cm^{-1} for the aromatic groups in the chain of PVBCz can be observed in both PVBCz and PVBCz-*b*-PDMAEMA [18]. In addition, after copolymerization with DMAEMA using PVBCz-Br as the macro-initiator, the characteristic absorption peaks at 1750 cm^{-1} (C=O stretching vibration) and 1300, 1100 cm^{-1} (C-O-C stretching vibration) [18] in figure 6 indicate the presence of the PDMAEMA block for PVBCz-*b*-PDMAEMA.

3.3. Optical properties of PVBCz and PVBCz-b-PDMAEMA

The fluorescence (FL) spectra of PVBCz and PVBCz-*b*-PDMAEMA in the THF solution at ambient temperature are shown in figure 7. The FL intensity of PVBCz is stronger than the intensity of PVBCz-*b*-PDMAEMA under the same mass concentration due to the existence of more carbazole moieties in PVBCz than in PVBCz-*b*-PDMAEMA.

Figure 8 shows the fluorescence changes of PVBCz-*b*-PDMAEMA in solvent mixtures (THF/water, the water volume fraction changed), and figure 9 exhibits the fluorescence change following temperature of PVBCz-*b*-PDMAEMA in aqueous solution. Both PVBCz and PDMAEMA are soluble in THF. PVBCz is hydrophobic. PDMAEMA is a classical thermo-responsive polymer, which is hydrophilic below the lower critical solution temperature (LCST). As long as the temperature exceeds the LCST, the polymer chains begin to collapse from coil to globule in aqueous solutions [19, 20]. In other words, it becomes hydrophobic above LCST. Due to the longer hydrophilic PDMAEMA segments below LCST, PVBCz-*b*-PDMAEMA could be dispersed in the aqueous medium.

As shown in figure 8, with the solution's water fraction increasing, the FL intensity decreased. The FL intensity of the THF solution is almost 10 times higher than that of the aqueous solution. As shown in figure 9, the FL intensity increased as the temperature of the solution rose. When the temperature was below 35°C, the FL intensity changed mildly. The FL intensity presented dramatical change as the temperature reached 40°C.

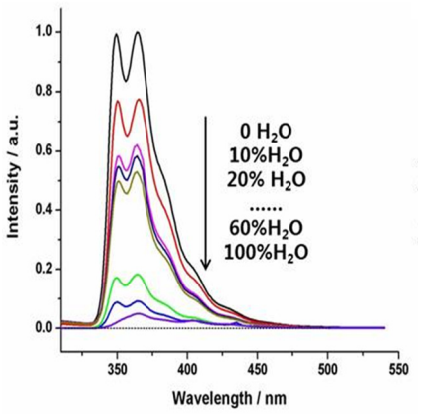


Figure 8. The fluorescence spectra of PVBCz-*b*-PDMAEMA in solvent mixtures (THF/water) at ambient temperature. The concentration of the sample was 1 mg/mL. The excitation wavelength was 280 nm.

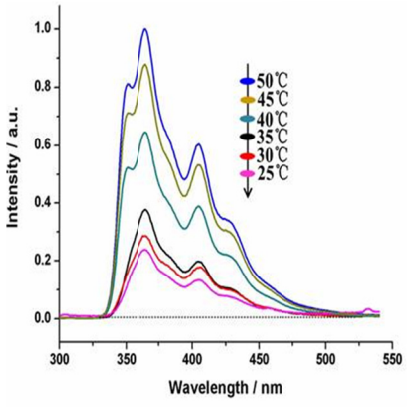
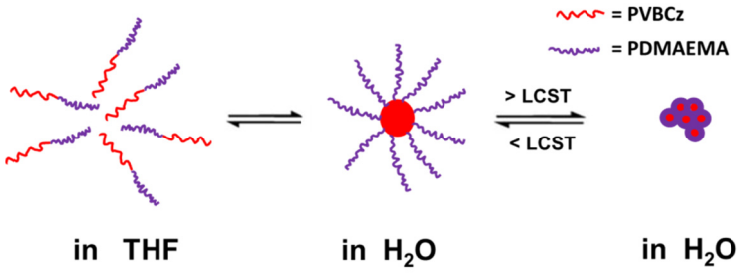


Figure 9. The fluorescence spectra of PVBCz-*b*-PDMAEMA in aqueous solution with variable temperature. The concentration of the sample was 1 mg/mL. The excitation wavelength was 280 nm.

3.4. Structure−property relationship

The mechanism of the unique optical properties of PVBCz-*b*-PDMAEMA is given in scheme 3. For linear conjugated polymers, the FL emission can be quenched by the π−π stacking of the conjugated segments during self-assembly easily (so-called "aggregation-caused quenching" (ACQ)) [21, 22]. In the THF solution, both polymer chains kept coiled. As the water fraction increased, the PVBCz chains aggregated to form solid-like cores while the PDMAEMA segments formed the shell. The FL intensity

decreased due to the aggregation of PVBCz. As the temperature rose, the PDMAEMA chains also collapsed from coil to globule. The PVBCz cores were well wrapped in the interior of the micelles by PDMAEMA. Therefore, the aggregation of PVBCz cores was prevented effectually by the PDMAEMA shell, which is the reason why the FL intensity increased when the temperature was above the LCST.



Scheme 3.

4. Conclusions

In this work, the functional polymers PVBCz and PVBCz-*b*-PDMAEMA were prepared via homopolymerization of 9-(4-vinylbenzyl)-9H-carbazole (VBCz) and copolymerization with DMAEMA initiated by macro-initiator PVBCz-Br, respectively. The controlled features of ATRP homopolymerization were confirmed by the kinetic study. The resulting PVBCz and PVBCz-*b*-PDMAEMA in the THF solution both exhibited fluorescence emission mainly at 350-400nm (λex=280 nm). The fluorescent intensity of PVBCz-*b*-PDMAEMA in the THF/water mixture solution decreased as the water fraction increased. The fluorescent intensity of PVBCz-*b*-PDMAEMA in the aqueous solution increased as the temperature rose to the LCST of the polymer, which could be attributed to the coupling of two different functional segments. Future work will focus on the self-assembly of the copolymers. Morphologic study is ongoing.

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