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# Synthesis and photoluminescent property of star polymers with carbzole pendent and a zinc porphyrin core by ATRP

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### ABSTRACT

Styrene-type monomer 9-(4-vinylbenzyl)-9H-carbazole (VBCz) and methacrylate-type monomer 2-(9Hcarbazole-9-yl)-ethyl methacrylate (CzEMA) were polymerized to star polymers respectively via atom transfer radical polymerization (ATRP) using zinc 5,10,15,20-tetrakis(4-(2-methyl-2-bromopropoxy) phenyl) porphyrin as an initiator. The emission spectra of two star polymers (star poly(VBCz) and star poly(CzEMA)) in the solid state displayed red light emission, while those of two monomers showed blue light emission. The result demonstrates that effective energy transfer occurs from the carbazole to the Zn porphyrin core. However, two star polymers in DMF solution emit week red light and strong UV light at 350–400 nm, it points that energy transfer cannot occur from the carbazole to the Zn porphyrin core effectively. They exhibit good thermal stability with  $T_{d poly(VBCz)} = 374 \text{ °C}$  and  $T_{d poly(CzEMA)} = 297 \text{ °C}$ at 5% weight loss. The DSC curves show that the glass transition temperature of styrene-type  $(T_{g \text{ poly}(VBCz)} = 177 \text{ °C})$  was better than that of methacrylate-type  $(T_{g \text{ poly}(CzEMA)} = 148 \text{ °C})$ .

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## 1. Introduction

Much attention has been paid to star-shaped derivatives and dendrimers from porphyrin and metal porphyrin owing to their special chemical and physical features relevant in various fields such as red light-emitting dyes [1–7], light harvesting materials [8], hemoprotein mimic and dioxygen binding [9,10], photodynamic therapy [11], and oxidation catalysis [12]. A variety of dendrimers built from porphyrin subunits have been reported [13–20]. Their regularly layered and symmetrically branched three-dimensional architecture and accurately controlled placement of functionalities made them useful in either photochemically, electrochemically, or catalytically active [16,20]. As its analogs, star polymers have recently received particular attention due to less synthetic steps and many end group functionalities within a single molecule. which are helpful for various applications. The synthesis of star polymers from porphyrin has been successful by polymerization of an epoxide system [21,22], ring opening polymerization [23-28], Suzuki polycondensation [29] and controlled radical polymerization (CRP) [30,31]. Atom transfer radical polymerization (ATRP), one of the most powerful CRP techniques [32-34], has been successfully used to prepare star polymers with a controlled architecture, narrow molecular weight distribution, and high chain-end functionality that allows further chemical modifications via one of three strategies: (i) "core-first" (ii) "arm-first" and (iii) "coupling onto" [35–37]. In the "core-first" strategy, a multifunctional initiator is used to initiate the monomers to obtain multiarm star polymers. Holder et al. first reported that well-defined fourarm star polymer of styrene and alkyl (meth)acrylates could be synthesized from tetrabromo porphyrin-based initiators via ATRP and the coordination of zinc ion and porphyrin initiator could avoid copper ion as catalyst into porphyrin in star polymers [31].

In addition, it is well-known that carbazole is electron-donor group and attaching a carbazole moiety to the molecular scaffold can significantly enhance the thermal stability and HOMO energy level of light-emitting polymers [38]. The doping of fluorescent red dye tetraphenylporphyrin into the blue light-emitting polymer can provides efficient transfer of energy from blue to red [39]. For efficient Förster energy transfer to the dopant, the spectral overlap between the photoluminescence band of the host material and the absorption band of the dopant is indispensable [40]. However, the emission peak of chromophore in solid state compared to in dilute solution may appear red-shifted in a certain degree [41].

To the best of our knowledge, only a few literatures have been found on the properties and functions of the well-defined energy donor-acceptor star polymers [2,24]. In the present work, we report the synthesis of two red light-emitting star polymers



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together with their absorption spectra, fluorescent spectra and thermal properties. Two star polymers were prepared using zinc 5,10,15,20-tetrakis (4-(2-methyl-2-bromo-propoxy) phenyl) porphyrin as initiator, 9-(4-vinylbenzyl)-9H-carbazole (styrenetype) and 2-(9H-carbazole-9-yl)-ethyl methacrylate (methacrylatetype) as monomer, respectively, via ATRP. To better understand the fluorescent properties of two star polymers and the energy transfer from carbazole to zinc porphyrin, the fluorescent spectra of star polymers and the monomers both in solid state and in solution were investigated.

## 2. Experimental section

### 2.1. Materials

4-Chloromethyl styrene was purchased from Sinopharm and passed through a short column of alumina to remove inhibitors prior to use, and was finally purified by distillation in vacuum. Copper(I) bromide (CuBr) (CP, Sinopharm) was agitated in acetic acid, filtered, washed with ethanol absolute, and dried in vacuum. 1,1,4,7,7-Pentamethyldiethylenetriamine, PMDETA (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuum. Cyclohexanone (AR, Sinopharm) was dried with magnesium sulfate overnight and distilled in vacuum. Other reagents were supplied as analytic pure and were used without further purification.

### 2.2. Instruments and methods

<sup>1</sup>H NMR spectra were measured on INOVA 400 MHz NMR or Bruker AV 500 MHz spectrometers at ambient temperature, using CDCl<sub>3</sub> as solvent. Element analyses were obtained with a Carlo Erba-MOD1106 instrument. UV–vis absorption spectra were recorded with a Shimadzu UV-3150 spectrometer. Monomer conversion was determined by gravimetry, molecular weight and the polydispersity relative to polystyrene was measured using a Waters1515 GPC with THF as eluent and a column temperature of 30 °C. Room temperature emission and excitation spectra were recorded using an Edinburgh-920 fluorescence spectrophotometer. The thermal gravimetric analysis (TGA, 2960 SDT V3.0F, TA Instruments) and differential scanning calorimetry (DSC, 2010DSC V4.4E, TA Instruments) measurements were carried out under a nitrogen atmosphere at a heating rate of 20 °C/min.

### 2.3. Tetrafunctional porphyrin initiator

5,10,15,20-Tetrakis(4-(2-methyl-2-bromopropoxy) phenyl)-21*H*, 23*H*-porphine was prepared according to the literature recipe [31] and the following parameters were obtained: Purple powder yield 90% from 5,10,15,20-tetrakis(4-hydroxyl phenyl)-21*H*, 23*H*-porphine. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) –2.82 (s, 2H, N–H), 2.24 (s, 24H, C(CH<sub>3</sub>)<sub>2</sub>Br), 7.56–7.58 (d, 8H, *J* = 8.0Hz, Ar–H), 8.24–8.26 (d, 8H, *J* = 8.0Hz, Ar–H), 8.88 (s, 8H, pyrrole–H). Anal. Calcd for C<sub>60</sub>H<sub>50</sub>Br<sub>4</sub>N<sub>4</sub>O<sub>8</sub>: C, 56.54; H, 3.95; N, 4.40. Found: C, 56.34; H, 3.89; N, 4.38. Absorption spectra data in CH<sub>2</sub>Cl<sub>2</sub>: 419, 516, 549, 588, 646 nm.

### 2.4. Tetrafunctional Zn porphyrin initiator

Zinc 5,10,15,20-tetrakis(4-(2-methyl-2-bromopropoxy) phenyl) porphyrin was synthesized by heating with 5,10,15,20-tetrakis(4-(2-methyl-2-bromopropoxy) phenyl)-21*H*,23*H*-porphine and ZnBr<sub>2</sub> in dichloromethane/methanol under reflux conditions for 4 h. After cooling to room temperature, the mixture was poured into methanol and the purple precipitate was filtered off, washed

with methanol and dried in vacuum. Characteristics were as follows: Purple powder yield 95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) 2.24 (s, 24H, C(CH<sub>3</sub>)<sub>2</sub>Br), 7.56–7.58 (d, 8H, *J* = 8.5Hz, Ar–H), 8.24–8.26 (d, 8H, *J* = 8.5Hz, Ar–H), 8.98 (s, 8H, pyrrole–H). Anal. Calcd for C<sub>60</sub>H<sub>50</sub>Br<sub>4</sub>N<sub>4</sub>O<sub>8</sub>Zn: C, 53.86; H, 3.62; N, 4.19. Found: C, 53.45; H, 3.59; N, 4.16. Absorption spectra data in CH<sub>2</sub>Cl<sub>2</sub>: 425, 554, 596 nm.

### 2.5. Synthesis of the monomers pendant carbazole [42]

### 2.5.1. Preparation of 9-(4-vinylbenzyl)-9H-carbazole (VBCz)

A mixture of carbazole (4.17 g, 25.0 mmol), potassium hydroxide (2.10 g, 37.5 mmol), 4-vinyl benzyl chloride (4.18 g, 27.5 mmol) and hexadecyl trimethyl ammonium bromide (40 mg, 0.11 mmol) in THF 50 mL was stirred at 75 °C for 24 h. After cooling to room temperature, the mixture was poured into deionized water 500 mL and the resultant white precipitate was filtered off and dried in vacuum. The crude product was purified by recrystallization from acetone to yield 4.45 g (62.9%) of white crystals. Parameters were: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) 5.18–5.21 (d, 1H, vinyl), 5.51 (s, 2H, -CH<sub>2</sub>), 5.65–5.70 (d, 1H, vinyl), 6.59–6.69 (m, 1H, vinyl), 7.08–7.13 (d, 2H, Ar–H), 7.22–7.45 (m, 8H, Ar–H), 8.12–8.15 (d, 2H, Ar–H). Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.89; H, 5.87; N, 4.89.

# 2.5.2. Preparation of 2-(9H-carbazole-9-yl)-ethyl methacrylate (CzEMA)

2.5.2.1. 2-(9H-Carbazole-9-yl) ethanol. A mixture of carbazole (4.17 g, 25.0 mmol) and potassium hydroxide (2.10 g, 37.5 mmol) in DMF 50 mL was stirred for 1 h and chloroethanol (2.95 g, 37.5 mmol) was added in drops. After stirring for 12 h at room temperature, the mixture was poured into deionized water 500 mL and the resultant white precipitate was filtered off. The reactant was dissolved in aqueous alcohol (70%Vol) 20 mL and insoluble matter was removed by filtering. The filtrate was poured into deionized water 100 mL, and the white flocculent precipitate was filtered off and dried in vacuum. Yield 4.01 g (75.4%).

2.5.2.2. 2-(9H-Carbazole-9-yl)-ethyl methacrylate. Methacryloyl chloride (7.95 g, 40.0 mmol) was added dropwise into a solution of 2-(9H-carbazole-9-yl) ethanol (4.00 g, 19.0 mmol) in chloroform 50 mL and triethyl-amine (7.60 g, 75.0 mmol) at 0–5 °C and reacted for 12 h. The crude product was isolated by evaporating the solvent and purified twice by recrystallization from 95% alcohol to yield 4.34 g (82.1%) of the white crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) 1.80 (s, 3H, –CH<sub>3</sub>), 4.52–4.55 (t, 2H, –CH<sub>2</sub>), 4.61–4.64 (m, 2H, –CH<sub>2</sub>), 5.47–5.48 (m, 1H, vinyl), 5.93 (m, 1H, vinyl), 7.23–7.27 (m, 4H, Ar–H), 7.44–7.47 (m, 2H, Ar–H), 8.09–8.11 (m, 2H, Ar–H). Anal. Calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.21; H, 6.05; N, 4.99.

### 2.6. ATRP procedures

Zinc porphyrin initiator (13.4 mg,  $1.0 \times 10^{-5}$  mol), CuBr (5.8 mg  $4.0 \times 10^{-5}$  mol), PMDETA (13.8 mg,  $8.0 \times 10^{-5}$  mol), VBCz (2.27 g,  $8.0 \times 10^{-3}$  mol), and cyclohexanone (9.1 g,  $9.2 \times 10^{-2}$  mol) were mixed in a round-bottomed flask. The flask was sealed and cycled between vacuum and N<sub>2</sub> four times. The polymerization took place in 90 °C under N<sub>2</sub> atmosphere. Samples were taken at regular intervals for conversion and molecular weight analysis. The products were dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.5, v/v). The precipitate was filtered and dried under vacuum. The crude polymers were purified by Soxhlet extractor with ethanol to remove the starting monomers. Star poly(CZEMA) was carried out similar experimental procedure.

Polymerization condition: zinc porphyrin initiator (13.4 mg,  $1.0 \times 10^{-5}$  mol), CuBr (5.8 mg  $4.0 \times 10^{-5}$  mol), PMDETA (13.8 mg,  $8.0 \times 10^{-5}$  mol), CzEMA (2.23 g,  $8.0 \times 10^{-3}$  mol), and cyclohexanone(8.9 g,  $9.2 \times 10^{-2}$  mol), reaction temperature 45 °C and reaction time 2 h (Scheme 1).

### 3. Results and discussion

### 3.1. Characterization of ATRP initiator

Tetrafunctional zinc porphyrin initiator was obtained by metallization of the tetrafunctional porphyrin initiator with zinc bromide. Zinc porphyrin initiator was characterized by <sup>1</sup>H NMR spectroscopy, which showed no signal at chemical shift -2.82 ppm that was ascribed to the hydrogen (N–H) in the porphyrin ring. In addition, the chemical shift of the hydrogen (C–H) in the pyrrole ring changed from 8.88 ppm to 8.98 ppm due to zinc coordination. It confirmed that hydrogen (N–H) was substituted by zinc completely (Supplementary data).

### 3.2. ATRP from tetrafunctional Zn porphyrin initiator

Herein, ATRP was processed by using zinc 5,10,15,20-tetrakis (4-(2-methyl- 2-bromopropoxy) phenyl) porphyrin as initiator, CuBr/ PMDETA as a catalyst system, and cyclohexanone as a solvent. We selected proper ratio of polymerization is that: [monomer]/[initiator]/[CuBr]/[PMDETA] = 800:1:4:8, cyclohexanone = 80 wt %. VBCz polymerized at 90 °C and CzEMA at 45 °C is according to typical ratio of ATRP of functional styrene-type and methacrylatetype monomers in our previous work [43] and keep a relatively low radical concentration. Gnanou has mentioned that the radical concentration can be kept low by using high ratio of monomer to initiator and stopping polymerization at lower conversions to prevent star-star termination [44].

The kinetic plots of polymerization of VBCz are presented in Fig. 1. The linearity of the semi-logarithmic plot of  $\ln([M]_0/[M])$  vs time indicates that the polymerization is first-order with respect to the monomer and that the concentration of the growing radicals remains constant. The number average molecular weights  $(M_n)$ 



Scheme 1. Synthesis of star poly(VBCz) and poly(CzEMA).





increased linearly with conversion. Size exclusion chromatographic (SEC) analysis of the star polymers was performed using refractive index detector. Overlay of molecular weight distribution plots of star poly(VBCz) and star poly(CzEMA) are shown in Fig. 2. As shown in Table 1, the polydispersity indexes (PDI) of star polymers are relatively narrow ( $M_w/M_n = 1.09-1.32$ ). All of these results suggest a "living" polymerization process.

# 3.3. Characterization of star polymers

The <sup>1</sup>H NMR spectra of star poly(VBCz) and star poly(CzEMA) were illustrated in Fig. 3. For star poly(VBCz), broad peak at 0.97 ppm was assigned to the hydrogen ( $-CH_2$ ), signals at 1.55 ppm are assigned to the hydrogen ( $-CH_2$ ), broad peak at 4.88 ppm is assigned to the hydrogen ( $-CH_2$ ), and broad peaks at 6.02, 6.36, 7.02 and 7.98 ppm are assigned to the hydrogen (Ar-H). For star poly(CzEMA), broad peaks at 0.14 ppm are assigned to the hydrogen ( $-CH_3$ ), signals at 1.28 ppm are assigned to the hydrogen ( $-CH_2$ ), broad peaks at 3.95 and 4.16 ppm are assigned to the hydrogen ( $N-CH_2-CH_2-$ ), and broad peaks at 7.06, 7.22 and 7.90 ppm are assigned to the hydrogen in the vinyl group of monomers (5.2, 5.7 and 6.6 ppm for VBCz and 5.5 and 5.9 ppm for CzEMA) are absent in the <sup>1</sup>H NMR spectrometry of star



Fig. 2. Overlay of molecular weight distribution plots obtained by SEC illustrating distribution of star poly(VBCz) and poly(CzEMA).

polymers which indicate that the unconverted monomer had been removed entirely. Unfortunately, the result of <sup>1</sup>H NMR analysis of star polymers is hard to do calculations of molecular weights via porphyrin core analysis, because the signal at 8.98 ppm from the hydrogen in the pyrrole ring for star poly(VBCz) ( $M_n = 7600$  g/mol) was obscure and no signal at 8.98 ppm for star poly(CzEMA) ( $M_n = 9300$  g/mol) was observed. (Expansion of <sup>1</sup>H NMR spectra was given in Supplementary data.) We conjecture that the signal was completely obscured by the polymer chains.

Table 1

Monomer, reaction time, molecular weight parameters and monomer conversion of the star polymers made by ATRP.

Monomer	Time (h)	Conversion (%)	M <sub>n, GPC</sub>	$M_w/M_n$
VBCz	1	3.4	7600	1.12
VBCz	2	5.1	9200	1.09
VBCz	3	7.3	15,800	1.18
VBCz	4	8.7	17,900	1.23
VBCz	5	11.7	24,700	1.25
VBCz	6	14.1	30,100	1.20
VBCz	7	15.3	32,900	1.24
CzEMA	2	5.4	9300	1.32



**Fig. 3.** <sup>1</sup>H NMR spectra of star poly(VBCz) ( $M_n = 7600$  g/mol) and poly(CzEMA) ( $M_n = 9300$  g/mol) with CDCl<sub>3</sub> as solvent (400 MHz).

### 3.4. Absorption spectra

In Fig. 4, absorption spectra of two star polymers in DMF solution exhibit similar absorption pattern, in which two bands appear at 280–350 nm, an inferior intense Soret band at 427 nm, and two



**Fig. 4.** Absorption spectra of the star poly(VBCz) ( $M_n = 7600 \text{ g/mol}$ ) and star poly(-CzEMA) ( $M_n = 9300 \text{ g/mol}$ ) in DMF solution. The inset is a locally enlarged graph.

weak Q bands at around 560 and 600 nm. The bands in the UV region are ascribed to carbazole group absorption, whereas the bands in the visible are associated with Zn porphyrin absorption. The Soret band is attributed to the singlet state, whereas the Q band originates from the spin-triplet excited state.

### 3.5. Fluorescent properties

With excitation at 345 nm in DMF solution, the emission maximum of the carbazole chromophore of the monomer is at 364 nm. However, the emission maximum of VBCz and CzEMA in the solid state are found to be at 420 and 409 nm respectively (figures were given in Supplementary data). Circa 50 nm redshifted may be caused by  $\pi - \pi$  stacking interactions of carbazoles. Similar red-shifted of other chromophores in the solid state vs in solution has been reported in our recent work [41]. The fluorescent properties of the star poly(VBCz) and poly(CzEMA) were investigated both in solution and solid state. As shown in Fig. 5, in DMF solution with excitation at 345 nm, the carbazole unit emits strong fluorescence with two peaks at 353 and 366 nm, while the Zn porphyrin emits weak fluorescence with the intensity of the Q(0,0)peak at 607 nm and the Q(0,1) sideband at 658 nm. The weak fluorescence could be attributed to weak excitation of Zn porphyrin core. It should be mentioned that energy absorbed by the carbazole chromophore is not transferred to the Zn porphyrin core effectively. It indicates that the carbazole units of the star polymers are completely dispersed in the dilute solution and the  $\pi$ - $\pi$  stacking interactions may be weakened. Excitation bands of star poly(VBCz) and poly(CzEMA) in the solid state (figures were given in Supplementary data) are at 400–450 nm, overlap the emission bands of VBCz and CzEMA in the solid state. It indicates that energy absorbed by the carbazole chromophores can be transferred effectively to the Zn porphyrin core in the solid state because more carbazole units come into close proximity for fluorescent resonance energy transfer (FRET) to occur. As shown in Fig. 6, with excitation at 345 nm in solid state, two star polymers emit obviously strong red fluorescence with two peaks at 607 and 658 nm in visible region. The molecular weight influences the energy transfer efficiency, with lower molecular weight leading to higher efficiency. Generally, the porphyrin chromophore in the solid state can form aggregates that lead to fluorescence quenching. Our strategy ensures that the Zn porphyrin chromophores are completely wrapped by carbazole groups at the molecular level.



Fig. 5. Emission spectra of star poly(VBCz) ( $M_n$  = 9200 g/mol) and star poly(CzEMA) ( $M_n$  = 9300 g/mol) in DMF solution at  $\lambda_{ex}$  = 345 nm.



Fig. 6. Emission spectra of (a) star poly(VBCz) and (b) star poly(CzEMA) in the solid state.

### 3.6. Thermal stability

Thermal stability of Zn porphyrin-cored star poly(VBCz)  $(M_n = 9200 \text{ g/mol})$  and poly(CzEMA)  $(M_n = 9300 \text{ g/mol})$  were investigated by thermogravimetric analyses (TGA) from 20 to



Fig. 7. TGA trace of star poly(VBCz) ( $M_n = 9200$  g/mol) and star poly(CzEMA) ( $M_n = 9300$  g/mol).

600 °C and differential scanning calorimetry (DSC) from 20 to 300 °C. Star poly(CzEMA) exhibited less than 5% weight loss at 297 °C and star poly(VBCz) at 374 °C (in Fig. 7). The thermal stability of the styrene-type star polymer was superior to that of methacrylate-type due to existence of benzene ring. The glass transition was observed in the second heating scan of the DSC curves for the star polymers, with the glass state temperatures for star poly(CzEMA) and poly(VBCz) being 148 °C and 177 °C respectively. The  $T_g$  of star poly(VBCz) is higher than that of star poly(CzEMA), which can presumably be attributed to the rigid molecular structure. The  $T_g$  for homopoly(CzEMA) ( $M_n = 20900 \text{ g/}$ mol, PDI = 3.01) was 131 °C [42], the  $T_g$  of star poly(CzEMA) was higher than that of homopoly(CzEMA). High  $T_g$  and  $T_d$  are important requisites for light-emitting materials.

### 4. Conclusion

ATRP of two type monomers containing a carbazole group using zinc 5,10,15,20-tetrakis (4-(2-methyl-2-bromopropoxy) phenyl) porphyrin as an initiator enable star poly(VBCz) and poly(CzEMA) with controlled molecular weights and narrow polydispersity index. The content of Zn porphyrin in the star polymers can be regulated by the arm length. Star polymers exhibit good thermal stability and their red light emission in the solid state due to the effective energy transfer. Furthermore, the flexible arms of star polymers can effectively hinder  $\pi - \pi$  interaction of porphyrin cores and prevent aggregation which would lead to fluorescent self-quenching in the solid state. All above points support that Zn porphyrin-cored star polymers will be promising in red-light-emitting materials for optical devices.

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## Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.07.025.

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