Synthesis and properties of well-defined carbazole-containing fluorescent star polymers of different arms

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Abstract: A series of fluorescent carbazole-containing star polymers with different arms were successfully synthesized using 9-(4-vinylbenzyl)9H-carbazole (VBCz) as monomer and multifunctional bromide as initiators via atom transfer radical polymerization (ATRP). The effect of the poly(9-(4-vinylbenzyl)-9H-carbazole) (PVBCz) star polymer architecture on their optical and electrochemical properties was investigated. All of the PVBCz star polymers absorbed light in the range of 280–360 nm both in solution and as polymer films. Meanwhile, the star polymers exhibited maximum fluorescent emission at 350 nm in solution, while at 406 nm as films. Moreover, the star polymers with different arm numbers showed different photoluminescence quantum efficiency and highest and lowest occupied molecular orbital (HOMO, LOMO, respectively) energy levels. It is proved that the PVBCz star polymers exhibited different photoelectronic properties by varying the molecular architectures.

Keywords: atom transfer radical polymerization (ATRP); carbazole; fluorescence; star polymer; 9-(4-vinylbenzyl)-9H-carbazole (VBCz).

1 Introduction

Due to the unique mechanical, viscoelastic and crystalline properties caused by the unique branching architectures (1–3), star polymers have been intensively investigated on the morphologies, properties and functions by varying polymeric arm types, arm numbers, and arm lengths (4, 5). The well-defined branching architectures afford a better-knit structure and higher density of segment compared with linear polymeric counterparts (6, 7), which are of remarkable importance to be applied in diversified fields including nano-medicine (8, 9), catalyst carriers (10) and photonics (11). Star polymers containing carbazole rings possess diverse unique properties, including fluorescence, high hole and current carrier transporting abilities, and some other photoconductive features (12–14) resulting from their particular molecular structure with large π-conjugated systems and strong intramolecular charge transfer. Thus the series of polymers have attracted plenty of scientific and industrial interest. Moreover, carbazole-containing star polymers belong to potential organic photoelectric and photovoltaic functional materials possessing wide developing prospect (15).

Previously, star polymers with well-defined molecular architectures and weight could only be obtained via living anionic polymerization (16). However, this method requires very harsh reaction conditions and strict polymerization procedures (16). In the last decade, with the rapid development and maturing of living radical polymerization (LRP) techniques, for instance, atom transfer radical polymerization (ATRP) (17), reversible addition-fragmentation chain transfer (RAFT) polymerization (18), and nitroxide-mediated stable free-radical polymerization (NMP) (19), the synthetic method of star polymers has been significantly simplified. ATRP, which is considered to combine the best of living polymerization and conventional free-radical polymerization, has greatly facilitated the synthesis of a series of peculiar macromolecular architectures, including graft, comb and block copolymers, star and dendritic, even hyperbranched polymers with preset and relatively uniform molecular weights and diverse functional groups (20). The strategies of synthesizing star polymers via ATRP can be roughly divided into the following three categories (21): (i) “core-first” method by germinating polymer arms from the initial multifunctional core; (ii) “coupling-onto” strategy by coupling prepared linear polymer arms onto a multifunctional agent center; (iii) “arm-first” way by cross-linking prepared linear polymer arms onto a multifunctional agent center. Compared with the other two
approaches, the “core-first” strategy is the simplest and most efficient to synthesize star polymers with predetermined arm numbers and well-defined arm length (22–24). Poly(9-(4-vinylbenzyl)-9H-carbazole) (PVBCz) is a utility fluorescent polymer with specific electrochemical and photoelectric performance, which is expected to be used in multiple photoelectric applications. By employing VBCz as the monomer and 1, 2, 4, 6-arm multifunctional initiators, carbazole-containing star polymers with varied arm numbers and lengths were first obtained via ATRP through “core-first” approach in this work. The effect of these polymer architectures on their absorption, fluorescence, and electrochemical properties were studied in detail. To understand thoroughly the optical properties of the star PVBCz, the UV-vis absorption and fluorescence emission spectra of the star PVBCz both as spin-coated films and in solution were analyzed.

2 Experimental

2.1 Materials and methods

1-(Chloromethyl)-4-ethenyl-benzen with inhibitors was bought from J&K Chemical and Scientific Ltd. (China) as a bright yellow mixed liquor, which was passed through a short neutral alumina column to remove inhibitors, and finally purified by distillation under vacuum to give a colorless liquid. Purified copper(I) bromide (CuBr) (J&K, China, 98%) was obtained by continuous stirring with ethyl alcohol overnight, washing with ethanol, ether and acetone, and then drying under vacuum to give white powders. 

Cyclohexanone (AR, Sinopharm, Shanghai, China) was dried using magnesium sulfate overnight and distilled in a vacuum. Tetrahydrofuran (THF) (AR grade) was purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Anhydrous and oxygen-free THF was distilled under Hi-purity Ar from sodium sands and benzophenone ketyl. Triethylamine (TEA) (Sinopharm, Shanghai, China, AR grade) was purified by distillation from CaH2.

All reactions in this article were conducted under an inert atmosphere of oxygen-free nitrogen using standard Schlenk techniques unless specially stated. 1H, 13C-NMR spectra were measured on an Agilent 400/54 NMR instrument (USA). Element analyzes were performed on a PerkinElmer PE-2400-II analyzer (USA). Molecular weight and the polydispersity index (PDI) were measured on a Wyatt gel permeation chromatography (GPC) equipped with a Dawn Heleos-II detector (USA), using polystyrene as the standard samples for calibration. Fluorescence (FL) spectra were measured on a JY FL-3 spectrometer (HORIBA Jobin Yvon Ltd., France). Ultraviolet-visible absorption (UV-vis) spectra were recorded with a Hitachi U2810 spectrometer for solution samples, and a Hitachi U4100 spectrometer (Japan) for the film samples, respectively. Cyclic voltammetry was operated on a CHI660E electrochemical workstation (Chenhua Instruments Ins., Shanghai, China) with a scan rate of 50 mV/s at room temperature. Measurements were all conducted using a conventional three-electrode cell (A Pt wire as the counter electrode, Ag/AgCl as the reference electrode and glass carbon electrode coated with thin polymer films as the working electrode) in an anhydrous dichloromethane solution with (n-Bu)4NClO4 (0.1 M) as the supporting electrolyte. Ferrocene/ferrocenium (Fc/Fc+) redox couple was used to calibrate the Ag/AgCl electrode.

2.2 Synthesis of monomer (VBCz)

Monomer VBCz was synthesized referring to the previous literature (25). The reaction equation is shown as Scheme 1A, and the procedure has also been described in detail in our previous study (26).

2.3 Synthesis of initiators

Multifunctional initiators were synthesized according to the references (27–29).

2-Arm initiator Ethylene glycol (2.79, 50.0 mmol), TEA (171 ml, 120.0 mmol) were injected into a Schlenk flask along with anhydrous THF (100 ml) by syringe under argon. Cooling the mixture to -18°C, and 2-bromo-iso-butyl bromide (BiBB) (13.7 ml, 110.0 mmol) dissolved in anhydrous THF (40 ml) was added dropwise (Scheme 1B). The reaction solution was subjected to continuous stirring for 24 h at room temperature and then diluted with CH2Cl2. The resulting organic extracts were washed twice with 200 ml HCl (2 M), twice with 200 ml saturated NaHCO3, and twice with 200 ml saturated NaCl in turn. The solution was then dried with anhydrous MgSO4. The resultant mixture was filtered, concentrated, recrystallized from hot methanol and filtered to afford 13.9 g (yield: 77%) of 2-arm initiator as a colorless crystalline powder. 1H-NMR(CDCl3, 400 MHz): (δ, ppm) 1.94 (s, 12H, 4CH3), 4.44 (s, 4H, 2CH2). 13C-NMR(CDCl3, 100 MHz): (δ, ppm) 29.4 (4C Br), 62.0 (2C Br), 170.1 (2C=O).

4-Arm initiator The procedure was the same as the synthesis of the 2-arm initiator except that pentaerythritol (3.29 g, 24.2 mmol) was used instead of ethylene glycol. TEA (15.2 ml, 108.7 mmol), anhydrous THF (100 ml) and BiBB (13.5 ml, 110.0 mmol) in 40 ml anhydrous THF was added sequentially (Scheme 1B). This procedure afforded...
11.5 g (yield: 65%) of 4-arm initiator as a colorless crystalline powder. $^1$H-NMR(CDCl$_3$, 400 MHz, $\delta$, ppm): 1.88 (s, 24H, 8CH$_3$), 4.27 (s, 8H, 4CH$_2$). $^{13}$C-NMR(CDCl$_3$, 100 MHz): ($\delta$, ppm) 29.7 (8CH$_3$), 42.9 (C(CH$_2$)$_4$O), 54.3 (4Br), 61.8 (4CH$_2$O), 169.8 (4C=O).

6-Arm initiator Dipentaerythritol (2.20 g, 7.85 mmol) used instead of ethylene glycol was the only difference in this procedure from that discussed in the previous section. TEA (10.0 ml, 71.5 mmol), anhydrous THF (100 ml) and BiBB (8.8 ml, 70.9 mmol) in 20 ml anhydrous THF was added sequentially in this reaction (Scheme 1B). This procedure afforded 5.1 g (yield: 52%) of 6-arm initiator as a colorless crystalline powder. $^1$H-NMR(CDCl$_3$, 400 MHz): ($\delta$, ppm) 1.94 (s, 36H, 12CH$_3$), 3.60 (s, 4H, CCH$_2$OCCH$_2$), 4.29 (s, 12H, 6CH$_2$O). $^{13}$C-NMR(CDCl$_3$, 100 MHz): ($\delta$, ppm) 30.6 (12CH$_3$), 43.9 (2C(CH$_2$)$_4$), 55.2 (6CB), 63.2 (6CH$_2$O), 69.3 (CH$_2$OCH$_2$), 170.6 (6C=O).

### 2.4 ATRP procedure of VBCz

A typical ATRP (30) was carried out to synthesize 1-arm PVBCz. We have described the polymerization process in detail in the previous study (26). (The ATRP procedure can give 1.85 g of 1-arm PVBCz with a yield of 81%.) The 2-, 4-, 6-arm PVBCz were prepared using the same procedure of the 1-arm PVBCz with the exception that 2-, 4-, 6-arm initiators were used in place of EBIB, and the yield was 79%, 72%, and 69%, respectively.

### 3 Results and discussion

#### 3.1 Preparation of the star polymers

PVBCz is a versatile fluorescent polymer with unique electrochemical properties that render it a widespread research interests in multiple photoelectric applications (31). The linear and cyclic PVBCz have been prepared and reported previously (26, 31, 32), but reports of the star PVBCz were exceedingly rare before. Inspired by this, we try to study the different photoelectric properties of star PVBCz with different arm numbers. Herein, we report the first example of a series of star PVBCz prepared via ATRP through the “core-first” approach using functional monomer VBCz and 1-, 2-, 4-, 6-arm multifunctional initiators. The feed ratios of the reagents are listed in Table 1. The ratio of VBCz to the initiator was kept the same while the ratio of CuBr and PMDETA was changed according to the number of active sites of the initiator.

The kinetic curve of the ATRP of 1-arm PVBCz is given as Figure 1A and B shows by the measured number-average molecular weights ($M_n$,GPC) and PDI as a function of monomer conversion. As demonstrated in our preceding article (26), the polymerization belongs to a first-order reaction and the radicals remain constant during the whole process of polymerization. Moreover, it is indicated that the ATRP of VBCz can be considered as a “living” polymerization process.

Figure 2A gives the $^1$H-NMR spectra of monomer and 1-arm PVBCz. It can be found that, after the polymerization, the characteristic peaks of the unsaturated C=H disappear from $\delta=5.20$ and 5.70 ppm. However, the emergence of peaks belonging to saturated C-H at $\delta=1.0-2.5$ ppm is

<table>
<thead>
<tr>
<th>Polymer</th>
<th>VBCz (mmol)</th>
<th>Initiator (mmol)</th>
<th>CuBr (mmol)</th>
<th>PMDETA (mmol)</th>
<th>Solvent (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-arm PVBCz</td>
<td>8.0</td>
<td>0.08</td>
<td>0.08</td>
<td>0.16</td>
<td>10</td>
</tr>
<tr>
<td>2-arm PVBCz</td>
<td>8.0</td>
<td>0.08</td>
<td>0.16</td>
<td>0.32</td>
<td>10</td>
</tr>
<tr>
<td>4-arm PVBCz</td>
<td>8.0</td>
<td>0.08</td>
<td>0.32</td>
<td>0.64</td>
<td>10</td>
</tr>
<tr>
<td>6-arm PVBCz</td>
<td>8.0</td>
<td>0.08</td>
<td>0.48</td>
<td>0.96</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 1: The kinetic curve (A) and Plots of $M_n$GPC, $M_n$ and PD vs. monomer conversion (B) of the ATRP of 1-arm PVBCz.

Figure 2: $^1$H-NMR spectra of VBCz and 1-arm PVBCz (A), the PVBCz star polymers (B).

Figure 3: GPC traces of the PVBCz star polymers.

noticeable. Figure 2B gives the $^1$H-NMR spectra of PVBCz star polymers, indicating that the PVBCz star polymers obtained have the similar molecule architectures. Due to the existence of a long polymeric chain, the characteristic proton signals of multifunctional initiators (core) could not be found in these spectra.

Figure 3 gives the GPC traces of all the star polymers. Meanwhile, the molecular weight parameters of the star polymers are listed in Table 2. The PDI of the PVBCz star polymers are relatively low (1.31~1.41). The DP is close to the feed ratio, which equals the theoretical DP of the resulting polymers. However, the molecular weights are enlarged with the increment of polymer arm numbers, indicating decrement of conversion of the initiator.

3.2 UV-vis absorption properties of the star polymers

Carbazole, VBCz and 1-arm PVBCz exhibit maximum UV-vis absorption at about 300 nm in THF solution, which could be ascribed to the $\pi-\pi^*$ transition of the aromatic chromophores, including carbazole units and benzene rings (32). Additionally, the spectra show two relatively
small peaks at around 330 nm and 345 nm, the characteristic absorption peak of carbazole molecules (33). The absorption peaks of VBCz appeared at 293 nm, 328 nm and 342 nm, which are relatively longer compared with those of carbazole. The slight red-shift of the absorption peaks of VBCz is probably caused by the introduction of 4-vinylbenzyl to 9-N of carbazole. Moreover, the absorption peaks of 1-arm PVBCz also appear at relatively longer wavelength compared with peaks of the monomer VBCz, which could be considered as a result of the interaction of adjacent chromophores (mainly aromatic rings) in the polymer chains (34).

The resulting star polymers were characterized to investigate their optical properties. Figure 4A and B show the UV-vis absorption spectra of the star polymers both in THF solution and as spin-coated films, respectively. The PVBCz star polymers with different molecular architectures exhibit almost the same UV-vis absorption in both THF solution and film. However, the UV-vis absorption peaks of star polymer films exhibited slight red-shift

Table 3: Optical properties of VBCz and the PVBCz star polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{abs}$ (nm) in THF</th>
<th>$\lambda_{abs}$ (nm) polymer film</th>
<th>$\lambda_{onset}$ (nm)</th>
<th>$\lambda_{em}$ (nm) in THF</th>
<th>$\Phi$ (%)</th>
<th>$\lambda_{em}$ (nm) polymer film</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBCz</td>
<td>293, 328, 342</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-arm PVBCz</td>
<td>295, 330, 344</td>
<td>298, 332, 345</td>
<td>359</td>
<td>351, 366</td>
<td>40.2</td>
<td>380, 406, 428</td>
</tr>
<tr>
<td>2-arm PVBCz</td>
<td>295, 330, 344</td>
<td>298, 332, 345</td>
<td>359</td>
<td>351, 366</td>
<td>39.8</td>
<td>379, 406, 428</td>
</tr>
<tr>
<td>4-arm PVBCz</td>
<td>295, 330, 344</td>
<td>298, 332, 345</td>
<td>359</td>
<td>351, 366</td>
<td>34.7</td>
<td>370, 406, 429</td>
</tr>
<tr>
<td>6-arm PVBCz</td>
<td>295, 330, 344</td>
<td>298, 332, 345</td>
<td>359</td>
<td>351, 366</td>
<td>33.9</td>
<td>380, 406, 427</td>
</tr>
</tbody>
</table>

Figure 4: UV-vis absorption spectra of PVBCz star polymers (A) in THF solution ($1 \times 10^{-5}$ m) and (B) polymer film.

Figure 5: The fluorescence spectra of the PVBCz star polymers (A) in THF solution (the concentration of carbazole units: $1 \times 10^{-5}$ m) and (B) polymer film. The excitation wavelength was 292 nm.
compared with those in THF solution. This phenomenon could arise from the closer molecular packing and more ordered molecular arrangement in the spin-coated films (35). The interaction of adjacent molecules in polymer chains was stronger as films than in solution. The results are listed in Table 3.

3.3 Fluorescent properties of the star polymers

The fluorescent properties of the PVBCz star polymer film and THF solution were investigated with an excitation at 292 nm. The spectra and parameters are shown in Figure 5 and listed in Table 3. It can be found that the PVBCz star polymers exhibit strong fluorescent emission in solution and film. Specifically, the maximum emission of VBCz is at 349 nm and 365 nm in THF solution. The fluorescent emission of the star polymers exhibit a slight red-shift compared with that of VBCz, which is a result of the interaction of neighboring chromophores in the polymer chains (34). Meanwhile, the maximum emission of the star polymers as film is found to be at 406 nm. The ~40 nm red shift may be due to π-π stacking interactions of VBCz in the solid state (36). The π-π stacking effect may be markedly weakened when dissolved in THF solution (37).

Photoluminescence quantum efficiency of VBCz and the star polymers in THF solution was also investigated, using quinine sulfate solution as standard (38). The calculated values of quantum efficiency for VBCz and the 1-, 2-, 4-, and 6-arm polymers are 43.1%, 40.2%, 39.8%, 34.7% and 33.9%, respectively. It is indicated that the quantum efficiency decreases from the monomer to the corresponding polymers, and decreases with the increment of the number of polymer arms, which may be due to the reduction of VBCz units in every arm of the star polymers. The results indicate that the star polymers and VBCz exhibit approximate fluorescent intensity when the concentration of carbazole moieties is kept the same. Although the quantum efficiency drops down, it is still acceptable.

3.4 Electrochemical properties of the star polymers

The HOMO energy level of the star PVBCz can be calculated by cyclic voltammetry (CV) via the equation of \( E_{\text{HOMO}} = - \left( E_{\text{onset}}^0 - E_{\text{CV}}^0 + 4.8 \right) \) eV (the value of the internal potential for VBCz) and the CV onset potential is from the cyclic voltammograms of the PVBCz star polymers coated on glass carbon electrode and Ag/AgCl as the reference electrode in CH\(_2\)Cl\(_2\) solution with 0.1 m \((n\text{-Bu})_4\text{NClO}_4\) as the supporting electrolyte operated at room temperature.

![Cyclic voltammograms of the PVBCz star polymers](image-url)
standard is -4.8 eV with the vacuum level as a benchmark) (39), where $E_{\text{ox}}$ is the onset potential for oxidation (40). $E_{\text{PC}}$ is the potential for oxidation of ferrocene vs. Ag/AgCl, the value of which was 0.60 V under the measurement condition. Thus, the lowest occupied molecular orbital (LUMO) energy level was available by calculating from the highest occupied molecular orbital (HOMO) value and band gap, which can be obtained from the UV absorption edge (onset wavelength). The spectra are shown in Figure 6, while the experimental and calculation results are summarized in Table 4.

The HOMO values of the star PVBCz range from 4.99 to 5.12 eV, while the LUMO from 1.53 to 1.67 eV. The star polymers possess high HOMO levels, so the energy barriers from the star polymers to ITO anodes ($W_F$ =5.0 eV) are narrow, leading to competent hole injection. This property enables them to be used potentially as luminescent hole transporting layer for photoelectronic devices (41). The results indicate that the star polymers possess higher HOMO and LUMO levels than their linear counterparts. Furthermore, 4-arm PVBCz has the highest HOMO and LUMO levels, which may owing to its excellent symmetry of molecular architecture. Therefore, it is proved that the HOMO and LUMO levels of the star PVBCz could be regulated by varying the molecular architectures.

### Table 4: Electrochemical properties and energy levels of the PVBCz star polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{\text{F}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-arm PVBCz</td>
<td>0.79</td>
<td>4.99</td>
<td>1.53</td>
<td>3.45</td>
</tr>
<tr>
<td>2-arm PVBCz</td>
<td>0.80</td>
<td>5.00</td>
<td>1.55</td>
<td>3.45</td>
</tr>
<tr>
<td>4-arm PVBCz</td>
<td>0.92</td>
<td>5.12</td>
<td>1.67</td>
<td>3.45</td>
</tr>
<tr>
<td>6-arm PVBCz</td>
<td>0.82</td>
<td>5.02</td>
<td>1.57</td>
<td>3.45</td>
</tr>
</tbody>
</table>

4 Conclusions

In this work, the fluorescent carbazole-containing star polymers were successfully prepared via ATRP of functional monomer VBCz initiated by 1-, 2-, 4-, 6-arm initiators. The effect of the PVBCz star polymer architecture on their optical and electrochemical properties was investigated. All of the resulting PVBCz star polymer absorb light in the range of 280–360 nm both in solution and as films. The maximum fluorescent emission of the PVBCz star polymers in solution exhibit ~40 nm red shift compared to them as films. As the absorption and emission mainly depend on the characteristic properties of monomer units and π–π stacking interaction of neighboring chromophores, the different macromolecular architectures of the star polymers do not contribute too much. However, the star polymers with different arm numbers show different photoluminescence quantum efficiency and HOMO, LUMO energy levels. Specifically, the star polymers possess higher HOMO and LUMO levels than their linear counterparts. The fluorescence and electrochemistry results indicate that the PVBCz star polymers are potential materials that can be used in photoelectronic devices. Future work will focus on the study on morphology, thermal and mechanical properties of the PVBCz star polymers.

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