Cyclic Polymers

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# Cyclic Polymers with Pendent Carbazole Units: Enhanced Fluorescence and Redox Behavior**

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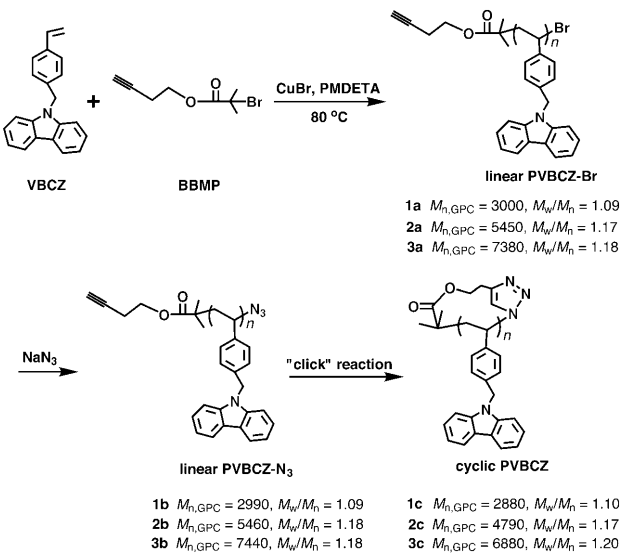
Cyclic polymers, which are also referred to as polymer rings or macrocycles, have specific properties that because of the absence of chain ends are in stark contrast to linear polymers, such as smaller hydrodynamic volume, reduced viscosity, larger refractive index, and higher glass transition temperature.[1] These unique properties of cyclic polymers have attracted extensive attention in macromolecular science in the last decades.[1b,h,2] To date, cyclic polymers that are based on homopolymers and copolymers and have various shapes, such as sun-shaped,[3] tadpole-shaped,[4] eight-shaped,[5] and θ-shaped[6] structures, have been extensively investigated. Moreover, cyclic polymers with functional monomers have also been designed and prepared. Among the strategies for preparation of cyclic polymers, α-alkyne–ω-azide click chemistry combined with living free radical polymerization (LFRP) was shown to be highly efficient and popular.[7] Liu et al.[8] and Winnik et al.[9] have reported the syntheses of cyclic poly(N-isopropylacrylamide) by LFRP and click chemistry, respectively. Very recently, Liu et al. reported the synthesis of cyclic block copolymers by selective click cyclization at a relatively high concentration.[10] However, cyclic topological polymers that bear functional mesogens have been underexplored to date because of the limited availability of well-defined linear precursors. The sole example was reported by Zhao et al. in which a liquid crystalline side chain with azobenzene as mesogen unit was introduced to a cyclic polymer.[11] These cyclic polymers with functional moieties have exhibited improved or unique properties compared with their linear precursors. Therefore, it is of great interest to design and fabricate cyclic topologic polymers with multifunctional moieties, and especially to investigate their topological effects on characteristic properties by comparing with linear counterparts.

Poly(4-vinylbenzyl-carbazole) (PVBCZ) is a versatile polymer with strong fluorescence and specific electrochemical properties[12] that render it particularly attractive for use in a variety of optoelectronic applications.[13] Inspired by this, cyclic PVBCZ is believed to significantly improve optoelectronic properties. Herein, we present the first example of a cyclic PVBCZ synthesized by the combination of atom transfer radical polymerization (ATRP) and a click reaction. The synthetic route to cyclic PVBCZ is depicted in Scheme 1.[4] The thermal properties, fluorescence, and redox behaviors of cyclic PVBCZ were investigated and compared with those of its linear precursor.




***Scheme 1.*** Routes to the synthesis of cyclic poly(4-vinylbenzyl)carbazole) (PVBCZ). PMDETA = pentamethyl diethylenetriamine.

Three series of PVBCZ with different molecular weights were synthesized to evaluate the diversity of our synthetic procedure and their properties with an increase in molecular weight. The successful preparation of cyclic polymers was verified by GPC, MALDI-TOF mass spectrometry, FTIR, and $^1$H NMR spectroscopy (Supporting Information, Figures S1–S4).

As a ring compound has fewer configurations compared to its open-chain counterpart, Di Marzio and Guttman[14] found that the configurational entropy $\Delta S$ of a cyclic system

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was always less than that of a linear system. According to the second law of thermodynamics, $\Delta G = \Delta H - T\Delta S$, the temperature must be lowered further in the linear system to reach $\Delta G = 0$. Briefly, the glass transition temperature, $T_g$, of cyclic systems is always higher than that of linear systems of an equal length.[14]

The $T_g$ of both cyclic PVBCZ and its linear precursor were determined by differential scanning calorimetry (DSC; Table 1). The results indicate that the $T_g$ of cyclic PVBCZ compounds are higher than the respective linear precursors. The difference $\Delta T_g$ between cyclic and linear polymer increases to as much as about 44 °C for a molecular weight of about 3000 g mol$^{-1}$. When the molecular weight reaches 5000 g mol$^{-1}$ and 7000 g mol$^{-1}$, $\Delta T_g$ between cyclic polymers and its linear form decreases to about 22 °C and about 11 °C, respectively. Based on the theories of Huggins[15] and of Gibbs and Di Marzio,[16] $T_g$ for linear polymers is higher with increasing molecular weight. However, for cyclic polymers, Di Marzio and Guttman[14] showed that the number of configurations in a small ring system were always less than that in a large ring system, which indicates that $T_g$ should become higher when decreasing the molecular weight. Thus, there is a larger $\Delta T_g$ between cyclic and linear polymers with lower molecular weights.

***Table 1:*** $T_g$ data for cyclic and linear PVBCZ.[a]

| Sample | $M_n$[b] | $T_g$ [°C] | $\Delta T_g$ [°C][c] |
|---|---|---|---|
| **1b** | 2990 | 116.3 | 43.9 |
| **1c** | 2880 | 160.2 | |
| **2b** | 5490 | 138.5 | 21.8 |
| **2c** | 4900 | 160.3 | |
| **3b** | 7440 | 155.5 | 10.9 |
| **3c** | 6880 | 166.4 | |

[a] $T_g$: glass transition temperature. [b] Number average molar mass [g mol$^{-1}$] determined by GPC. [c] $\Delta T_g$: the difference between values of $T_g$ for cyclic and linear PVBCZ.

Another possible explanation for the $T_g$ values is the end-group effect.[17] The fact that the difference in $T_g$ between linear and cyclic chains decreases with increasing molecular weight implies that the end group had a strong effect on the linear chains. We compared the $T_g$ values of the linear chains before and after bromide was replaced by $N_3$. The results indicated that the $T_g$ values for PVBCZ-$N_3$ were uniformly larger than the corresponding PVBCZ-Br. Similarly, the difference in $T_g$ values between PVBCZ-Br and the corresponding PVBCZ-$N_3$ decreased with increasing molecular weight (Supporting Information, Table S2). This study thus provides a way to demonstrate end-group effects, and confirms current theories on the influence of end groups on $T_g$.

There are few reports on the fluorescence of cyclic polymers.[18] We were therefore interested in investigating the fluorescence of the cyclic and linear polymer. Most of the polymers containing carbazole groups showed intense fluorescence emission, and we recently reported the fluorescence property of linear PVBCZ.[12] Herein, the fluorescence spectra of the cyclic and the linear PVBCZs are shown in Figure 1. Identical fluorescence emission peaks were observed in both of the cyclic and linear PVBCZ. However, the emission intensities of these cyclic polymers were different from the linear polymers. The emission intensity dramatically enhanced if the linear polymers were converted into their cyclic analogues for the low-molecular-weight polymers (Figure 1 a).

It would be very interesting to explore the mechanism of the various emission behaviors for the cyclic PVBCZ with different molecular weights. Hogen-Esch et al.[18] observed that the emission intensity was enhanced when linear polystyrene (PS) transformed to cyclic PS; this result was interpreted by the conjugation effect between phenyl groups in adjacent units located at the same plane because of the restriction of topological structures. For cyclic PVBCZ, the bathochromic shift caused by conjugation in Hogen-Esch's case was not observed, and therefore the conjugation might not take place in this case. The restriction of intramolecular rotation (RIR) could explain the emission enhancement.[19] The RIR included two main channels: the restriction of distortion by main-chain topological structures (defined as the first channel of RIR) and the block effect between adjacent carbazole segments (defined as the second channel of RIR).

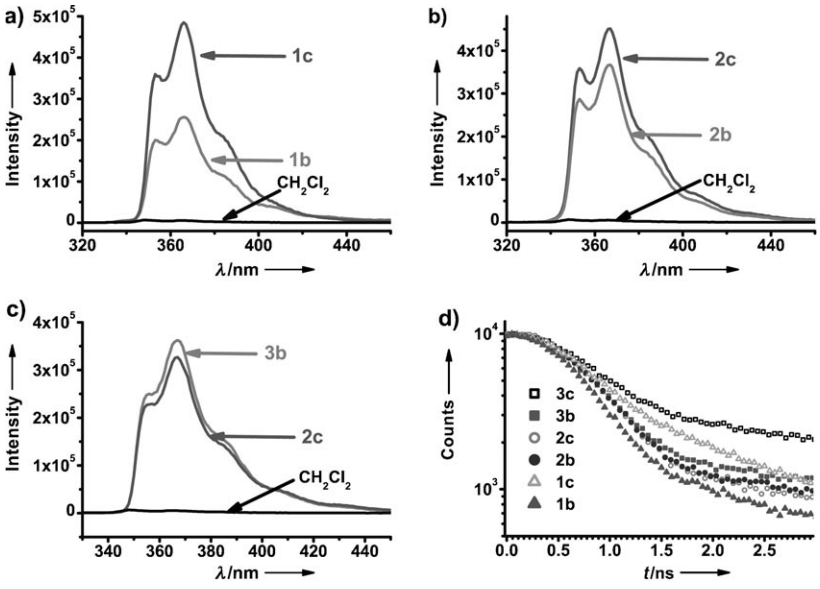


***Figure 1.*** The fluorescence emission spectra of cyclic and linear PVBCZ in $CH_2Cl_2$ (excitation wavelength at 314 nm). a) The concentration of **1b** and **1c** is $2.4\times10^{-2}$ g L$^{-1}$; **1b**: $M_{n,GPC}$ = 2990 g mol$^{-1}$, $M_w/M_n$ = 1.09; **1c**: $M_{n,GPC}$ = 2880 g mol$^{-1}$; $M_w/M_n$ = 1.10. b) The concentration of **2b** and **2c** is $2.3\times10^{-2}$ g L$^{-1}$; **2b**: $M_{n,GPC}$ = 5460 g mol$^{-1}$, $M_w/M_n$ = 1.18; **2c**: $M_{n,GPC}$ = 4790 g mol$^{-1}$, $M_w/M_n$ = 1.17. c) The concentration of **3b** and **3c** is $2.5\times10^{-2}$ g L$^{-1}$; **3b**: $M_{n,GPC}$ = 7440 g mol$^{-1}$, $M_w/M_n$ = 1.18; **3c**: $M_{n,GPC}$ = 6880 g mol$^{-1}$, $M_w/M_n$ = 1.20. d) Fluorescence lifetime decay for cyclic and linear PVBCZ measured at their fluorescence peak emission in $CH_2Cl_2$ of $2\times10^{-4}$ mol L$^{-1}$ (excitation wavelength at 380 nm).

  

The first channel of RIR was the major factor of the system with low molecular weights (series **1** in Scheme 1). The strong rigidity of the small rings led to carbazole groups being isolated, thus the distortion of adjacent carbazole segments was restricted. As the rigidity of the ring decreases with increasing molecular weight, when the restriction of distortion on the chain backbone decreased, the second channel of RIR was considered as the major factor for the system with large molecular weights (series **3** in Scheme 1). The lower hydrodynamic volume for cyclic PVBCZ made the carbazole groups between adjacent locations more compact than that of linear PVBCZ, and therefore the block effect dominated. The block effect led to an emission enhancement, while the self-quenching resulting from compact chain segments deteriorated fluorescence. The results in Figure 1 b,c confirm such hypotheses. The fluorescence of cyclic and linear PVBCZ with comparably large molecular weights did not show any intensity differences.

The fluorescence lifetime was measured to explore the restriction effect of the RIR on cyclic polymer. In Figure 1 d, the cyclic polymer displayed a slower fluorescence decay in comparison with its respective linear form, which further verifies the existence of the RIR in cyclic PVBCZ. As the excitation energy was limited by the restriction, it cannot relax from the twisting form, which resulted in a longer decay time for cyclic PVBCZ. For the system with low molecular weight (series **1** in Table 1), the restriction caused by the first channel of RIR was the dominant factor. With an increasing length of the main backbone of the polymers, the restriction of distortion caused by the rigidity of small rings decreased and entanglements between the main chains became easier. The effect of the second channel of RIR turned out to be the dominating factor. The polymer with a large molecular weight displayed a longer fluorescence lifetime than those of small polymers because the restriction effects of the block were strengthened by an increase of chain segments. Given that the cyclic polymer has a smaller volume compared with its respective linear form, both compact and obstruction effects between adjacent segments in cyclic PVBCZ were stronger than those of linear PVBCZ, which collectively led to the longer fluorescence lifetime in the cyclic polymer.

It has been reported that polymers containing the carbazole groups exhibit a redox response.[20] The reversible redox activities of cyclic PVBCZ and linear PVBCZ were estimated by cyclic voltammetry (CV) in $CH_2Cl_2$ (Supporting Information, Figure S5, Table S1). It was observed that $\Delta I_p$ vaules (the difference between anodic $I_{pa}$ and cathodic peak electric current $I_{pc}$) for the cyclic PVBCZ were larger than those of corresponding linear precursor, suggesting that the cyclic PVBCZ could have an efficient charge-transport site.[21] The electrochemical properties of cyclic PVBCZ is now being explored in detail.

In our present work, well-defined cyclic PVBCZ with pendent functional carbazole moieties was efficiently synthesized by successive ATRP and intramolecular end-to-end click cyclization. Cyclic PVBCZ exhibited unique properties in comparison with its linear form: a higher $T_g$, enhanced fluorescence with a longer fluorescence lifetime, and higher $\Delta I_p$. A lower molecular weight can induce a larger difference between cyclic PVBCZ and its linear precursor. Owing to its unique properties, cyclic PVBCZ may be a potential candidate for a charge injection/transport layer for organic electronic devices. Moreover, the remarkable enhanced fluorescence lifetime of cyclic polymers may aid in the rapid determination of the structure of cyclic polymers. The interesting finding of enhanced functions of cyclic polymer, especially at low molecular weights, may pave a new way to improve properties of functionalized polymers. Further investigations into this issue are currently ongoing.

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