Liquid crystal block copolymer micelles with aggregation-induced emission from corona chains

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Abstract. Aggregation-induced emission (AIE) is a very useful tool to study the self-assembly process of block copolymers. However, most of the studies have been focused on the AIE process of the micelle core block. In this study, a typical AIEgen tetraphenylethylene (TPE) was introduced into the corona-forming block of the liquid crystal diblock copolymer. Although the coronal chains were still soluble in solution and the TPE group content was very low, due to the highly crowded and stretched chains, there was significant fluorescence emission after micellization. This provides a new research direction for the AIE process of diblock polymers and is of great significance for the study of the star micelle models.

1. Introduction
In recent years, aggregation-induced emission (AIE) has been one of the important research topics in the fields of chemistry and materials science [1-3]. It has been used to detect many physical properties and visual monitoring of materials [4], biological probes [5], and cell imaging materials [6], etc. AIE luminous agents (AIEgens) usually show strong emission in a highly aggregated state, and emit weak emission light in a free state, due to the restriction on intramolecular motion in the former case [2]. This mechanism makes AIEgen extremely sensitive to changes in the molecular environment [7], allowing them to be used as fluorescent molecular probes [8]. Generally, polymer systems are difficult to characterize on a single chain scale, but the AIE process provides an excellent tool for studying the interactions between chains in polymer systems [9].

Many studies on block copolymers containing AIEgens have been reported, usually involving the partial incorporation of AIEgens into the core-form blocks. The core formed during block aggregation or micelleization is highly aggregated and thus emits fluorescence [10]. However, the assembly process and final morphology of this polymer will also be affected by additional bulky moities [11].

In this study, the classical AIE structure tetrastyrrene (TPE) moieties were randomly incorporated into the corona-forming block of the block copolymer by atom transfer radical polymerization (ATRP). The TPE content in the corona-forming block was low and dispersed evenly (each molecular chain contained one TPE on average). The polymer was thermodynamically stable and the molecular weight
was controllable. The polymer had obvious aggregation-induced emission under selective solvent environment.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and were used as received unless otherwise stated. The cholesteryl methacryloxy ethyl carbonate (CholMA) and the TPE-containing acrylate monomer (TPEA), was synthesized according to literatures [12, 13]. For the atom transfer radical polymerization (ATRP), cuprous bromide (99%, CuBr) was purified with acetic acid before use. All other solvents were used as received without further purification.

Figure 1. Synthetic routes of PtBA-1 and BCP-1.

2.2. Random copolymerization of tBA and TPEA

5 mL of dry toluene, TPEA (160 mg, 0.4 mmol), CuBr (2.9 mg, 0.02 mmol), PMDETA (3.5 mg, 0.02 mmol), EBiB (3.9 mg, 0.02 mmol) and tBA (512 mg, 4 mmol) were introduced into a Schlenk tube and degassed with three freeze–pump–thaw cycles. The solution was heated at 60 ℃ with vigorous stirring, and sample were taken from every two hours for 1H NMR experiments. The residual monomers ratios were obtained by comparing two peak integrations from the vinyl group of tBA and TPEA. The reactor conversions and the ratio of tBA and TPEA in polymers were also calculated based on these results. The exemplary 1H NMR spectrum for the initial moment of the reaction was shown in Figure 2 and the calculated results were summarized in Table 2.

2.3. Polymerization

2.3.1. P(tBA-r-TPEA) (PtBA-1). 1 mL dry toluene, TPEA (16 mg, 0.04 mmol), CuBr (2.9 mg, 0.02 mmol), PMDETA (3.5 mg, 0.02 mmol), EBiB (3.9 mg, 0.02mmol) and tBA (512 mg, 4 mmol) all these chemicals were introduced into a Schlenk tube and degassed with freeze–pump–thaw cycles for three times. The polymerization was reacted at 60 ℃ for 4 h under vacuum with vigorous stirring. The polymer solution was purified by Al2O3 and repeated precipitations 3 times from THF into mixture of methanol and water, and dried under reduced pressure without heated. White solid was obtained as final product (257 mg, yield 47 %).

2.3.2. Polymerization of P(tBA-r-TPEA)-b-PCholMA (BCP-1). 1.5 mL dry toluene and macroinitiator PtBA-1 (144 mg, 0.01 mmol), CuBr (1.5 mg, 0.01 mmol), CholMA (792 mg, 1.5mmol) and PMDETA (1.7 mg, 0.01 mmol) were introduced into a Schlenk tube and degassed with freeze–pump–thaw cycles for three times. The polymerization solution was heated at 80 ℃ for 3.5 h under a nitrogen atmosphere with vigorous stirring. The polymer was purified by Al2O3 and repeated precipitations from THF into methanol then dried at reduced pressure. White solid was obtained as final product (427 mg, yield 54 %).
3. Results and discussion

The diblock copolymers were synthesized via ATRP, as depicted in Figure 1, and their detailed characteristics are included in Figure 2-3 and Table 1. The TPE monomer was copolymerized with tert-butyl acrylate (tBA) to achieve a random corona-forming block. By using PtBA-1 as macro-initiator, the core forming block was synthesized by the cholesterol-containing methacrylate monomer (CholMA). The liquid crystal diblock copolymer BCP-1 (PtBA0.99-r-TPEA0.01)109-b-PCholMA84) was subsequently obtained.

### Table 1. Molecular characteristics of the PtBA-1 and BCP-1

| Sample | Mn (kDa) | Mw (kDa) | Mw / Mn | m | n |
|--------|----------|----------|---------|---|---|
| PtBA-1 | 15.8     | 14.4     | 1.10    | 109 | N.A. |
| BCP-1  | 68.7     | 58.7     | 1.17    | 109 | 84 |

*a: obtained from gel permeation chromatography (GPC);

*b: degree of polymerization (DP) of the PtBA-1, calculated by dividing the Mn of the by the molecular weight of tBA;

*c: DP of the PCholMA block, calculated from the DP of PtBA-1 and the Mn from GPC.

The degree of polymerization and molecular weight distribution were precisely controlled by the ATRP reaction. For the two blocks of PtBA and PCholMA, the degree of polymerization was controlled at around 100 and 85, respectively (as shown in Table 2). Considering that the molar ratio of TPEA is 1% during the synthesis of PtBA-1, the TPE moiety was randomly distributed in the first block, while BCP-1 contained one TPE moiety per chain.

![Figure 2](image)

Figure 2. 1H NMR spectrum of (a) the TPE-A monomer, (b) the PtBA-1, (c) the polymerization solution of tBA (90 mol%) and TPEA (10 mol%) at time 0 s, and (d) BCP-1.

In order to verify that the reaction activity of TPE-acrylate and tBA were similar, the peak integration of residual vinyl groups at different polymerization time was compared, by using the solvent toluene as an internal standard (from 1H NMR spectra). 10 mol% TPE was used to reduce the
system error and make the conclusion more accurate. However, it is worthy pointing out the content of TPEA would not influence the activity of the monomer and the random nature of the PrBA-1 copolymerization. The polymerization rate of tBA (90 mol%) and TPEA (10 mol%) was calculated by the peak integration (Table 2). A constant molar ratio of TPEA to tBA was obtained at different molecular weights, with the same conversion rates of the two monomers, indicating that TPEA had similar activities between tBA units, and the polymerization process proceeds randomly. Therefore, when the TPEA content in PrBA-1 was reduced to 1 mol%, it would be randomly distributed in the PrBA-1 block.

Table 2. Results from the $^1$H NMR characterization of the copolymerization experiment of tBA (90 mol%) and TPEA (10 mol%)

|          | 0h     | 1h     | 2h     | 4h     | 6h     | 8h     | 10h    | 14h    |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| Integration from tBA ($\times 10^{-2}$) | 10.68  | 10.62  | 10.20  | 9.66   | 9.36   | 9.11   | 9.04   | 8.73   |
| Conversion of tBA (%) | 0      | 0.56   | 4.50   | 9.55   | 12.36  | 14.70  | 15.36  | 18.26  |
| Integration from TPEA ($\times 10^{-2}$) | 1.16   | 1.15   | 1.10   | 1.05   | 1.02   | 0.98   | 0.97   | 0.95   |
| Conversion of TPEA (%) | 0      | 0.86   | 5.17   | 9.48   | 12.07  | 15.52  | 16.38  | 18.10  |
| % of TPEA in polymer$^a$ | 0      | 13.30  | 10.32  | 9.03   | 8.89   | 9.55   | 9.64   | 9.02   |

$^a$: calculated by the comparing the integration of residual TPEA and tBA monomers.

The liquid crystalline nature of second PCholMA block has been well established [14], and was characterized by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). PrBA homopolymer begins to thermally decompose above 200 °C, as shown in (Figure 3(a)) and there were two stages from the side chain to the main chain decomposition. The first stage of weight loss was 40% on the decomposition of ester bonds in tert-butyl groups. For the block copolymer that started to decompose at 230 °C, the ester bond from the side chain of PtBA broke and lost 10% weight, and then 60% weight loss with the decomposition of ester bonds in cholesterol ethyl methacrylate. From the DSC analysis results (Figure 3(b)), it showed that the glass transition temperature of the PtBA homopolymer was 52 °C, and the liquid crystal phase transition for the block polymer BCP-1 was 193 °C. The thermodynamic analysis showed that both polymers were stable.

The results of UV-visible absorption and PL spectra verified our hypothesis (Figure 4). Polymers PrBA-1 and BCP-1 had very similar UV-vis absorption spectra in the mixture solution of THF and n-BuOH (5:95, v / v). The BCP-1 solution had a broad peak around 310 nm absorption from TPE. It was obvious that the polymerization had no effect on the absorbance of TPE moieties. Although the fluorescence intensity of the PtBA polymer solution was negligible, the photoluminescence of the block polymer caused by micellization was significantly enhanced. It was because the TPE moieties were randomly distributed in the coronal layer at low density (1%), after the BCP-1 micellization. According to the classical physical model of star micelles [15], one end of the micelle coronal chain was bound to the surface of the liquid crystal core that made the PrBA chain stretching and very crowded, which reducing the movement and flexibility of the TPE group on the corona-forming blocks. As shown in the Figure 4(d), BCP-1 self-assembled into spherical micelles with a diameter of about 100-200 nm in the selective solvent. After the formation of micelles, the TPE groups on the PtBA chain was subjected to interchain interaction and had strong fluorescence emission.
4. Conclusion

In conclusion, we have synthesized a liquid crystalline diblock copolymer and introduced a very low AIE moieties content (1%) in the corona-forming blocks, which were distributed randomly in the corona. This random copolymerization process was verified by comparing the conversion rates of these two monomers during the polymerization reaction. And the block polymer synthesized by this method had a very narrow molecular weight distribution and stable thermodynamic properties. When the block copolymer formed micelles, the TPE moieties were stretched by the coronal chains, restricting the intramolecular motion. This induced luminescence without the spatial aggregation of AIEgens. Therefore, we believe that this study not only provides a novel and more direct method for the diblock copolymer star micelle model, but also provides some different insights into the application and mechanism of the AIE phenomenon.

Acknowledgments

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