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Article

Synthesis of Hyperbranched Poly(ε-caprolactone) Containing Terminal Azobenzene Structure via Combined Ring-Opening Polymerization and "Click" Chemistry

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Abstract: A novel well-defined linear poly(ε-caprolactone) (P1) containing terminal azobenzene and ethyne groups was successfully synthesized through tin-catalyzed ring-opening polymerization of ε-caprolactone in the presence of *N*,*N*′-bis(2-hydroxyethyl)-4-(3-ethynylphenylazo)aniline (BHA) in bulk. Subsequent reactions allowed the synthesis of the corresponding bromoester end-functionalized polymer (P2), which was converted into AB_2 type polymer (P3) containing terminal azide groups with NaN_3. Consequently, hyperbranched poly(ε-caprolactone) (HPCL) was prepared with AB_2 macromonomer (P3) by "click" chemistry under the catalysis of $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O. The structure of the resultant HPCL was characterized by gel permeation chromatography (GPC), proton nuclear magnetic resonance (^{1}H-NMR), ultraviolet-visible (UV-Vis) spectroscopy and fourier transform infrared spectroscopy (FT-IR). Thermal and crystallization properties of P1 and HPCL were further studied by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarised optical microscopy (POM). These results indicated that the crystallinity of HPCL was slightly lower than that of P1 due to the hyperbranched structure of HPCL. Additionally, the photo-induced *trans-cis* isomerization behaviors of BHA, P1 and HPCL containing terminal azobenzene were investigated in chloroform solution, and the photoisomerization rate constant (k_{exp}) of small molecule (BHA) was nearly three times faster than that of polymers P1 and HPCL, which was due to the sterically hindering effect of the polymer-chain configuration.

Keywords: hyperbranched polymer; "click" chemistry; photoresponsive behavior; ring-opening polymerization; poly(ε-caprolactone)

1. Introduction

In recent years, biodegradable aliphatic polyesters have attracted considerable research attention, and are widely applied in the specialty biomedical areas (such as drug delivery materials), as well as in the environmental and marine fields [1,2]. Poly(ε-caprolactone) (PCL), an aliphatic polyester synthesized through ring-opening polymerization, is also considered an ideal biodegradable material with flexibility and suitable biodegradability [3–5]. Meanwhile, the living ring-opening polymerization (ROP) technique of ε-caprolactone (CL) has been used to prepare various complex polymer structures, such as hyperbranched, block, star-shaped, and dendritic polymers [6–10].

In 1952, Flory [11] first presented hyperbranched polymers in theoretical work. Until 1988, the first example of this type of macromolecule was reported by Kim and Webster [12]. Since then, hyperbranched polymers have attracted much attention in polymer science owing their unique physical and chemical properties [13–15], such as less entanglement in the solid state, fast molecular motion and high solubility in various solvents. Compared with dendrimers obtained from step-by-step synthesis, hyperbranched polymers could be considered as irregular analogues of the dendrimers with narrow polydispersity and predictable molecular weights [16], Moreover, hyperbranched polymers can easily be synthesized by direct one-pot polymerization based on functional AB_x-type ($x \geq 2$) monomers [17,18], which were better suited for application in highly functionalized globular production. Recently, hyperbranched PCLs (HPCLs) have been increasingly studied, because a homologous series of HPCLs with a range of molecular architectural variations (*i.e.*, different lengths of linear backbone segments and different numbers of branching points) could be obtained by a series of novel synthetic approaches [19–21]. For instance, a series of HPCLs were synthesized through the moisture-sensitive catalyst-free polycondensation of AB_2 macromonomers, and Jeongsoo Choi *et al.* [22] investigated the thermal characteristics of HPCLs in conjunction with their branching features. In 2004, Jeongsoo Choi and his colleagues [23] conducted a detailed study on the crystallization behaviors of three HPCLs with different molecular architectures. However, few methods are available to synthesize HPCLs [19–23].

Recently, the Huisgen 1,3-dipolar cycloaddition between azide and alkyne to yield 1,2,3-triazole using a copper-catalyzed system [24] was named "click" chemistry. This concept of popular "click" chemistry had attracted much attention because of its high efficiency, quantitative yield and selectivity under mild reaction conditions [25–27]. This novel method had been successfully applied in the area of polymer materials with different topologic structures, including linear, block, and star-shaped polymers and dendrimers [28–34]. In very recent years, "click" chemistry has also been used for the synthesis of hyperbranched polytriazole through step-growth polymerization. Zhong'an Li and his co-workers [35] reported two new azobenzene hyperbranched polytriazoles from AB_2 monomers via "click" chemistry under copper(I) catalysis, and demonstrated excellent nonlinear optical properties (NLO). Qin *et al*. [36] synthesized hyperbranched polytriazoles by the polycycloaddition of diazide (A_2) and triyne (B_3) monomers, and succeeded in generating fluorescent images with different emission colors.

Moreover, azobenzene-terminated polymers have been applied to photochromic probes [37,38] due to their unique optical *trans-cis-trans* isomerization [39–41]. Crostoam Peptu *et al.* [42] prepared well defined poly(ε-caprolactone) (PCL) and polylactide (PLA) end capped with azobenzene by noncatalyzed ring-opening polymerization in the presence of Disperse Red 1 (DR1). Xiulin Zhu *et al.* also prepared well-defined azobenzene-terminated poly(methyl methacrylate) (PMMA) [43] poly(methyl acrylate) (PMA) and poly(styrene) (PS) [44,45] via living radical polymerization. However, there were few reports about light-responsive polymers containing only a middle azobenzene moiety [29,46,47].

Therefore, we proposed a new type of azobenzene functionalized HPCL prepared by "click" chemistry of AB_2 macromonomer (P3) containing terminal ethyne and azide groups. The azobenzene group was inside the HPCL chain, distinguishing this polymer from other azobenzene-terminated polymers. The structural characterizations of HPCL were provided by gel permeation chromatography (GPC), proton nuclear magnetic resonance (^{1}H-NMR), ultraviolet-visible (UV-Vis) spectroscopy and fourier transform infrared spectroscopy (FT-IR). Thermal and crystallization properties of linear PCL (LPCL) and HPCL were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD) and polarized optical microscopy (POM), which indicated that the hyperbranched structure of HPCL rendered crystallization more difficult than LPCL. Furthermore, owing to steric hindrance of the polymer-chain configuration, the photoisomerization rate constant (k_{exp}) of HPCL was much lower than that of the small molecule (BHA). This process could provide a useful alternative method for synthesizing a well-defined HPCL containing terminal functional group in the presence of a branch point.

2. Experimental Section

2.1. Materials

3-Ethynylaniline (≥98%; Sigma Aldrich: St. Louis, MO, USA), *N*-phenyldiethanolamine (≥95%; Fluka: Buchs, Switzerland), 2-bromopropiomyl bromide (98%; Sigma Aldrich: St Louis, MO, USA), tin 2-ethylhexanoate (96%; Alfa Aesar: Karlsruhe, Germany) and sodium azide (≥99.5%; Aldrich, Sigma Aldrich: St. Louis, MO, USA) were used as received. ε-Caprolactone (CL; Sigma Aldrich: St. Louis, MO, USA) was dried by distillation over calcium hydride. Concentrated HCl (37%), acetic acid (analytical reagent), sodium nitrite (analytical reagent), NaOH (analytical reagent), tetrahydrofuran (THF, analytical reagent), petroleum ether (boiling point: 60–90 °C), triethylamine (analytical reagent), dichloromethane (analytical reagent), Na_2CO_3 (analytical reagent), $MgSO_4$ (analytical reagent), DMF (analytical reagent), $CuSO_4 \cdot 5H_2O$ (analytical reagent), sodium ascorbatewere (analytical reagent) and methanol (analytical reagent) were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). THF, DMF and triethylamine were dried by distillation over sodium. Other reagents were purified using standard procedure before use.

2.2. Analysis and Characterizations

^{1}H-NMR and ^{13}C-NMR spectra of the polymers were recorded on an INOVA 300 MHz nuclear magnetic resonance (NMR, Varian: Palo Alto, CA, USA) instrument, using $CDCl_3$ as a solvent, tetramethylsilane (TMS) as the internal standard. Conversion of the reactants was determined using an HP-689 gas

chromatography (GC, Kexiao: Shanghai, China) equipped with an HP-5 column (30 m × 0.54 mm × 0.5 μm). The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were determined with a Waters 1515 gel permeation chromatograph (GPC: Milford, MA, USA) equipped with a refractive index detector, a Wyatt multi angle laser light scattering (MALLS, Santa Barbara, California, USA) and a Wyatt Visco Star viscometer detector (MALLS, Santa Barbara, California, USA) using HR1, HR3, and HR4 column with a molecular weight range of 100–500,000 calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL·min^{-1} operated at 30 °C. Elemental analysis of C, H, and N were conducted with an EA1110 CHNO-S (Carlo-Erba Co.: Cornaredo, Italy) instrument. The UV-vis spectra were determined on a Hitachi U-3900 spectrophotometer (Hitachi, Tokyo, Japan) at room temperature. Thermal analysis was performed by differential scanning calorimetry (DSC) using a TA instruments DSC2010 (TA, New Castle, DE, USA) with a heating/cooling rate of 10 °C·min^{-1} under a continuous nitrogen flow. FT-IR spectra were recorded on a Nicolette-6700 FT-IR spectrometer (Thermo Fisher, Madison, WI, USA). The XRD analysis was performed with a Rigaku D/max-γ rotation anode X-ray diffractometer (Rigaku, Woodlands, TX, USA), using graphite-monochromatized Cu K_α radiation sources (λ = 1.5406 Å). A scanning rate of 0.005 °/s was applied in the 2θ range of 0–60°. Polarized optical microscope (POM, Leica, Wetzlar, Hesse-Darmstadt, Germany) observation was performed on a Leica DM 4000M with a Leitz 350 hot stage.

2.3. Synthesis of N,N′-Bis(2-hydroxyethyl)-4-(3-ethynylphenylazo)aniline (BHA)

3-Ethynylaniline (1.17 g, 10 mmol) was added dropwise to a solution of concentrated HCl (37%, 3 mL) in deionized water (10 mL). The mixture was stirred in an ice bath to keep the reaction temperature at 0–5 °C. Then an aqueous solution (5 mL) of sodium nitrite (0.70 g, 10.1 mmol) was added within 5 min. The mixture was stirred at 0–5 °C for further 60 min. A yellow transparent diazonium salt solution was obtained. *N*-Phenyldiethanolamine (1.81 g, 10 mmol) was dissolved in acetic acid (5 mL) and deionized water (5 mL) at 0 °C, and then added dropwise to the reaction solution under vigorous stirring at 0–5 °C for 10 min. The pH value of the reaction system was then adjust to pH 5–6 with a NaOH (40%) solution. The mixture was stirred at 5 °C for 3 h. A red-orange precipitate was formed by adding this reaction solution to NaOH solution (5%, 100 mL) under stirring, which was then collected through filtration, and washed with deionized water. The crude product, *N*,*N*′-bis(2-hydroxyethyl)-4-(3-ethynylphenylazo)aniline (BHA), was purified by column chromatography (silica gel, EtOAc/petroleum ether = 2:1), m_{BHA} = 2.56 g, yield: 83.0%.

The characteristic analytical data involved are as follows (Italic text means objective proton form the NMR signal): ^{1}H-NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.06–7.78 (s, 1H, Ar*H*), 7.58–7.38 (m, 2H, Ar*H*), 5.86–6.70 (d, 2H, Ar*H*), 4.10–3.87 (m, 4H, C*H*$_2$–OH), 3.84–3.68 (m, 4H, C*H*$_2$–N), 3.12 (s, 1H, ArC≡C*H*); Elemental analysis: Calculated (%): C 69.88, H 6.19, N 13.58; Found (%): C 70.01, H 6.34, N 13.21.

2.4. Synthesis of Poly(ε-caprolactone) Containing Terminal Azobenzene and Ethyne Groups (P1)

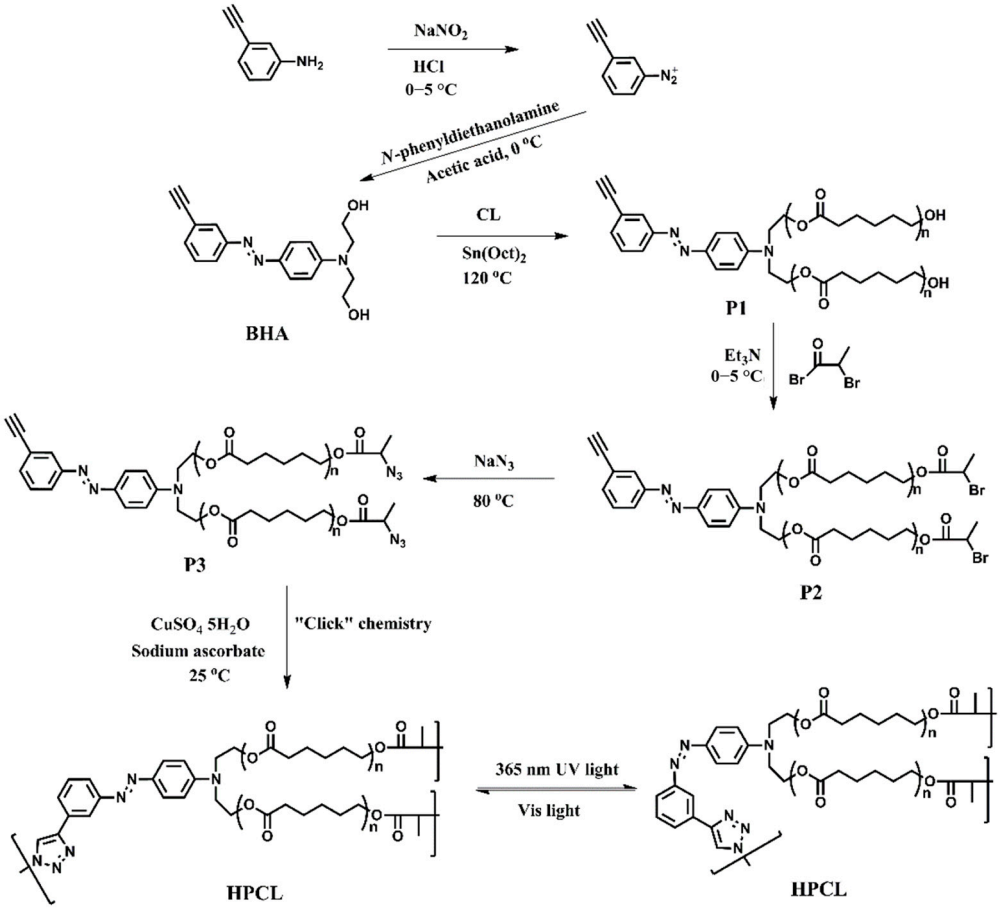
A typical polymerization was described as follows: A solution of ε-caprolactone (CL, 1.00 g, 8.77 mmol), BHA (0.0271 g, 0.0875 mmol) and tin 2-ethylhexanoate ($Sn(Oct)_2$, 3.54 mg, 8.75 μmol) with the molar ratio of $[CL]_0$:$[BHA]_0$:$[Sn(Oct)_2]_0$ = 100:1:0.05 was added to a dry 2 mL ampule tube. The reaction

mixture was purged with argon for approximately 10 min to eliminate oxygen. Afterward, the ampule was flame sealed. The polymerization reaction was performed in an oil bath with a thermostat set at 120 °C. After the desired reaction time, the reaction mixture was cooled to room temperature, dissolved in a minimal amount of tetrahydrofuran (THF, 10 mL), and precipitated by dropwise addition to 250 mL of petroleum ether. The precipitate was filtrated and dried to a constant weight at room temperature in vacuum.

The characteristic analytical data involved are as follows: ^{1}H-NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.01–7.94 (Ar*H*), 7.93–7.77 (Ar*H*), 7.58–7.36 (Ar*H*), 6.94–6.74 (Ar*H*), 4.40–4.25 (NCH_2–CH_2), 4.18–3.90 (CH_2OC=O), 3.82–3.54 (NCH_2 and OC=O$(CH_2)_4CH_2OH$), 3.20–3.05 (ArC≡CH), 2.45–2.15 (OC=OCH_2CH_2), 1.80–1.50 (OC=O$CH_2CH_2CH_2CH_2$), 1.50–1.20 (OC=OCH_2CH_2C*H*$_2CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 173.8 (*C*OOCH_2), 64.2 (COO*C*H_2), 33.8 (*C*H_2COOCH_2), 29.3 ($COOCH_2$*C*H_2), 25.5 (COO$(CH_2)_3$*C*H_2), 24.1 (COO$(CH_2)_2$*C*H_2); FTIR (KBr): γ_{max}/cm^{-1} 2950, 2870, 1720, 1600, 1510, 1470, 1420, 1400, 1370, 1300, 1240, 1190, 1100, 1050, 962, 800 and 733.

2.5. Synthesis of AB$_2$ Type Macromonomer (P3)

An AB_2 type macromonomer (P3) containing terminal azide and ethyne groups was synthesized according to Scheme 1.



Scheme 1. The synthetic route of the hyperbranched poly(ε-caprolactone) (HPCL).

Poly(ε-caprolactone) (P1, 0.74 g, 0.1 mmol, M_n = 7400 g/mol, M_w/M_n = 1.15), dry THF (25 mL) and dry triethylamine (0.14 mL, 1.0 mmol) was added to a 100 mL three-necked flask under strong stirring.

The mixture was cooled with an ice bath (0–5 °C). Then 2-bromopropionyl bromide (1.73 g, 8.0 mmol) in dry THF (10 mL) was added dropwise to the mixture with the temperature at 0–5 °C. The reaction mixture was vigorously stirred overnight at room temperature. After filtration, the filtrate was evaporated under vacuum. The remaining yellow mixture was dissolved in dichloromethane and washed with 5% Na_2CO_3 aqueous solution followed with deionized water three times. The organic solution was dried with anhydrous $MgSO_4$ overnight. Afterward, the solution was concentrated to 5–10 mL under a reduced pressure, and followed by precipitation by dropwise addition to 250 mL methanol. The precipitate (P2) was filtrated and dried to a constant weight at room temperature in vacuum (0.68 g, yield: 91.9%).

The characteristic analytical data of P2 involved are as follows: ^{1}H-NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.01–7.94 (Ar*H*), 7.93–7.78 (Ar*H*), 7.60–7.40 (Ar*H*), 6.95–6.75 (Ar*H*), 4.45–4.25 (NCH_2–CH_2), 4.25–3.90 (CH_2OC=O), 3.90–3.50 (NCH_2 and OC=O$(CH_2)_4$CH_2OH), 3.18–3.10 (ArC≡C*H*), 2.45–2.15 (OC=OCH_2CH_2), 1.96–1.80 (OC=OCH(CH_3)Br), 1.80–1.52 (OC=OCH_2CH_2CH_2CH_2), 1.52–1.25 (OC=OCH_2CH_2CH_2CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 173.8 (*C*OOCH_2), 64.1 (COO*C*H_2), 33.8 (*C*H_2COOCH_2), 29.2 ($COOCH_2$*C*H_2), 25.6 ($COO(CH_2)_3$*C*H_2), 24.2 ($COO(CH_2)_2$*C*H_2); FTIR (KBr): γ_{max}/cm^{-1} 2950, 2870, 1720, 1600, 1510, 1420, 1400, 1370, 1300, 1240, 1190, 1110, 1050, 962, 800 and 733.

P2 (0.6 g, 0.08 mmol), dimethylformamide (DMF, 10 mL), sodium azide (0.064 g, 1.0 mmol) and deionized water (1.0 mL) were added to a 25 mL round-bottomed flask equipped with a stir bar and a condenser. The mixture was vigorously stirred under reflux at 80 °C for 24 h and then cooled to room temperature. After filtration, the filtrate was precipitated by dropwise addition to 250 mL methanol. The precipitates (P3) were filtrated and dried to a constant weight at room temperature in a vacuum (0.52 g, yield: 86.6%).

The characteristic analytical data of P3 involved are as follows: ^{1}H-NMR (P1, 400 MHz, $CDCl_3$), δ (TMS, ppm): 8.01–7.95 (Ar*H*), 7.93–7.79 (Ar*H*), 7.60–7.41 (Ar*H*), 6.95–6.74 (Ar*H*), 4.46–4.25 (NCH_2–CH_2), 4.26–3.90 (CH_2OC=O), 3.90–3.49 (NCH_2 and OC=O$(CH_2)_4$CH_2OH), 3.18–3.10 (ArC≡C*H*), 2.45–2.15 (OC=OCH_2CH_2), 1.96–1.79 (OC=OCH(CH_3)N_3), 1.79–1.52 (OC=OCH_2CH_2CH_2CH_2), 1.52–1.25 (OC=OCH_2CH_2CH_2CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 173.8 (*C*OOCH_2), 64.3 (COO*C*H_2), 33.8 (*C*H_2COOCH_2), 29.2 ($COOCH_2$*C*H_2), 25.6 ($COO(CH_2)_3$*C*H_2), 24.2 ($COO(CH_2)_2$*C*H_2); FTIR (KBr, P3): γ_{max}/cm^{-1} 2950, 2860, 1720, 1600, 1510, 1470, 1420, 1400, 1370, 1300, 1240, 1190, 1110, 1050, 962, 802 and 733.

2.6. Synthesis of Hyperbranched Poly(ε-caprolactone) (HPCL)

Hyperbranched poly(ε-caprolactone) (HPCL) was synthesized from AB_2 type macromonomer (P3) through "click" chemistry under the catalysis of $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O (Scheme 1). Wherefore, P3 (0.4 g, 0.054 mmol) and $CuSO_4 \cdot 5H_2O$ (0.0005 g, 0.1 mmol) were dissolved in 10 mL DMF under vigorous stirring at room temperature. Sodium ascorbate (0.0393 g, 0.2 mmol) in deionized water (0.5 mL) was added dropwise to the mixture. Sequentially, the mixture was vigorously stirred for 24 h. The mixture was poured into 250 mL of methanol. The precipitate (HPCL) was collected by filtration and desiccation in vacuum (0.38 g yield: 95.0%).

The characteristic analytical data of HPCL involved are as follows: ^{1}H-NMR (HPLC, 400 MHz, $CDCl_3$), δ (TMS, ppm): 8.30–8.20 (C*H*N_3Ar), 8.12–8.02 (Ar*H*), 7.98–7.74 (Ar*H*), 7.62–7.46 (Ar*H*), 6.95–6.74 (Ar*H*),

5.60–5.40 (OC=OC*H*(CH_3)CHN_3Ar), 4.35–4.23 (NCH_2–C*H*$_2$), 4.23–4.12 (C*H*$_2$OC=OCH(CH_3)CHN_3Ar), 4.12–3.84 (C*H*$_2$OC=O), 3.84–3.40 (NC*H*$_2$ and OC=O$(CH_2)_4$C*H*$_2$OH), 2.42–2.14 (OC=OC*H*$_2$$CH_2$), 1.94–1.78 (OC=OCH(C*H*$_3$)Br), 1.77–1.47 (OC=OCH_2C*H*$_2$$CH_2$C*H*$_2$), 1.47–1.10 (OC=O$CH_2$$CH_2$C*H*$_2$$CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 173.7 (*C*OOCH_2), 64.2 (COO*C*H$_2$), 33.9 (*C*H$_2$$COOCH_2$), 29.2 ($COOCH_2$*C*H$_2$), 25.6 ($COO(CH_2)_3$*C*H$_2$), 24.3 ($COO(CH_2)_2$*C*H$_2$); FTIR (KBr, HPCL): γ_{max}/cm^{-1} 2940, 2870, 1730, 1620, 1470, 1420, 1400, 1370, 1300, 1140, 960, 792 and 733.

3. Results and Discussion

3.1. Ring-opening Polymerization of ε-Caprolactone (CL)

Poly(ε-caprolactone) (PCL) containing terminal azobenzene and ethyne groups was synthesized through tin-catalyzed ring-opening polymerization of ε-caprolactone (CL) in the presence of *N*,*N*′-bis(2-hydroxyethyl)-4-(3-ethynylphenylazo)aniline (BHA) in bulk. According to reference [42,49], BHA initiated the ring-opening polymerization of CL, and azobenzene and ethyne groups of BHA did not participate in any side reactions. Therefore, the ring-opening polymerization of CL was carried out in bulk using BHA as initiator, and the results are presented in Figures 1 and 2 and Table 1. Figure 1 showed the kinetic plots of the ring-opening polymerization of CL in bulk using BHA as initiator and $Sn(Oct)_2$ as the catalyst with molar ratio of $[CL]_0$:$[BHA]_0$:$[Sn(Oct)_2]_0$ = 100:1:0.05 at 120 °C. Figure 1 presents a first-order kinetic relationship between $\ln([M]_0/[M])$ and the reaction time. However, a rearrangement of the coordinative aggregates of the initiator (*i.e.*, BHA) [48] resulted in an induction period of approximately 6 h. With the extended polymerization time, a highly viscous system was generated. Moreover, polymerization resulted in strong conversion growth, which deviated from linearity. As shown in Figure 2 and Table 1, the molecular weights ($M_{n\ GPC}$, PS standard) of PCL from 1800 to 10,300 g/mol increased linearly with monomer conversions up to high monomer conversions. However, $M_{n\ GPC}$ were slightly lower than the theoretical values ($M_{n\ th}$, Equation (1)) in the polymerization, which could be due to discrepancies between PCL and PS standards [49]. Furthermore, as shown in Figure 2, the molecular weight distributions were relatively narrow (M_w/M_n < 1.2, Table 1). The theoretical values $M_{n\ th}$ of PCL were calculated via Equation (1):

$$M_{n\ th} = 2[CL]_0/[BHA]_0 \times M_{CL} \times \text{Conversion} + M_{BHA} \quad (1)$$

where $[CL]_0$ and $[BHA]_0$ were the initial concentration of CL and BHA, respectively; M_{CL} and M_{BHA} were the molecular weights of CL and BHA, respectively.

The detailed polymerization results are shown in Table 1. The monomer conversions for the polymerizations catalyzed $Sn(Oct)_2$ reach up to nearly 100% in 16 h. The molecular weights measured ($M_{n\ NMR}$) by ^{1}H NMR were close to the $M_{n\ th}$, which further indicated that the ring-opening polymerization of ε-caprolactone (CL) was well controlled with the high initiation efficiency of BHA.

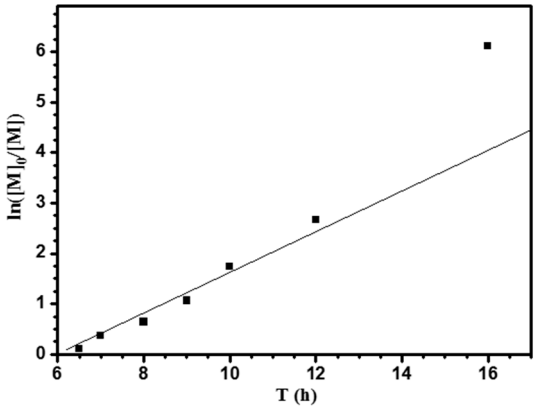


Figure 1. The kinetic plots of the ring-opening polymerization of CL in bulk using BHA as initiator and $Sn(Oct)_2$ as the catalyst with molar ratio of ($[CL]_0$:$[BHA]_0$:$[Sn(Oct)_2]_0$ = 100:1:0.05) at 120 °C. [M] is the concentration of monomer at *t* h, and $[M]_0$ is the concentration of monomer at 0 h.

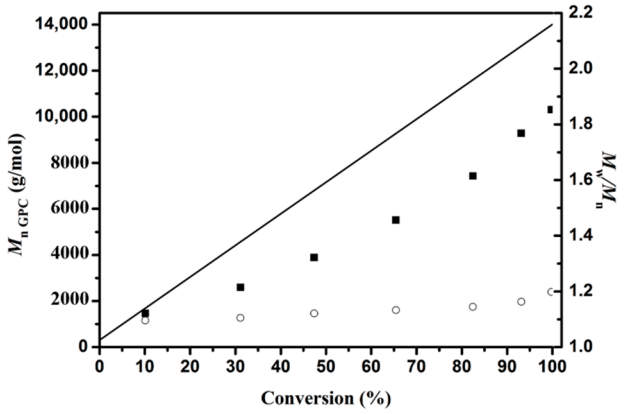


Figure 2. Dependence of the molecular weights and the molecular weight distributions on the monomer conversions for the ring-opening polymerization of CL. The polymerization conditions are same as in Figure 1. "■" means the molecular weight ($M_{n\ GPC}$) of PCL with monomer conversion, and "○" means the molecular weight distribution (M_w/M_n) of PCL with monomer conversion.

Table 1. Characteristics of poly(ε-caprolactone)s (PCLs).

Sample [a]	Time [b] (h)	Conversion [c] (%)	$M_{n\ GPC}$ [d] (g/mol)	$M_{n\ th}$ [e] g/mol	M_w/M_n [f]	$M_{n\ NMR}$ [g] (g/mol)
PCL1	6.5	10.10	1,400	1,700	1.10	1,500
PCL2	7	31.11	2,600	4,500	1.10	4,200
PCL3	8	47.37	3,900	6,800	1.12	6,600
PCL4	9	65.44	5,500	9,300	1.13	8,600
P1	10	82.45	7,400	11,600	1.14	11,300
PCL5	12	93.12	9,300	13,100	1.16	13,200
PCL6	16	99.78	10,300	14,000	1.20	13,500

[a], $[CL]_0$:$[BHA]_0$:$[Sn(Oct)_2]_0$ = 100:1:0.05, at 120 °C, in bulk; [b], The polymerization time; [c], Conversion determined by GC chromatograms; [d], the number-average molecular weight determined by gel permeation chromatography (GPC); [e], The theoretical number-average molecular weight calculated via Equation (1); [f], molecular weight distribution.; [g], the number-average molecular weight calculated via ^{1}H NMR. $M_{n\ NMR} = M_{BHA} + (I_{4.20–3.90}/2I_{8.03–7.93}) \times M_{CL}$.

3.2. "Click" Chemistry for Hyperbranched Poly(ε-caprolactone) (HPCL)

"Click" chemistry has been shown to be a versatile synthetic tool in polymer science for preparing polymers with different topologic structures due to its high efficiency, selectivity and quantitative yields under mild reaction conditions. In the present study, the copper-catalysized Huisgen 1,3-dipolar cycloaddition of azides and alkynes, a typical "click" chemistry, was employed to synthesize hyperbrached poly(ε-caprolactone) (HPCL) from the α-alkyne and ω-azide functionalized poly(ε-caprolactone) (P3 in Scheme 1). The linear PCL (P1) with α-alkyne was firstly reacted with 2-bromopropionyl bromide to introduce bromine into the polymer's ω terminal of the polymer. The formed polymer was labeled as P2. Then, this bromine group reacted easily with sodium azide under mild conditions to convert into azide group, forming the AB_2 type macromonomer (P3). Finally, P3 was further polymerized under the catalysis of $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O in DMF solution at room temperature to form the hyperbranched poly(ε-caprolactone), e.g., HPCL. The GPC curves of the polymers (P1, PCL4, P2, P3, HPCL and HPCL4) were shown in Figure 3. The M_n and M_w/M_n of P1, P2 and P3 changed a little, because P2 and P2 was obtained by only the terminal reaction of P1. There was an obvious peak shift from the macromonomer P1 to final HPCL with the molecular weight increasing from 7400 to 25,500 g/mol. The GPC elution profile of HPCL showed two peaks and one shoulder, which indicated that HPCL contains multi-components from the slightly branched chains to the highly branched chains with much more than three primary chains. Thus, the molecular weight distribution of the HPCL (2.38) was much broader than that of the original polymer (1.15). From the measurements using GPC equipped with a light scattering photometer, the weight-average molecular weight of HPCL was 47,000 g/mol. On average, Approximately 6.4 linear polymer chains on average were found in each HPCL. When the molecular weight of the linear PCL4 was 5500 g/mol (M_w/M_n = 1.13), the corresponding the molecular weight of HPCL2 was 20,000 g/mol through "click" chemistry, and the molecular weight distribution of the HPCL was 2.04 as measured GPC measure. The GPC curve of HPCL2 in Figure 3 was similar to that of HPLC containing more multi-components in the branched polymer. Moreover, when measured using GPC equipped with a Wyatt Visco Star viscometer detector, the polymer structure in solution affected the intrinsic viscosity (IV). Therefore, the Zimm branching factor, g' ($g' = IV_{branched}/IV_{linear}$), is typically used as a qualitative indicator to the degree of branching [50,51]. The g' of the linear polymer is 1, and the higher branching degree for the branched polymer results in a smaller g' under the equal molecular weights. Through GPC, the g' of HPCL (M_w = 25,000 g/mol) was 0.43, which was less than 1, identifying that the HPCL had a branched structure. On the other hand, the g' of HPCL4 (M_w = 20,000 g/mol) was 0.50.

This reaction procedure was also tracked by ^{1}H NMR and FT-IR spectra. Figure 4 showed the ^{1}H NMR spectra of P1, P3 and HPCL. In the ^{1}H NMR spectrum of P1 in $CDCl_3$, the chemical shifts at around 7.77–8.01 ppm were due to the phenyl protons of the azobenzene group (b–e) at the end of the polymer chain. The protons of the alkyne group (a) still had been found at about 3.13 ppm in the ^{1}H NMR spectrum of P1, which indicated that the alkyne group did not participate in the ring-opening polymerization of CL [52]. Resonance at 3.74 ppm (f) and 4.32 ppm (g) were the characteristic signals of the methylene protons of initiator (BHA) segment. The characteristic signals corresponding to the PCL methylene protons conjoint with the hydroxyl end group were observed at approximately 3.64 ppm. These results indicated that a segment of initiator BHA was attached to the end of P1. Furthermore, the molecular weight ($M_{n,NMR}$ = 8600 g/mol), calculated from the ^{1}H NMR spectrum can be determined

by relative integration ratio of resonances at 2.30 ppm of the PCL repeat units and 6.89 ppm of the azobenzene group. To achieve complete functionalization of P2, multiple 2-bromopropionyl bromide was added dropwise to P1, the characteristic signals corresponding to the PCL methylene protons in the end group were observed at around 3.64 ppm in Figure 4 (P1), and the signals disappeared completely after the reactions in Figure 5 (P2). The new characteristic signals corresponding to the protons of the methyl protons in the terminated P2 were observed at around 1.84 ppm, which confirmed successful complete functionalization of P2.

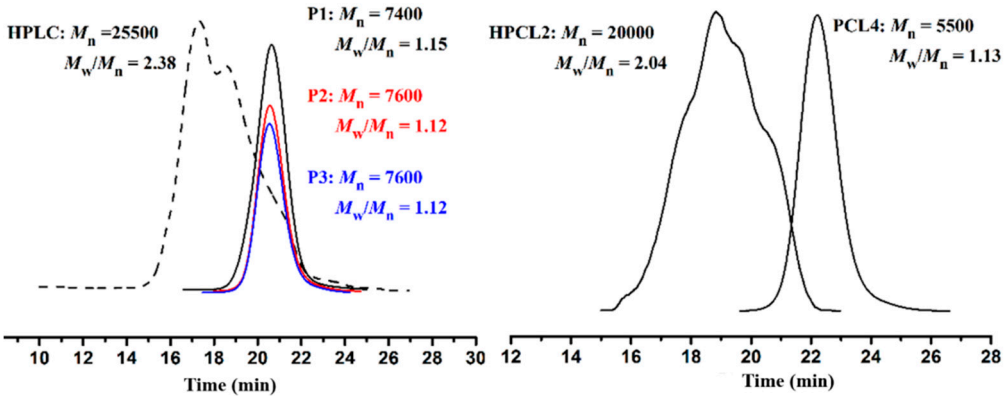


Figure 3. The GPC curves of the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15; PCL4, $M_{n\,GPC}$ = 5500 g/mol, M_w/M_n = 1.13), hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38; HPCL2, $M_{n\,GPC}$ = 20000 g/mol, M_w/M_n = 2.04).

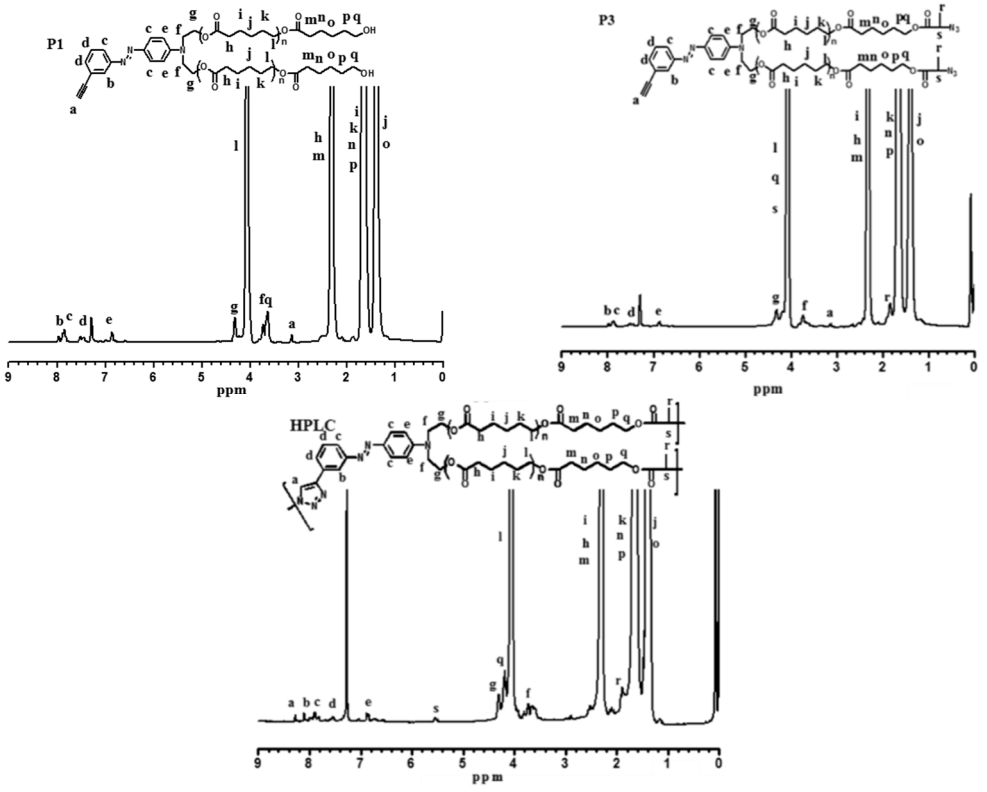


Figure 4. ^{1}H NMR spectra of the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15), AB_2 macromonomer (P3) containing terminal ethyne and azide groups and hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38).

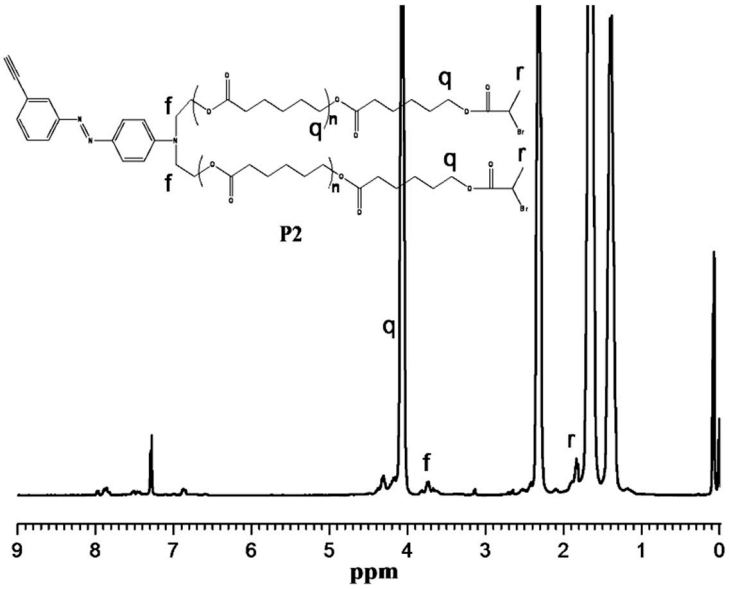


Figure 5. ^{1}H NMR spectrum of the poly(ε-caprolactone) (P2).

P3 was obtained by bromination and azidation procedures of PCL. Therefore, it was clear that the chemical shifts at around 3.64 ppm, and the characteristic signals of the PCL methylene protons conjoint with the hydroxyl end group were shown in Figure 4 (P1), which then disappeared completely after the reactions in Figure 4 (P3). The new characteristic signals corresponding to the protons of the methyl protons in the terminated P3 (r) were observed at around 1.84 ppm. The protons of the alkyne group (a) still can been found at about 3.13 ppm in Figure 4 (P3). Besides, a new signal was found at 2109 cm^{-1} corresponding to the vibration peak of the azide group in the terminated P3 from FT-IR spectroscopy in Figure 6 (P3), which confirmed the successful introduction of azide group in P3.

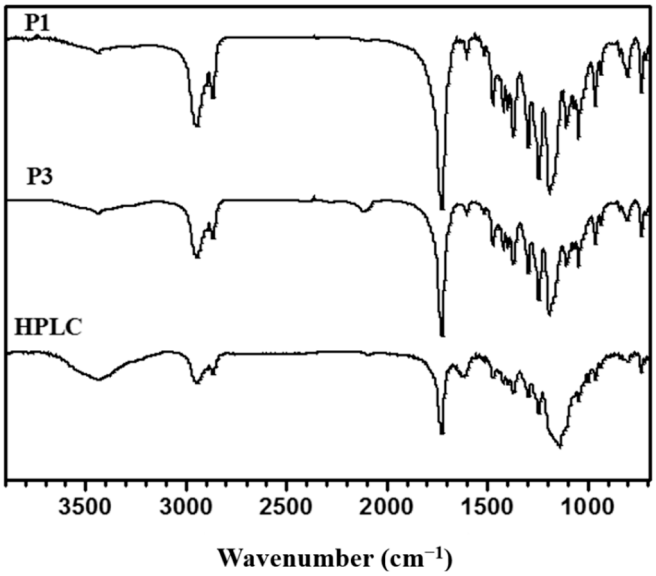


Figure 6. FT-IR spectra of the linear poly(ε-caprolactone) (P1, $M_{n\ GPC}$ = 7400 g/mol, M_w/M_n = 1.15), AB_2 macromonomer (P3) containing terminal ethyne and azide groups and hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\ GPC}$ = 25,500 g/mol, M_w/M_n = 2.38).

Afterwards, the resulting HPCL via "click" chemistry with P3 was also confirmed by ^{1}H NMR spectrum in Figure 4 (HPCL). Compared with the spectra of P1 and P3, the signals at approximately 1.84 ppm from the alkyne group in the terminated P3 were disappeared after the "click" reaction. New resonance at a chemical shift of 8.28 ppm was found in Figure 4, which can be attributed to the protons of the 1,2,3-trizole ring (a). Moreover, the resonance of methine protons (s) of the adjacent azide group in P3 shifted from 4.05 to 5.56 ppm after the polymerization. These results demonstrated the successful "click" reaction. Meanwhile, phenyl protons of the azobenzene group and the PCL repeat units appeared in those ^{1}H NMR spectra both before and after polymerization. This finding confirmed that HPCL containing azobenzene functionalized group was successfully obtained. However, from the GPC curve of HPCL in Figure 3, it seems that approximately 10% of the component had the low molecular weight as well as that of P1, which was due to cyclization of P1. FT-IR spectroscopy in Figure 6 further confirmed the success of the "click" polymerization. The signals at 2109 cm^{-1} (Figure 6, P3) assigned to the azide group in the terminated P3 were largely reduced after the reaction. An appreciable band at around 3400 cm^{-1} assigned to the alkyne group in the terminated P1 and P3. Only one alkyne and two azide groups were present at the end of the polymer P3. When the "Click" reaction complete, the obtained HPCL still had one remaining azide group per branched chain, and a number of azide groups remained at the end of HPCL. Therefore, the signals at 2109 cm^{-1} still existed after the reaction.

3.3. Thermal and Crystallization Characterization

Thermal and crystallinity properties of P1 and HPCL were evaluated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), and polarized optical micrographs (POM), respectively. Figure 7 showed secondary DSC heating curves of P1 and HPCL with a heating rate of 10 °C min^{-1} under a continuous nitrogen flow. The curves indicated the presence of melting temperature both in P1 and HPCL, which were characteristics of semicrystalline in PCL. HPCL ($M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38) showed a monomodal melting peak at 54.1 °C (ΔH_m = 73.5 J/g), and T_m (melting-point) of P1 with $M_{n\,GPC}$ of 7400 g/mol was 55.3 °C (ΔH_m = 79.4 J/g). Thus, no significant difference between the melting point of HPCL and P1 can be observed. The degrees of crystallinity (X_c) of HPCL as well as P1 were estimated from the enthalpy of melting through the following Equation (2):

$$X_c\ (\%) = (\Delta H_m/\Delta H_m^*) \times 100\% \quad (2)$$

where ΔH_m was the apparent melting enthalpy, and ΔH_m^* was the theoretical enthalpy corresponding to the 100% crystalline PCL sample with an average value of 136.4 J/g [53]. From the Equation (2), the calculation results showed that the X_c value of HPCL was 53.4%, which was lower than that of linear P1 (58.2%). Thus, the amorphous fractions in the samples were increased after hyperbranching of P3 by "click" chemistry. The lower X_c values of HPCL can be attributed to the increase in end-groups and the hyperbranched structure of HPCL, which made crystallisation more difficult [22,54].

The thermal stability of P1 and HPCL were characterized by thermogravimetric analysis (TGA) under a continuous nitrogen flow. HPCL was thermally stable up to 329.3 °C (onset decomposition temperature) under nitrogen atmosphere, which was higher than that of P1 (319.7 °C). The increase in thermal stability had been endowed by hyperbranching.

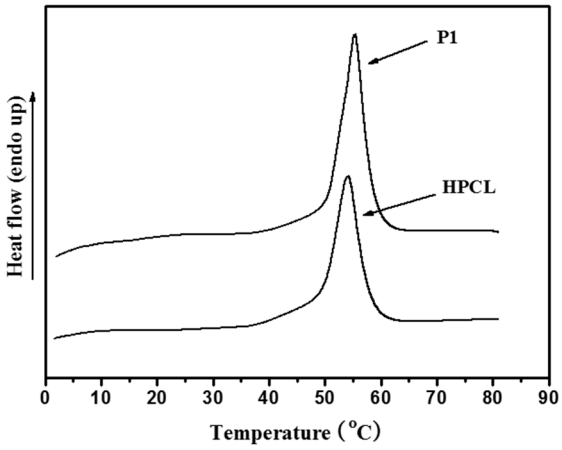


Figure 7. Second DSC heating curves of the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15) and hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38).

The degrees of crystallinity of P1 and HPCL were further investigated via WAXD. As shown in Figure 8, P1 exhibited three major peaks of 2θ at 15.6°, 21.4° and 23.6° (the strongest peak), because linear PCL had a semicrystalline structure. However, only one small diffraction peak of 2θ at 21.4° was observed in the WAXD spectrum of HPCL. These results indicated that the hyperbranched structure of HPCL could be attributed to the confinement of PCL crystallization and was unfavorable for the crystallization of linear PCL chain. The crystalline morphologies of HPCL and P1 were also investigated by polarized optical micrograph (POM). As shown in Figure 9 A,B, the spherulite morphology of P1 by POM was observed at 30 °C, which was in good agreement with the crystallization morphology of the linear PCL. However, the POM results of HPCL showed irregular crystallization morphology, which further confirmed that the crystallinity was slightly less than that of linear polymer chain (P1) due to the hyperbranched structure of HPCL.

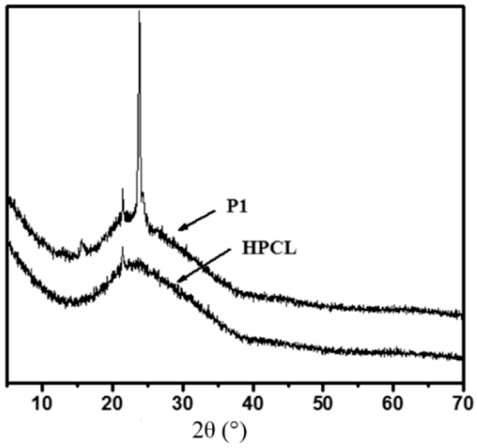


Figure 8. WAXD (wide-angle X-ray diffraction) spectra of the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15) and hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38) at room temperature.

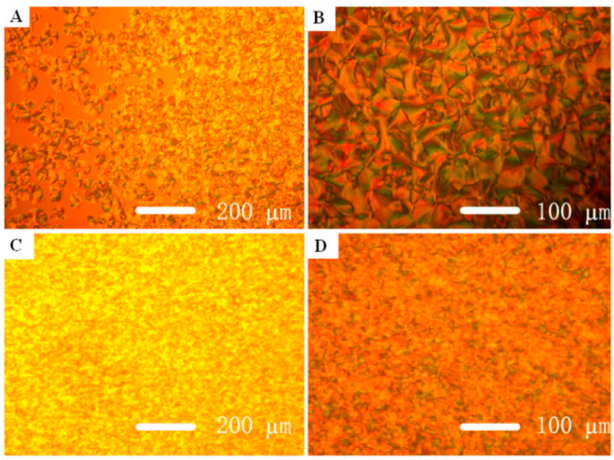


Figure 9. Polarized optical micrographs (POM) of poly(ε-caprolactone) (PCL) crystallized at 30 °C. (**A**) and (**B**): the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15); (**C**) and (**D**): the hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38)

3.4. Photoisomerization Behaviors

It is well-known that polymers containing azobenzene chromophores have showed reversible *trans-cis-trans* isomerization behaviors, which undergoes isomerization from *trans*- to *cis*-forms under the irradiation of 365 nm ultraviolet light, and reverse transformation from *cis*-to-*trans* forms under thermal energy [55–57]. The *trans-cis* photoisomerization of BHA, P1 and HPCL in chloroform solution were investigated at room temperature. All samples were irradiated with 365 nm ultraviolet light, and UV-vis spectroscopy was used to characterize the process of photoisomerization. The UV-vis absorption changes of BHA, P1, and HPCL were given in Figures 10, 11, and 12, respectively. As shown in Figure 10, the absorption bands at about 403 nm and 526 nm were attributed to the characteristic π–π^* transition of azobenzene (*trans*-form) and the n–π^* transition of azobenzene (*cis*-form). After irradiation with 365 nm UV light, the *trans*-form of the azobenzene changed to the *cis*-form. BHA showed typical isomerization behavior of azobenzene compound. However, in the cases of the polymers (both in P1 and HPCL) in Figures 11 and 12, the absorption intensity of *trans*-form azobenzene (403 nm) strong increased (about 50%) upon UV irradiation at the beginning of irradiation. This finding may be attributed to the PCL segment significantly affecting the *trans*- and *cis*- isomerization activity of the azobenzene chromophore. Generally speaking, the *trans*-form of azobenzene (the π–π^* transition) was more stable than the *cis*-form (the n–π^* transition), therefore, the content of *trans*-form azobenzene was much higher than that of *cis*-form. After irradiation with 365 nm UV light, the *trans*-form of the azobenzene changed to the *cis*-form. For this type polymer, azobenzene chromophore was in the middle of the PCL chain, and the PCL chain in the solution intertwined each other, which lead to becoming a much more stable *cis*-form. The content of *cis*-form was much higher because of winding PCL. When irradiated with 365 nm UV light in the beginning, the winding PCL untwist each other through UV light energy. Therefore, the "free" azobenzene chromophore in middle of PCL chain became an unstable structure, and the unstable *cis*-form with high content quickly transformed into the *trans*-form. This period was different between P1 and HPCL, *i.e.*, the period of 10 s and 15 s were found for P1 and HPCL respectively. After continuous

irradiation with 365 nm UV light, the absorption of *trans*-form azobenzene at 403 nm decreased remarkably, and the intensity of the *cis*- form azobenzene (526 nm) rapidly increased. This system reached a photostationary state after irradiation periods of 600, 1080 and 1450 s in BHA, P1 and HPCL solutions, respectively. However, the *trans*- form of the azobenzene did not completely disappear, and there was about 24.8% of *trans*- form in the azobenzene chromophore from the HPCL in the saturated systems. Moreover, the color of the HPCL solution changed gradually from faint yellow to pink under irradiation with 365 nm UV light in Figure 13. Similar characteristic behavior of BHA and P1 was also observed. However, the maximum absorptions of BHA at 411 nm and P1 at 407 nm were the characteristic intense π–π^* transition of azobenzene (*trans*-form), and the absorption at about 526 nm corresponded to the *cis*- form (weak n–π^* transition).

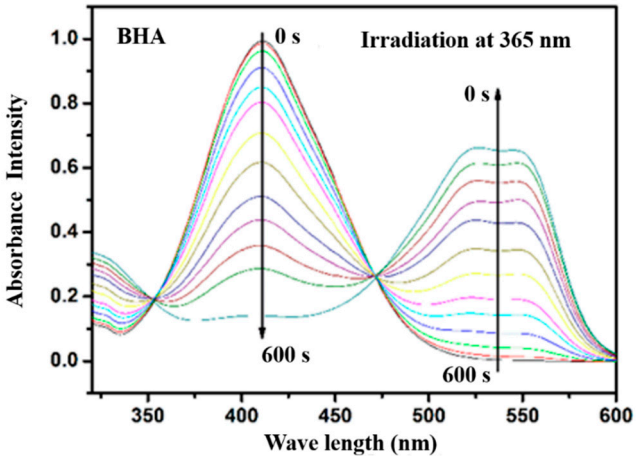


Figure 10. The UV-vis absorption changes of BHA during the irradiation with 365 nm UV light in chloroform solution (The concentration of azobenzene moieties is 5.00×10^{-5} M at room temperature). The arrows means that the time go on and the absorbance intensity decreased or increased.

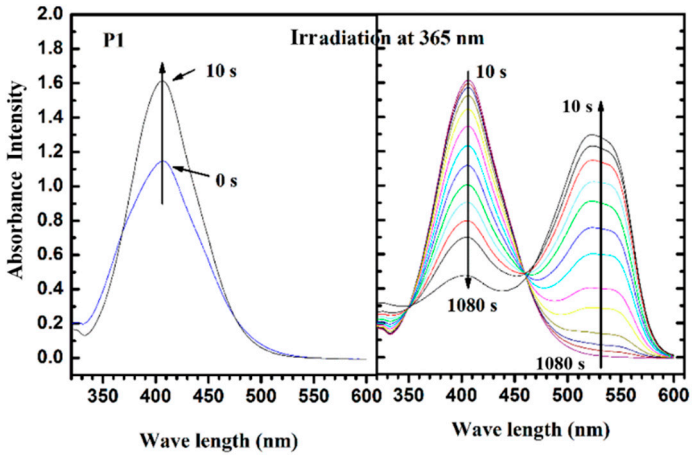


Figure 11. The UV-vis absorption changes of the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15) during the irradiation with 365 nm UV light in chloroform solution (The concentration of azobenzene moieties is 5.00×10^{-5} M at room temperature). The arrows means that the time go on and the absorbance intensity decreased or increased.

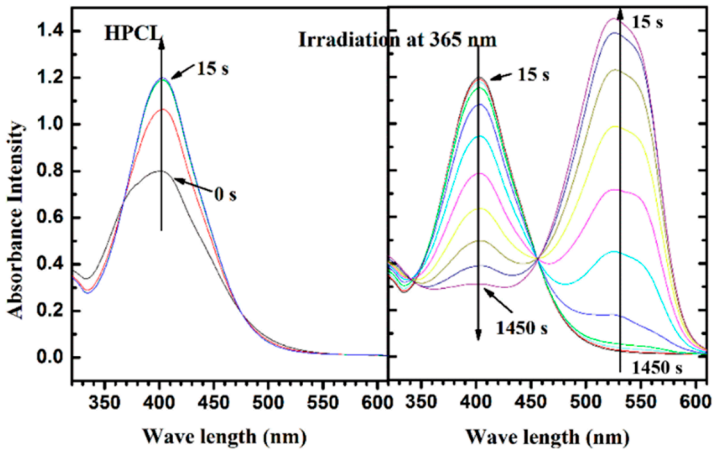


Figure 12. The UV-vis absorption changes of the hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\ GPC}$ = 25,500 g/mol, M_w/M_n = 2.38) during the irradiation with 365 nm UV light in chloroform solution (The concentration of azobenzene moieties is 5.00 × 10^{-5} M at room temperature). The arrows means that the time go on and the absorbance intensity decreased or increased.

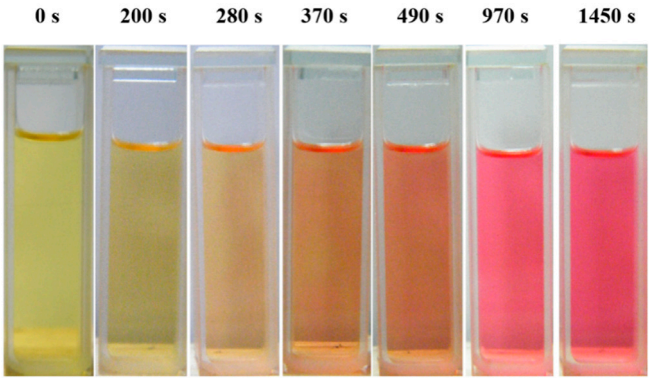


Figure 13. Color change of the hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\ GPC}$ = 25,500 g/mol, M_w/M_n = 2.38) during the irradiation with 365 nm UV light in chloroform solution (The concentration of azobenzene moieties is 5.00 × 10^{-5} M at room temperature).

The corresponding photoisomerization kinetics of BHA, P1 and HPCL in chloroform solution was plotted in Figure 14. The rate of *trans-cis* photoisomerization was analyzed from the absorption of 403 nm with different 365 nm light irradiation time. The first-order rate constant (k_{exp}) of photoisomerization was determined by Equation (3) [55] as follows:

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = -k_{exp}t \quad (3)$$

where A_∞, A_0 and A_t are absorbances at 401 nm for HPCL (BHA at 411 nm and P1 at 407 nm), after 365 nm light irradiation at infinite time, time zero, and time t, respectively. The photoisomerization rate constants k_{exp} of BHA, P1 and HPCL were 0.0054, 0.0016 and 0.0014 s^{-1}, respectively. From the results, the k_{exp} of small molecule BHA was nearly three times faster than that of polymers P1 and HPCL, which was consistent with the result obtained in the literature [58]. This finding was due to the sterically hindering effect of the polymer-chain configuration. When the samples were irradiated under 365 nm ultraviolet

light, azobenzene undergoes isomerization from *trans*- to *cis*-forms, which induced scale shape and dipole movement of the rigid azobenzene chromophore. The polymer chains containing the middle azobenzene moiety were more greatly affected by the *trans-cis* isomerization, which easily drive movement of the polymer segment.

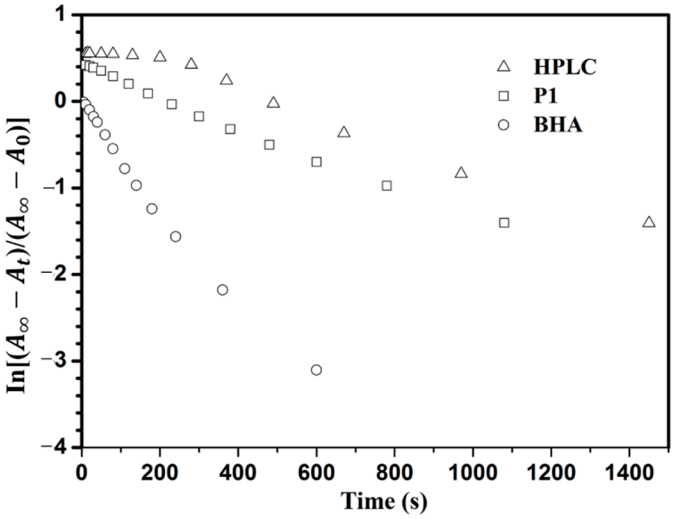


Figure 14. First-order for *trans-cis* photoisomerization of BHA, the linear poly(ε-caprolactone) (P1, $M_{n\,GPC}$ = 7400 g/mol, M_w/M_n = 1.15) and hyperbranched poly(ε-caprolactone) (HPCL, $M_{n\,GPC}$ = 25,500 g/mol, M_w/M_n = 2.38). The concentration of the solution is 5.0 × 10^{-5} M during the irradiation time with 365 nm UV light in chloroform solution at room temperature.

4. Conclusions

A hyperbranched azobenzene functionalized poly(ε-caprolactone) (HPCL) was successfully synthesized by "click" chemistry of AB_2 macromonomer (P3) containing terminal ethyne and azide groups. Moreover, P3 was obtained by bromination and azidation procedures of linear poly(ε-caprolactone) (P1), which was prepared through tin catalyzed ring-opening polymerization of ε-caprolactone in the presence of *N*,*N*′-bis(2-hydroxyethyl)-4-(3-ethynylphenylazo)aniline (BHA) in bulk. The obtained polymers P1 and HPCL were demonstrated by GPC, ^{1}H-NMR, and FT-IR spectra. Thermal and crystallization properties of P1 and HPCL were studied by DSC, TGA, WAXD and POM, which confirmed that the crystallinity of HPCL was slightly less than that of linear polymer chain (P1) due to the hyperbranched structure of HPCL. Furthermore, the photo induced *trans-cis* isomerization of BHA, P1, and HPCL containing terminal azobenzene were also investigated in chloroform solution. The photoisomerization rate constants k_{exp} of BHA, P1 and HPCL was 0.0054, 0.0016 and 0.0014 s^{-1}, respectively.

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Author Contributions

Bibiao Jiang and Xiaoqiang Xue designed the experiments. Xiaoqiang Xue and Jing Yang carried out the experiments. Bibiao Jiang, Xiaoqiang Xue, Jing Yang, Wenyan Huang and Hongjun Yang carried out instrumental analysis. Xiaoqiang Xue, Bibiao Jiang, Yang, Wenyan Huang and Hongjun Yang prepared the manuscript.

Conflicts of Interest

The authors declare no conflict of interest

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