

Synthesis and characterization of poly(ϵ -caprolactone) tetra-arm star polymer using tetra terminal alkynyl-substituted phthalocyanine by the combination of ring-opening polymerization and "click" chemistry

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Abstract. The synthesis of poly(ϵ -caprolactone) (PCL) tetra-arm star polymer was carried out using "click" chemistry and ring-opening polymerization techniques. For this purpose, poly(ϵ -caprolactone) azido (PCL-N₃) was acquired using ring-opening polymerization of ϵ -caprolactone and 2-[2-(2-azidoethoxy)ethoxy]ethanol (N₃ol). N₃ol was obtained using sodium azide and 2-[2-(2-chloroethoxy)ethoxy]ethanol. 4-(prop-2-ynyloxy)-phthalonitrile was obtained by using 4-nitrophthalonitrile and propargyl alcohol. 2(3),9(10),16(17),23(24) Tetrakis-[(prop-2-ynyloxy)-phthalocyaninato]zinc(II) (Pc-propargyl) was synthesized by using 4-(prop-2-ynyloxy)-phthalonitrile and a metal salt. By reacting Pc-propargyl and PCL-N₃, PCL tetra-arm star polymer was obtained by "click" chemistry. The products were characterized via scanning electron microscopy, ¹H-nuclear magnetic resonance spectroscopy, ultraviolet-visible spectrophotometry, Fourier-transform infrared spectroscopy, and gel permeation chromatography instruments. The spectroscopic analyses of PCL tetra-arm star polymer prove that the star polymer was built through the combination of ROP and "click" chemistry. We provided a protocol for PCL tetra-arm star polymer, and a statement of reproducibility with respect to the properties of this tetra-arm star polymer. This study is an example of a novel type of combination reaction, from ring-opening polymerization to "click" chemistry using phthalocyanine. This can open the door for diverse tetra-arm star polymer synthesis that could potentially cause major advances in synthetic macromolecular chemistry.

Keywords: tetra-arm star polymer; "click" chemistry; ring-opening polymerization; phthalonitrile derivative; metallophthalocyanine.

1. Introduction

Phthalocyanines are dyes and pigments used for many significant industrial applications thanks to their bright blue or green colors combined with remarkable thermal and photochemical stability [1-3]. Furthermore, phthalocyanines and their derivatives with the fascinating electrical and electrochemical properties are critical for applications including chemical sensors, nanotechnology, catalysis, optical data storage, nonlinear optics, organic light-emitting diodes (OLEDs), organic solar cell and liquid crystals [4-6]. In recent years, derivatives of phthalocyanines have been widely used as sensitizers in the photodynamic therapy (PDT) method of cancer cases [7, 8]. On the other hand, phthalocyanines have got a visible disadvantage owing to their low solubility properties in water or organic solvents. However, this problem is able to be overcome by implementing bulky or long-chain groups, e.g. alkyl, alkoxy/alkylthio into the peripheral positions of the framework of phthalocyanine. The ring-opening polymerization (ROP) technique was utilized for most of the cyclic monomers with the catalyst systems [9-11]. Poly(ϵ -caprolactone) (PCL), which is a biodegradable semi-crystalline polyester and has got a glass transition temperature and low melting point, is widely utilized for

many polymer syntheses [12, 13]. Lactones display special properties including biocompatibility, excellent mechanical properties, biodegradability, and no toxicity [14-16]. These days, copper-catalyzed azide-alkyne cycloaddition (CuAAC) reactions, which are the "click" chemistry methods, have emerged as the unique method for obtaining polymer [17-19]. Surface control and functionalization are done by "click" reactions which are key to the performance of the materials. Therefore, star polymer has a great interest [20-22]. Recently, "click" techniques have appeared in the synthesis of new structured macromolecules, which enable them to take place in many fields of science [23-25]. The principal characteristics of "click" chemistry are shown by simple reaction conditions, high tolerances of functional groups, lack of byproducts, light, and simple product isolations [26-28].

In our recent study [29], poly(ϵ -caprolactone-block-ethylene glycol methyl ether) block copolymer was synthesized by "click" chemistry of polyethylene glycol methyl ether propargyl and poly(ϵ -caprolactone) azido. This study was aimed at the synthesis of PCL tetra-arm star polymer which is a homopolymer by using tetra terminal alkynyl-substituted phthalocyanine via "click" chemistry. 2-[2-(2-azidoethoxy)ethoxy]ethanol (N₃ol) was obtained via reaction of sodium azide and 2-[2-(2-

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chloroethoxy)ethoxy]ethanol as the reference [30]. Poly(ϵ -caprolactone) azido (PCL- N_3) was obtained via the reaction between ϵ -caprolactone (CL), and N_3 ol by ROP technique as shown in the literature [29]. Pc-propargyl was synthesized by using 4-(prop-2-ynyloxy)-phthalonitrile and a metal salt as shown in the reference [31]. Finally, PCL- N_3 and Pc-propargyl were used to acquire the tetra-arm star polymer by "click" chemistry. The characterization of the products was particularly fulfilled.

2. Experimental

2.1. Materials

Sigma-Aldrich supplied 4-nitrophthalonitrile, anhydrous potassium carbonate, anhydrous zinc acetate [$Zn(CH_3COO)_2$], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 2-[2-(2-chloroethoxy)ethoxy]ethanol, sodium azide, chloroform, propargyl alcohol, N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA), ϵ -caprolactone, tin(II) 2-ethylhexanoate [$Sn(Oct)_2$], diethyl ether, tetrahydrofuran (THF), N,N -dimethylformamide (DMF), and copper(I) bromide, methanol. Potassium carbonate (K_2CO_3), dimethyl sulfoxide, and hexane were supplied by Merck. All the chemicals were not exposed to any further purification.

2.2. Equipment

1H -NMR spectra were obtained by Bruker Ultra Shield Plus ultra-long hold time 400 NMR spectrometers in dimethyl sulfoxide- d_6 as the solvent. FT-IR (ATR) spectra were acquired by Alpha-P Bruker FT-IR spectrometer between the range of 4000-400 cm^{-1} . SEM figures were obtained by Carl Zeiss Sigma 300 Field Emission electron microscope. UV-Vis studies were recorded using a Hitachi U-2900 spectrophotometer. Molecular weight and dispersity were studied by the Malvern GPCMax instrument at 22 °C using THF as a solvent with a 1 mL/min flow rate through the RI system.

2.3. Synthesis

Synthesis of poly(ϵ -caprolactone) azido (PCL- N_3)

PCL- N_3 was obtained via ROP as the procedure [29] as shown below: 1 mL of DMF, 2.0 mL of CL, 0.2 mL of N_3 ol (obtained as ref. [30]), 2 drops of $Sn(Oct)_2$ were separately placed in a tube. After nitrogen purging, the reaction mixture was stirred at 120 °C for 18 hours. Cold excess diethyl ether was poured into the reaction mixture to separate PCL- N_3 . The mixture was put in a deep freezer overnight. PCL- N_3 was dried under vacuum at 25 °C after decantation.

Synthesis of 4-(prop-2-ynyloxy)-phthalonitrile

4-(Prop-2-ynyloxy)-phthalonitrile was obtained as the reference [31]. For example, 4-nitrophthalonitrile (1 g,

5.77 mmol) and propargyl alcohol (0.389 g, 6.94 mmol = 0.408 mL) were solved in 10 mL dry dimethyl sulfoxide and mixed at 25 °C under nitrogen gas for 15 minutes. Anhydrous K_2CO_3 (12.68 mmol, 1.75 g) was inserted. The reaction was continued for 24 hours at 25 °C. Then, 100 mL of distilled water was inserted into the reaction mixture. The brownish crude product was extracted with chloroform, washed with distilled water, and dried with Na_2SO_4 . Dimethyl sulfoxide was separated using a rotary evaporator. In the end, the raw product was refined by column chromatography on silica gel by using eluent chloroform/methanol (10/1, v/v).

Synthesis of 2(3),9(10),16(17),23(24)-tetrakis-[(prop-2-ynyloxy)-phthalocyaninato] zinc (II) (Pc-propargyl) 2(3),9(10),16(17),23(24)-tetrakis-[(prop-2-ynyloxy)-phthalocyaninato] zinc (II) (Pc-propargyl) was synthesized as the literature [31]. For example, 4-(prop-2-ynyloxy)-phthalonitrile (0.105 g, 0.55 mmol) and anhydrous $Zn(CH_3COO)_2$ (0.025 g, 0.14 mmol) were heated at 170 °C for 5 minutes in the presence of 0.18 mL DBU. The dark green blend was cooled to 25 °C and then sedimented in hexane. The sediment was filtered and washed using a hexane/methanol mixture (1/1, v/v). The raw product was refined by column chromatography by using the eluent THF to obtain zinc phthalocyanine as a green solid on silica gel.

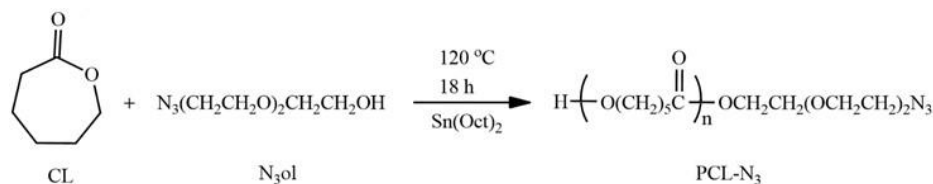
Synthesis of PCL tetra-arm star polymer via "click" chemistry

0.010 g of Pc-propargyl and 0.042 of PCL- N_3 were dissolved in 2 mL of DMF in a glass tube. 1 drop of PMDETA and 0.002 g of CuBr were inserted in the glass tube by purging argon gas for 5 minutes. The glass tube was dipped in a silicon bath at 35 °C on a magnetic hotplate for 24 hours. After this time, the tube content was sedimented in cold petroleum ether/diethyl ether (1/1, v/v). After decantation, the precipitate was dried in a vacuum oven at 30 °C for 72 hours.

3. Results and discussion

Synthesis of PCL- N_3

PCL- N_3 was obtained using N_3 ol and CL by ROP technique [29]. Scheme 1 includes the synthesis road for PCL- N_3 . PCL- N_3 was weighted as 2.01 g (91.36 wt. %). FT-IR (ATR) of PCL- N_3 (Figure 1B), wavenumber/ (cm^{-1}) : 3450 (-OH), 2940 (-CH aliphatic), 2104 (- N_3), 1721 (-C=O), 1238 (C-O-C). 1H -NMR of PCL- N_3 in Figure 2A monitored peaks at 4.4 ppm for -NCH, 4.0 ppm for -OCH, 2.3 ppm for -CH linked carbonyl, 1.5 and 1.3 ppm for -CH.



Scheme 1. Reaction pathway for synthesis of PCL- N_3 .

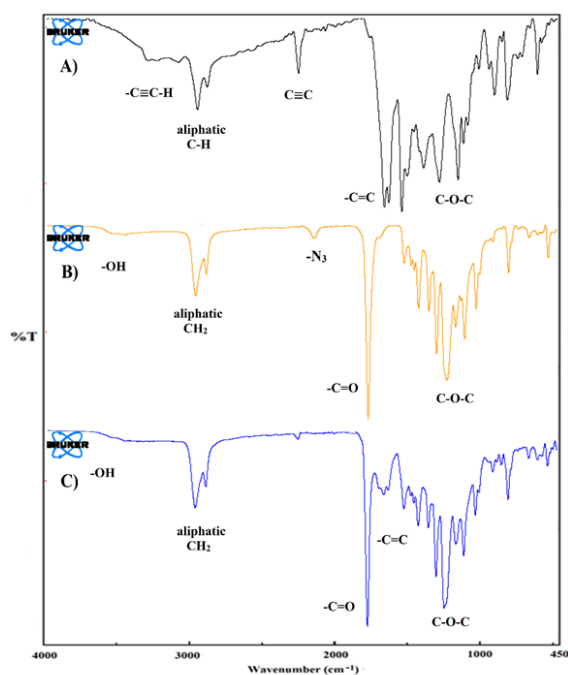


Figure 1. FT-IR spectra of Pc-propargyl (A), PCL- N_3 (B), and PCL tetra-arm star polymer (C).

Synthesis of 4-(prop-2-ynyloxy)-phthalonitrile

4-(Prop-2-ynyloxy)-phthalonitrile was synthesized through reaction of 4-nitrophthalonitrile and 2-propyn-1-ol [31]. Scheme 2 includes the synthesis pathway (step 1) for the synthesis of 4-(prop-2-ynyloxy)-phthalonitrile. 4-(prop-2-ynyloxy)-phthalonitrile was weighted as 0.87 g (83 wt. %); m.p. 152-158 $^{\circ}\text{C}$. FT-IR

(ATR), wavenumber/ cm^{-1} : 3284 ($\text{-C}\equiv\text{C-H}$), 3118 (C-H), 2987-2900 (C-H), 2229 ($\text{C}\equiv\text{N}$), 2135 ($\text{C}\equiv\text{C}$), 1593, 1492 (C=C), 1257, 1087 (C-O-C).

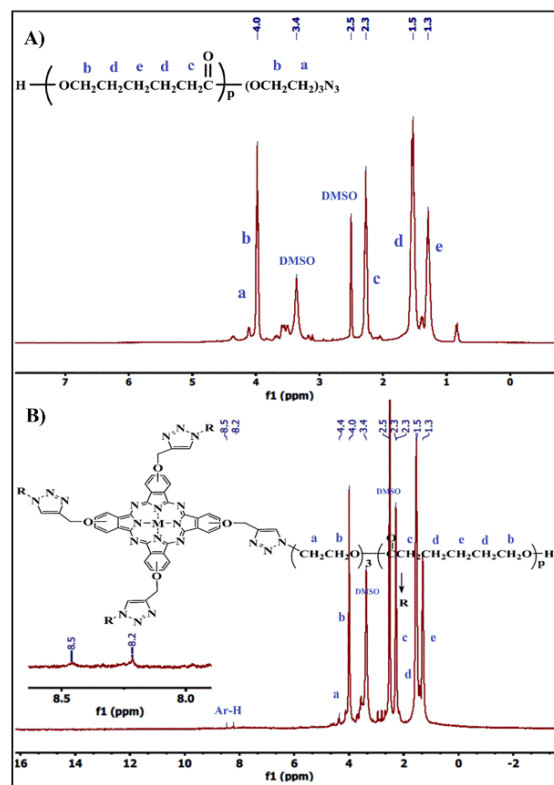
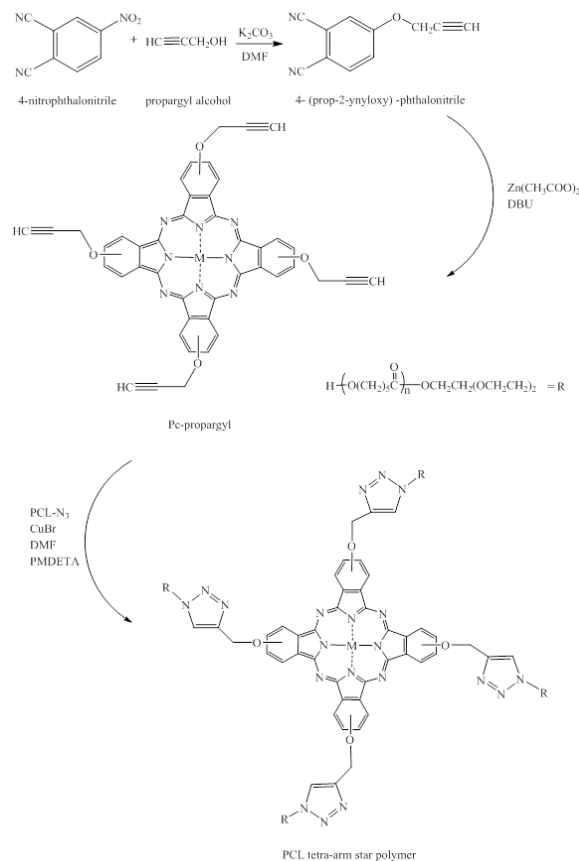


Figure 2. $^1\text{H-NMR}$ of PCL- N_3 (A), PCL tetra-arm star polymer (B).



Scheme 2. Reaction outlines for syntheses of 4-(prop-2-ynyloxy)-phthalonitrile, Pc-propargyl, and PCL tetra-arm star polymer.

Synthesis of Pc-propargyl

Pc-propargyl was synthesized by starting from 4-(prop-2-ynyloxy)-phthalonitrile [31]. The road for synthesis of Pc-propargyl was presented in Scheme 2 (step 2). Pc-propargyl was weighted as 0.33 g (75 wt. %), m.p. > 300 °C. UV-Vis (THF) λ_{max} , nm (log ϵ): nm: 680, 610, 346. FT-IR (ATR) of Pc-propargyl (Figure 1A), wavenumber/(cm⁻¹): 3288 (-C≡C-H), 2923 (C-H aliphatic), 2210 (C≡C), 1604, 1482 (-C=C aromatic), 1217 and 1084 (C-O-C).

Synthesis of PCL tetra-arm star polymer

PCL tetra-arm star polymer was obtained using PCL-N₃ and Pc-propargyl via "click" chemistry. The star polymer was weighted as 0.048 g (91.18 wt. %). FT-IR (ATR) (Figure 1C), wavenumber/(cm⁻¹): 3450 (-OH), 2938 (-CH aliphatic), 1722 (-C=O), 1607, 1465 (-C=C aromatic), 1238 (C-O-C). ¹H-NMR of the tetra-arm star

polymer in Figure 2B showed peaks at 8.5-8.2 ppm for aromatic -CH of triazole, 4.4 ppm for -NCH, 4.0 ppm for -OCH, 2.3 -C=OCH, 1.5 and 1.3 ppm for -CH. The signals at 8.5-8.2 ppm were demonstrated as proof for the synthesis of PCL tetra-arm star polymer. To examine the morphological properties of PCL tetra-arm star polymer, SEM was used. The tetra-arm star polymer was covered by a thin gold plate. The figures were obtained from different perspectives. The surface morphology of PCL tetra-arm star polymer was demonstrated in Figure 3. According to the SEM figures of the tetra-arm star polymer, homogenization of the star polymer was great. The rough surfaces that form a continuous phase were observed. GPC curve of PCL tetra-arm star polymer was demonstrated in Figure 4. Mw value of PCL tetra-arm star polymer was 3,778 Da. The dispersity of the star polymer was 1.35. The value was relatively narrow

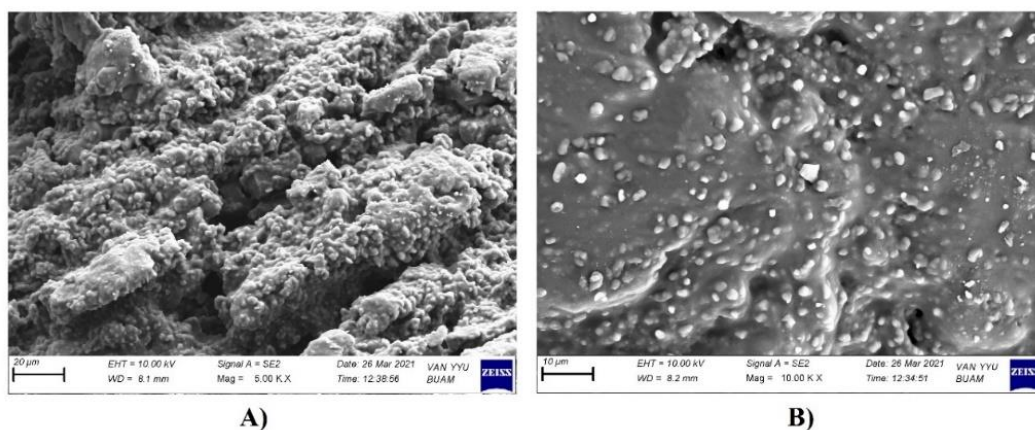


Figure 3. SEM displays of PCL tetra-arm star polymer: 5 000 X (A), 10 000 X (B).

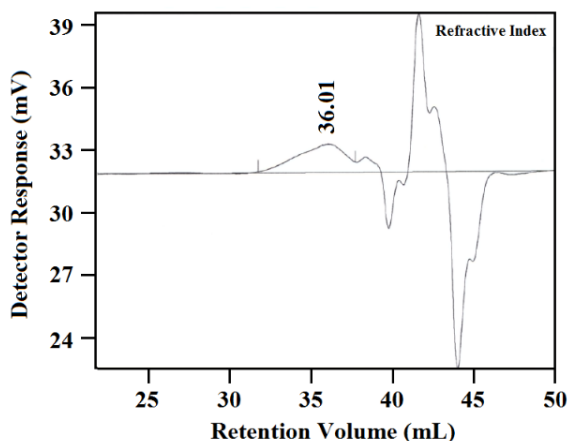


Figure 4. GPC diagram of PCL tetra-arm star polymer.

4. Conclusions

This work shows the synthesis of PCL tetra-arm star polymer. The synthesis strategy given in the study is easy and effective. This work can lead the way for well-conceived materials to be prepared by the combination of poly(ϵ -caprolactone) and phthalocyanine. ¹H-NMR, FT-IR, SEM, UV-Vis, and GPC were carried out for the product characterizations.

Conflict of interest

Authors declare no conflict of interest.

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