

## Synthesis and characterization of poly( $\epsilon$ -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( $\epsilon$ -caprolactone) (PCL) tetra-arm star polymer was carried out using "click" chemistry and ring-opening polymerization techniques. For this purpose, poly( $\epsilon$ -caprolactone) azido (PCL-N<sub>3</sub>) was acquired using ring-opening polymerization of  $\epsilon$ -caprolactone and 2-[2-(2-azidoethoxy)ethoxy]ethanol (N<sub>3</sub>ol). N<sub>3</sub>ol was obtained using sodium azide and 2-[2-(2-chloroethoxy)ethoxy]ethanol. 4-(prop-2-ynyl)oxy-phthalonitrile was obtained by using 4-nitrophthalonitrile and propargyl alcohol. 2(3),9(10),16(17),23(24) Tetrakis-[(prop-2-ynyl)oxy]-phthalocyaninato]zinc(II) (Pc-propargyl) was synthesized by using 4-(prop-2-ynyl)oxy-phthalonitrile and a metal salt. By reacting Pc-propargyl and PCL-N<sub>3</sub>, PCL tetra-arm star polymer was obtained by "click" chemistry. The products were characterized via scanning electron microscopy, <sup>1</sup>H-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( $\epsilon$ -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" technics 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( $\epsilon$ -caprolactone-block-ethylene glycol methyl ether) block copolymer was synthesized by "click" chemistry of polyethylene glycol methyl ether propargyl and poly( $\epsilon$ -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 (N<sub>3</sub>ol) was obtained via reaction of sodium azide and 2-[2-(2-

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chloroethoxy)ethoxy]ethanol as the reference [30]. Poly( $\epsilon$ -caprolactone) azido (PCL-N<sub>3</sub>) was obtained via the reaction between  $\epsilon$ -caprolactone (CL), and N<sub>3</sub>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<sub>3</sub> 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<sub>3</sub>COO)<sub>2</sub>], 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),  $\epsilon$ -caprolactone, tin(II) 2-ethylhexanoate [Sn(Oct)<sub>2</sub>], diethyl ether, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and copper(I) bromide, methanol. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), dimethyl sulfoxide, and hexane were supplied by Merck. All the chemicals were not exposed to any further purification.

### 2.2. Equipment

<sup>1</sup>H-NMR spectra were obtained by Bruker Ultra Shield Plus ultra-long hold time 400 NMR spectrometers in dimethyl sulfoxide-d<sub>6</sub> as the solvent. FT-IR (ATR) spectra were acquired by Alpha-P Bruker FT-IR spectrometer between the range of 4000-400 cm<sup>-1</sup>. 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( $\epsilon$ -caprolactone) azido (PCL-N<sub>3</sub>)

PCL-N<sub>3</sub> 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<sub>3</sub>ol (obtained as ref. [30]), 2 drops of Sn(Oct)<sub>2</sub> 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<sub>3</sub>. The mixture was put in a deep freezer overnight. PCL-N<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>SO<sub>4</sub>. 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<sub>3</sub>COO)<sub>2</sub> (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.*

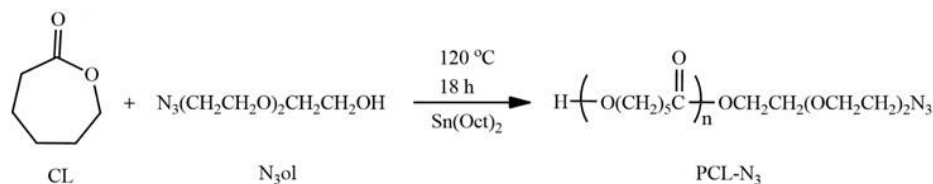
#### *Synthesis of PCL tetra-arm star polymer via "click" chemistry*

0.010 g of Pc-propargyl and 0.042 of PCL-N<sub>3</sub> 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.

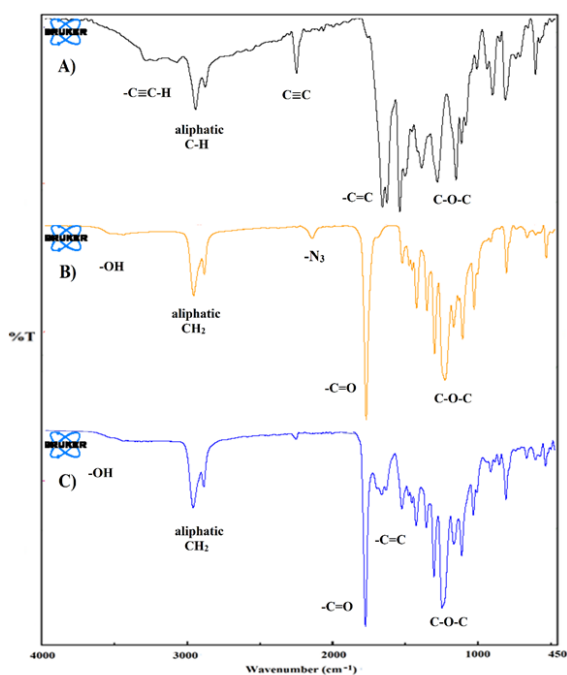
## 3. Results and discussion

### Synthesis of PCL-N<sub>3</sub>

PCL-N<sub>3</sub> was obtained using N<sub>3</sub>ol and CL by ROP technique [29]. Scheme 1 includes the synthesis road for PCL-N<sub>3</sub>. PCL-N<sub>3</sub> was weighted as 2.01 g (91.36 wt. %). FT-IR (ATR) of PCL-N<sub>3</sub> (Figure 1B), wavenumber/(cm<sup>-1</sup>): 3450 (-OH), 2940 (-CH aliphatic), 2104 (-N<sub>3</sub>), 1721 (-C=O), 1238 (C-O-C). <sup>1</sup>H-NMR of PCL-N<sub>3</sub> 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<sub>3</sub>.

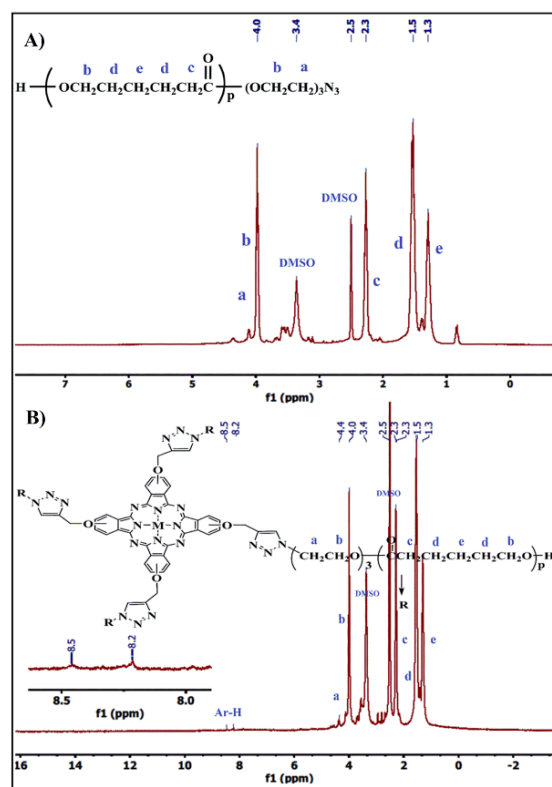


**Figure 1.** FT-IR spectra of Pc-propargyl (A), PCL-N<sub>3</sub> (B), and PCL tetra-arm star polymer (C).

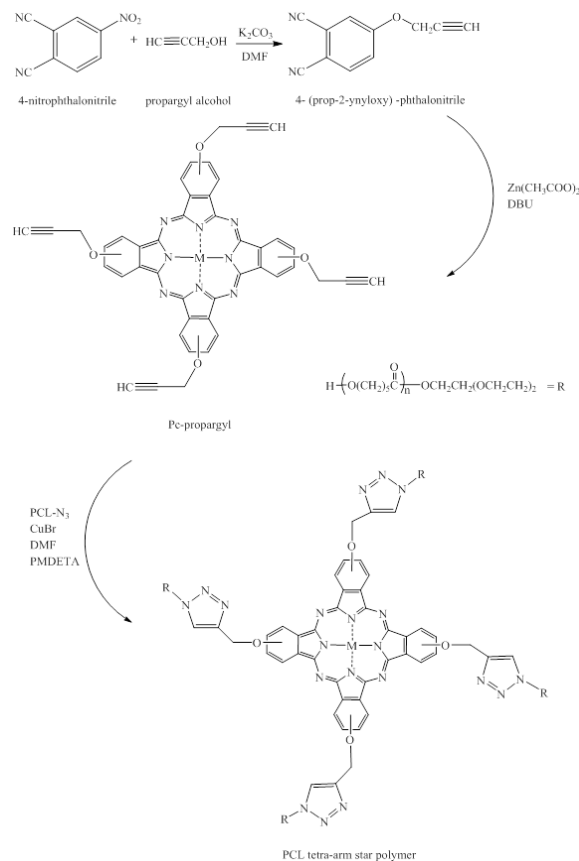
#### Synthesis of 4-(prop-2-ynyloxy)-phthalonitrile

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 °C. FT-IR

(ATR), wavenumber/(cm<sup>-1</sup>): 3284 (-C≡C-H), 3118 (C-H), 2987-2900 (C-H), 2229 (C≡N), 2135 (C≡C), 1593, 1492 (C=C), 1257, 1087 (C-O-C).



**Figure 2.** <sup>1</sup>H-NMR of PCL-N<sub>3</sub> (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-ynoxy)-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)  $\lambda_{\max}$ , nm (log  $\epsilon$ ): nm: 680, 610, 346. FT-IR (ATR) of Pc-propargyl (Figure 1A), wavenumber/(cm<sup>-1</sup>): 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-N<sub>3</sub> 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<sup>-1</sup>): 3450 (-OH), 2938 (-CH aliphatic), 1722 (-C=O), 1607, 1465 (-C=C aromatic), 1238 (C-O-C). <sup>1</sup>H-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

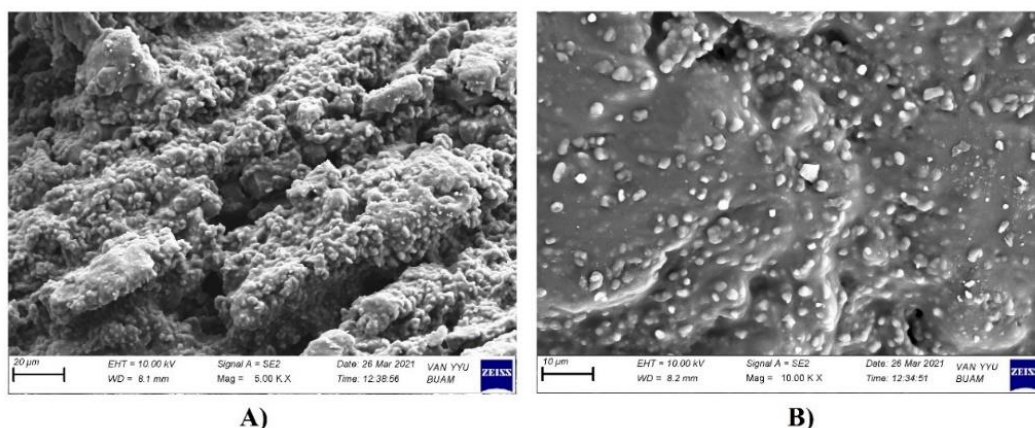


Figure 3. SEM displays of PCL tetra-arm star polymer: 5 000 X (A), 10 000 X (B).

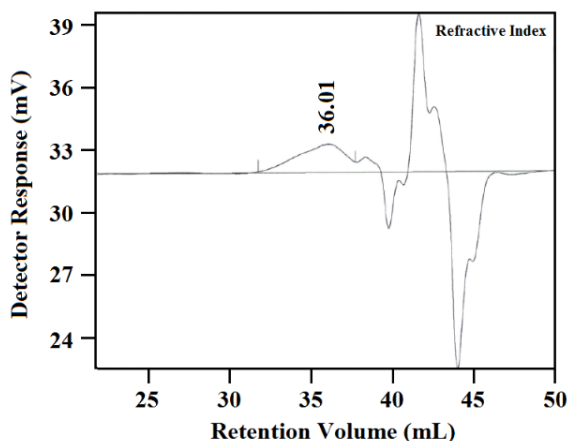


Figure 4. GPC diagram of PCL tetra-arm star polymer.

## 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( $\epsilon$ -caprolactone) and phthalocyanine. <sup>1</sup>H-NMR, FT-IR, SEM, UV-Vis, and GPC were carried out for the product characterizations.

## Conflict of interest

Authors declare no conflict of interest.

## References

- [1] M.S. Ağırtaş, B. Savaş, Characterization and synthesis of phthalocyanines prepared from 4-(5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy) phthalonitrile, *Journal of The Institute of Natural & Applied Sciences* 1 (2011) 12-16.
- [2] C.C. Leznoff, A.B.P. Lever, *Phthalocyanines properties and applications*, VCH-Wiley, New York, 1989, vol. 1, pp. 341-392.
- [3] S. Altun, A. Altındal, A.R. Özkaya, M. Bulut, Ö. Bekaroğlu, Synthesis, characterization, electrochemical and CO<sub>2</sub> sensing properties of novel mono and ball-type phthalocyanines with four phenolphthalein units, *Tetrahedron Letters* 49 (2008) 4483-4486.
- [4] K.M. Kadish, K.M. Smith, Guillard R The porphyrin handbook, Academic Press, New York, 18 (2003) 303-349.
- [5] Y. Li, P. Lu, X. Yan, L. Jin, Z. Peng, Non-aggregated hyperbranched phthalocyanines: single molecular nanostructures for efficient semi-opaque photovoltaics, *RSC Advances* 3 (2013) 545-558.

- [6] K.C. Lin, L. Wang, T. Doane, A. Kovalsky, S. Pejic, C. Burda, Combination of optical and electrical loss analyses for a Si-phthalocyanine dye-sensitized solar cell, *The Journal of Physical Chemistry B* 118 (2014) 14027-14036.
- [7] P. Zimcik, M. Miletin, V. Novakova, K. Kopecky, Z. Dvorakova, Tetrapyrrolineporphyrins with different number of peripheral pyridyl rings. Synthesis, photophysical and photochemical properties, *Dyes and Pigments* 81 (2009) 35-39.
- [8] V. Mantareva, I. Angelov, M. Aliosman, I. Stoineva, V. Kussovski, An overview on the impact of cationic phthalocyanine complexes for inactivation of drug-resistant microorganisms, *Photodiagnosis Photodynamic Therapy* 100 (2017) A43-A44.
- [9] G. Hizal, D. Sakar, U. Tunca, Synthesis of tri-arm star di-block co-polymer containing poly(tetrahydrofuran-*b*-methyl methacrylate) arms via combination of cationic ring-opening polymerization and photosensitized free radical polymerization routes, *Designed Monomers and Polymers* 8 (2005) 609-617.
- [10] T. Öztürk, A. Kılıçoğlu, B. Savaş, B. Hazer, Synthesis and characterization poly( $\epsilon$ -caprolactone-co-ethylene glycol) heteroarm star-type amphiphilic copolymers by "click" chemistry and ring-opening polymerization. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 55 (2008) 588-594.
- [11] T. Öztürk, M. Yavuz, M. Göktepe, B. Hazer, One-step synthesis of triarm block copolymers by simultaneous atom transfer radical and ring-opening polymerization, *Polymer Bulletin* 73 (2016) 1497-1513.
- [12] T. Öztürk, E. Meyvacı, Synthesis and characterization poly( $\epsilon$ -caprolactone-*b*-ethylene glycol-*b*- $\epsilon$ -caprolactone) ABA type block copolymers via "click" chemistry and ring-opening polymerization, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 54 (2017) 575-581.
- [13] E. Çatiker, T. Öztürk, M. Atakay, B. Salih, Synthesis and characterization of the ABA-type poly(ester-ether-ester) block copolymers. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 57 (2020) 600-609.
- [14] M. Chausson, A.S. Fluchère, E. Landreau, Y. Aguni, Y. Chevalier, T. Hamaide, N. Abdul-Malak, I. Bonnet, (2008) Block copolymers of the type poly(caprolactone)-*b*-poly(ethylene oxide) for the preparation and stabilization of nanoemulsions, *International Journal of Pharmaceutics* 362 (2008) 153-162.
- [15] T. Öztürk, C.A. Cavicchi, Synthesis and characterization of poly(epichlorohydrin-*g*- $\epsilon$ -caprolactone) graft copolymers by click chemistry, *Journal of Polymer Materials* 35 (2018) 209-220.
- [16] B. Savaş, E. Çatiker, T. Öztürk, E. Meyvacı, Synthesis and characterization of poly( $\alpha$ -methyl  $\beta$ -alanine)-poly( $\epsilon$ -caprolactone) tri arm star polymer by hydrogen transfer polymerization, ring-opening polymerization and "click" chemistry. *Journal of Polymer Research* 28 (2021) 1-10.
- [17] J.E. Moses, A.D. Moorhouse, The growing applications of click chemistry, *Chemical Society Reviews* 36 (2007) 1249-1262.
- [18] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click chemistry: diverse chemical function from a few good reactions, *Angewandte Chemie International Edition* 40 (2001) 2004-2021.
- [19] W.H. Binder, R. Sachsenhofer, 'Click' chemistry in polymer and materials science, *Macromolecular Rapid Communications* 28 (2017) 15-54.
- [20] O. Altıntaş, G. Hizal, U. Tunca, ABC-type hetero-arm star terpolymers through "click" chemistry, *Journal of Polymer Science Part A: Polymer Chemistry* 44 (2006) 5699-5707.
- [21] H. Dinçer, H. Mert, B.N. Şen, A. Dağ, S. Bayraktar, Synthesis and characterization of novel tetra terminal alkynyl-substituted phthalocyanines and their star polymers via click reaction, *Dyes and Pigments* 98 (2013) 246-254.
- [22] N.C. Yigit, G. Hizal, U. Tunca, Powerful tool for preparing peripherally post-functionalized multiarm star block copolymer, *Polymer Bulletin* 75 (2018) 3523-3538.
- [23] C.D. Hein, X. M. Liu, D. Wang, Click chemistry, a powerful tool for pharmaceutical sciences, *Pharmaceutical Research* 25 (2008) 2216-2230.
- [24] M.A. Taşdelen, Ç. Altınkök, In situ preparation of hetero-polymers/clay nanocomposites by CUAAC click chemistry, *Turkish Journal of Chemistry* 45 (2021) 50-59.
- [25] E. Çatiker, E. Meyvacı, M. Atakay, B. Salih, T. Öztürk, Synthesis and characterization of amphiphilic triblock copolymers including  $\beta$ -alanine/ $\alpha$ -methyl- $\beta$ -alanine and ethylene glycol by "click" chemistry, *Polymer Bulletin* 76 (2019) 2113-2128.
- [26] U. Tunca, Triple click reaction strategy for macromolecular diversity, *Macromolecular Rapid Communications* 34 (2013) 38-46.
- [27] A. Sethiya, N. Sahiba, S. Agarwal, Role of click chemistry in organic synthesis, *Current Topics in Chirality – From Chemistry to Biology*, T. Akitsu ed., IntechOpen Book Series, 2021.
- [28] U. Tunca, Click and multicomponent reactions work together for polymer chemistry, *Macromolecular Chemistry and Physics* 219 (2018) 1800163.
- [29] E. Meyvacı, T. Öztürk, B. Savaş, Syntheses and characterizations of poly( $\epsilon$ -caprolactone-*b*-ethylene glycol methyl ether) block copolymers via ring-opening polymerization and "click" chemistry, *Journal of the Institute of Science and Technology* 11 (2021) 1329-1340.
- [30] Y.R. Baker, W.R.J.D. Galloway, J.T. Hodgkinson, D.R. Spring, Design and synthesis of a biotinylated chemical probe for detecting the molecular targets of an inhibitor of the production of the pseudomonas aeruginosa virulence factor pyocyanin, *Molecules* 18 (2013) 11783-11796.
- [31] Ö. Koyun, S. Gördük, B. Keskin, A. Cetinkaya, A. Koca, U. Avcıata, Microwave-assisted synthesis,

electrochemistry and spectroelectrochemistry of phthalocyanines bearing tetra terminal-alkynyl functionalities and click approach, Polyhedron 113 (2016) 35-49.

*Received:* 25.10.2021

*Received in revised form:* 26.02.2022

*Accepted:* 28.02.2022