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Syntheses And Characterizations Of Poly(ϵ -Caprolactone-b-Ethylene Glycol Methyl Ether) Block Copolymers Via Ring-Opening Polymerization And "Click" Chemistry

Ergül MEYVACI¹, Temel ÖZTÜRK^{1*}, Bedrettin SAVAŞ²

ABSTRACT: Poly(ϵ -caprolactone-block-ethylene glycol methyl ether) [poly(RCL-b-mEG)] block copolymers were synthesized by "click" chemistry of polyethylene glycol methyl ether propargyl (mPEG-propargyl) and poly(ϵ -caprolactone) azido (RPCL-N₃). Thus, mPEG-propargyl was acquired through the reaction of polyethylene glycol methyl ether with propargyl bromine. 2-[2-(2-Azidoethoxy)ethoxy]ethanol (N₃ol) was synthesized by using 2-[2-(2-chloroethoxy)ethoxy]ethanol and sodium azide. Synthesis of RPCL-N₃ was acquired using ROP of ϵ -caprolactone and N₃ol. By using mPEG-propargyl and RPCL-N₃, poly(RCL-b-mEG) block copolymers were obtained via "click" chemistry. The monofunctional homopolymers in the study were utilized for the syntheses of poly(RCL-b-mEG) block copolymers. The outputs were identified by scanning electron microscopy, ¹H-nuclear magnetic resonance spectroscopy, differential scanning calorimetry, thermogravimetric analysis, Fourier-transform infrared spectroscopy, gel permeation chromatography, and dynamic light scattering instruments. The spectroscopic and thermal analysis of the block copolymers monitor that the copolymers were built through combination of ROP and "click" chemistry.

Keywords: Block copolymer, "click" chemistry, polyethylene glycol methyl ether propargyl, poly(ϵ -caprolactone) azido, ring-opening polymerization, 2-[2-(2-azidoethoxy)ethoxy]ethanol.

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INTRODUCTION

Polyethylene glycol (PEG) which is one of the most used hydrophilic segment (Adams, et al., 2003) is preferred in block copolymers possibly because it has got unique biocompatible properties (Çatıker, et al., 2020). PEG-based polymers are desirable materials of biomedical, industrial, and chemicals applications thanks to PEG's unique features (Erciyes et al., 1992; Adams, et al., 2003; Riess, 2003; Gacal, et al., 2006; Öztürk and Hazer, 2010; Çatıker, et al., 2020). Syntheses of block or graft copolymers were fulfilled because of their unique properties (Ruzette and Leibler, 2005; Öztürk, et al., 2011; Altıntaş et al., 2011; Bolton and Rzayev, 2012; Öztürk, Kaygın, et al., 2016; Öztürk, Cakmak et al., 2019; Çatıker, et al., 2019; Bağlan et al., 2018; Öztürk, Savaş, et al., 2020). The capability of amphiphilic block copolymers is owing to their chemical composition, which is described by a hydrophilic block chemically related to a hydrophobic block (Çatıker, et al., 2020). The ring-opening polymerization (ROP) technique was firstly carried out by Carothers et al. for lactones, cyclic anhydrides and carbonates (Hizal, et al., 2005; Coulembier, et al., 2006; Çatıker, et al., 2020;). ROP technique was widely used in the syntheses of new types of copolymers (Coulembier, et al., 2006; Göktaş et al., 2014; Öztürk, Yavuz, et al., 2016; Öztürk, et al., 2018). The applications in "click" chemistry have been examined (Moses and Moorhouse, 2007; Xu et al., 2007; Altıntaş and Tunca, 2011; Tunca, 2013; Xi et al., 2014; Zhu et al., 2015; Öztürk and Meyvacı 2017; Öztürk, et al., 2019) since "click" chemistry was presented by Sharpless et al. (Kolb et al., 2001) in 2001. Recently, "click" chemistry technique has been developed in the synthesis of polymers by increasing its place in science (Binder and Sachsenhofer, 2007; Barner-Kowollik et al., 2011; Şanal et al., 2017; Öztürk and Cavicchi, 2018; Tunca, 2018; Öztürk and Yörümez, 2020).

This paper demonstrates syntheses of poly(ϵ -caprolactone-block-ethylene glycol methyl ether) [poly(RCL-b-mEG)] block copolymers through ROP and "click" chemistry methods. Firstly, synthesis of polyethylene glycol methyl ether propargyl (mPEG-propargyl) obtained by reaction of polyethylene glycol methyl ether with 5,000 Da (mPEG-5000) and propargyl bromine was presented. Then, 2-[2-(2-azidoethoxy)ethoxy]ethanol (N₃ol) was synthesized by reaction of 2-[2-(2-chloroethoxy)ethoxy]ethanol and NaN₃ as ref. (Baker et al., 2013). After that, poly(ϵ -caprolactone) azido (RPCL-N₃) was acquired using ϵ -caprolactone (CL) and N₃ol by ROP technic. Lastly, RPCL-N₃ and mPEG-propargyl were utilized by "click" chemistry to obtain poly(RCL-b-mEG) block copolymers. Furthermore, the product characterization was provided in detail.

MATERIALS AND METHODS

Materials

Sigma-Aldrich supplied tin(II) 2-ethylhexanoate [Sn(Oct)₂], 2-[2-(2-chloroethoxy)ethoxy]ethanol, NaN₃, mPEG-5000, propargyl bromine, chloroform, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), ϵ -caprolactone (CL), CuBr. Triethylamine (TEA), methanol, diethyl ether were obtained from Merck, Kimetsan, and Carlo Erba Reagent, respectively.

Instrumentation

Records of ¹H-NMR spectra were obtained by ultra-long hold time 400 NMR spectrometers called as Bruker Ultra Shield Plus. FT-IR were obtained by Jasco FT/IR 6600 FT-IR spectrometer. Molecular weight and dispersity were studied by HPLC/GPC-Shimadzu RID-10A GPC instrument with THF at 40 °C through Refractive Index Detector. A calibration curve was generated with polystyrene standards of low dispersity (M_w = 1490, 2500, 5480, 9500, 20800 and 53500 Da). SEM displays were taken by using a Hitachi SU 1510 electron microscope. DSC measurement was obtained by Hitachi DSC 7000 series

thermal analysis system under N₂ gas. Dynamic light scattering (DLS) instrument was Malvern Zetasizer Nano Series Nano-ZS with Insmark IR120 model refractometer (solvent: DMF; concentration: 1 mg/mL, 0.5 mg/mL, and 0.25 mg/mL; temperature: 20 °C; λ = 633 nm). TGA were obtained by a Seiko II Exstar 6000 model instrument.

Synthesis of polyethylene glycol methyl ether propargyl (mPEG-propargyl)

Typically, 4.087 g (0.81 mmol) of mPEG-5000 and 0.110 g (1.08 mmol) of TEA in 10 mL of CHCl₃ was poured into a 250 mL clear flask with a N₂ input and cooled off to below 0 °C. 0.126 g (1.05 mmol) of propargyl bromine in 3 mL of CHCl₃ was put into this solution by a dropping funnel during 20 minutes. The solution was blended for 30 minutes below 0 °C. Next, the content slowly reached to ambient temperature. 24 hours later, CHCl₃ was to some extent vaporized. The residue was precipitated in cold excess diethyl ether. Following decantation, mPEG-propargyl was made dry at 40 °C in vacuum oven during 4 days. mPEG-propargyl output was obtained gravimetrically. The gravimetric yield was 98.79 wt% (4.162 g).

Synthesis of 2-[2-(2-azidoethoxy)ethoxy]ethanol (N₃ol)

N₃ol was synthesized as ref. (Baker et al., 2013). For instance, 2.227 g (0.01 mmol) of 2-[2-(2-chloroethoxy)ethoxy]ethanol, 4.039 g (0.06 mmol) of NaN₃, 60 mL of distilled water were poured into a 250 mL clear flask. Flask was dip in oil bath which was fixed at 70 °C on hot plate for reflux. After 22 hours, the reaction mixture was put into extraction process with diethyl ether (80 mL x 3). The organic layer was made dry on MgSO₄ and was vaporized until its drying to obtain N₃ol as a clear oil. Product yield was defined gravimetrically (0.475 g, 24.33 wt%).

Synthesis of poly(ϵ -caprolactone) azido (RPCL-N₃) through ROP

Poly(ϵ -caprolactone) azido which was presented RPCL-N₃ was achieved by ROP as procedures below: 4.100 g (0.041 mol) of CL, 0.475 g (0.002 mol) of N₃ol, Sn(Oct)₂ (1-2 drops) were placed separately in glass tube, then, N₂ gas was injected into tube for 5 min. Tube was covered with rubber septum, put into oil bath at 120 °C during 24 hours. After 24 hours, the content of the tube was mixed into cold excess diethyl ether for separation of RPCL-N₃. The product was placed in a fridge during a night. Following decantation, the polymer was made dry at 40 °C under vacuum during 4 days. Yield of RPCL-N₃ was 85.51 wt% (3.867 g).

Table 1. Syntheses of poly(RCL-b-mEG) copolymers by "click" chemistry.

Code	mPEG-propargyl (g)	RPCL-N ₃ (g)	Yield (g)	Yield (wt%)	Mw (g.mol ⁻¹)	Decomposition	
						Td1	Td2
E-1	0.243	0.144	0.303	78.15	9,160	306	411
E-2	0.242	0.244	0.455	93.72	6,510	340	399
E-3	0.247	0.344	0.445	75.25	10,400	334	399
E-4	0.245	0.417	0.550	83.12	8,620	343	394

Temperature: 35 °C, time: 48 hours, chloroform: 3 mL, copper(I) bromide: 0.003 g, PMDETA: 0.008 g.

Synthesis of poly(ϵ -caprolactone-block-ethylene glycol methyl ether) [poly(RCL-b-mEG)] by "click" chemistry

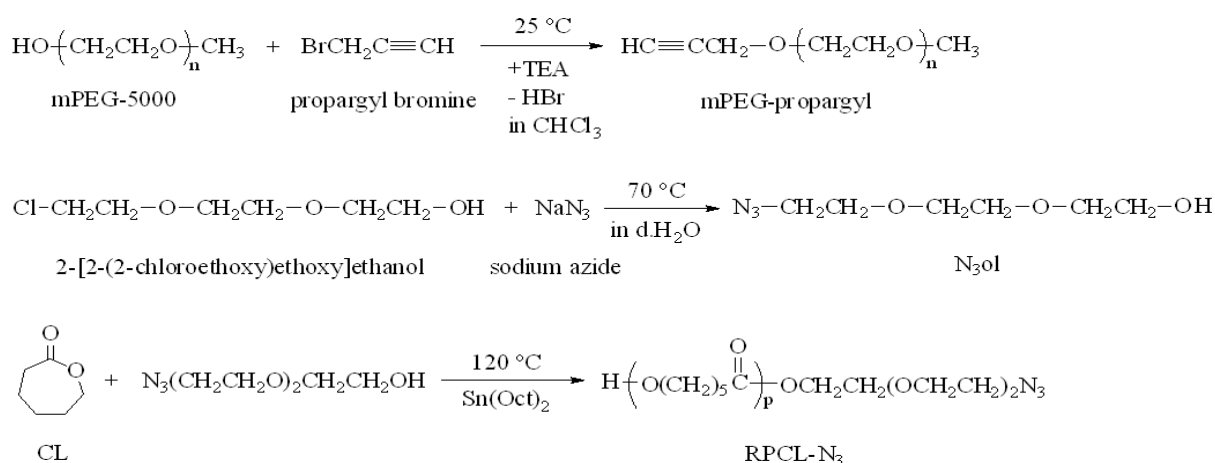
The amounts of the materials which were utilized in block copolymerization were presented in Table 1. mPEG-propargyl, RPCL-N₃, PMDETA, CuBr, chloroform was placed into glass tubes and then N₂ was injected into tube for 5 min. Tubes were placed in oil bath at 35 °C on a magnetic stirrer. 48 hours later, the contents of the tubes were strained out. CuBr left was removed with small alumina

columns from the block copolymers. The mixtures were poured into excess methanol for separation of precipitated poly(RCL-b-mEG) copolymers. The copolymers were dried in vacuum oven at ambient temperature during 4 days. Products were determined gravimetrically as shown in Table 1.

RESULTS AND DISCUSSION

Synthesis of mPEG-propargyl

mPEG-propargyl was acquired as white solid by mPEG-5000 ($^1\text{H-NMR}$ for mPEG-5000: 3.5 ppm for $-\text{OCH}_2$, 2.5 ppm for $-\text{OH}$). Reaction pathway is included on the first line of Scheme 1 for the synthesis of mPEG-propargyl. Figure 1.A shows FT-IR spectrum of mPEG-propargyl. The successful propargylation of mPEG-5000 is provided with the creation of acetylenic band at about 3150 cm^{-1} . $^1\text{H-NMR}$ spectrum of mPEG-propargyl in Figure 2A displayed peaks at 3.5 ppm for $-\text{OCH}_2$ of mPEG-5000, 3.4 ppm for $-\text{OCH}_2$ of propargyl group linked mPEG-5000 unit, 1.2 ppm for $-\text{C}\equiv\text{CH}$. Peak at 1.2 ppm for $-\text{C}\equiv\text{CH}$ in $^1\text{H-NMR}$ proved which mPEG-propargyl was successfully acquired.



Scheme 1. Reaction schemes for syntheses of mPEG-propargyl, N₃ol, and RPCL-N₃

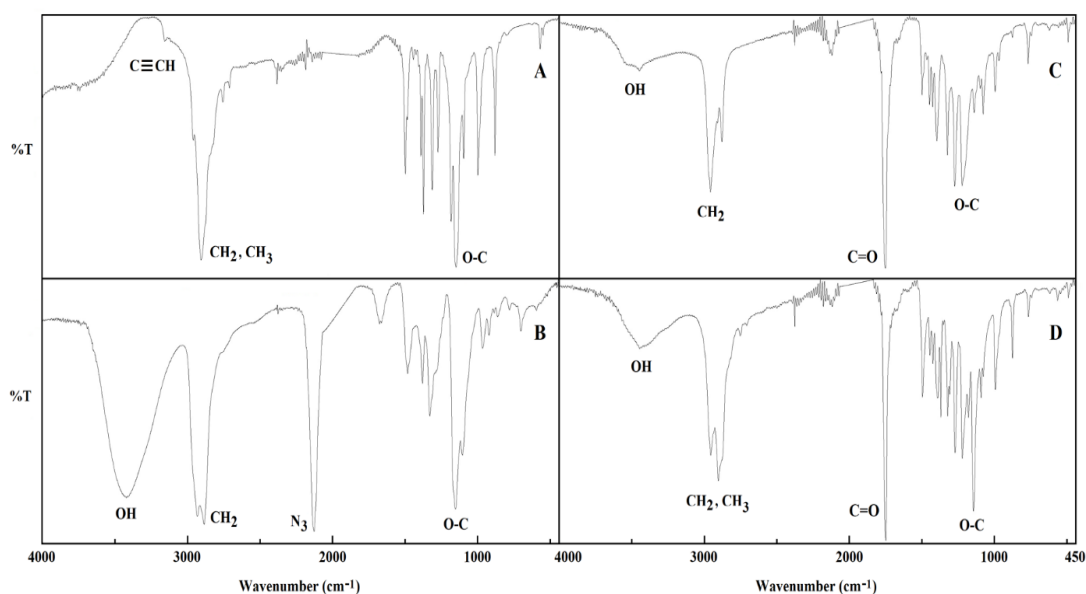


Figure 1. FT-IR spectra of mPEG-propargyl (A), N₃ol (B), RPCL-N₃ (C), and poly(RCL-b-mEG) block copolymer (D) (E-3 in Table 1).

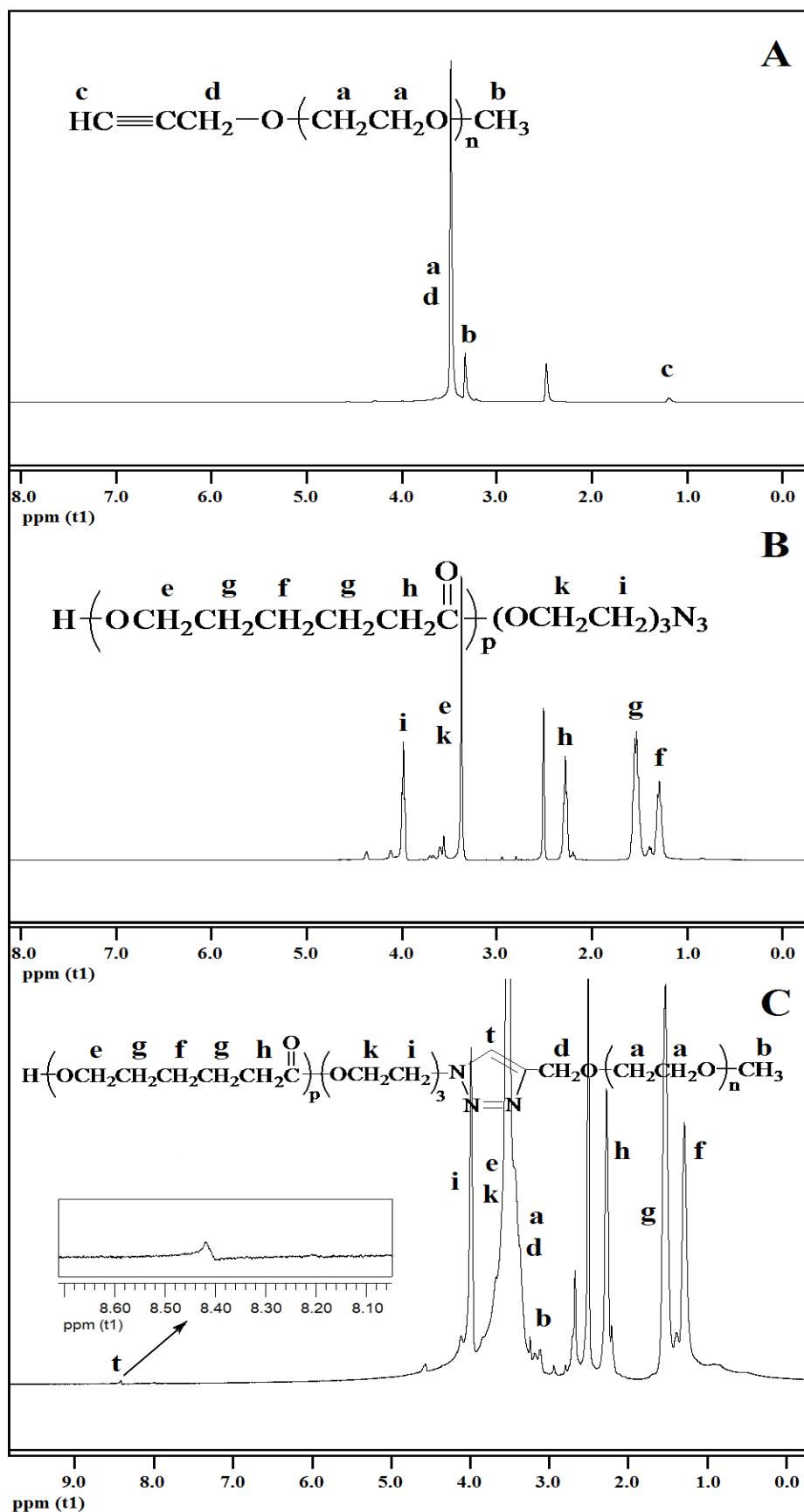


Figure 2. $^1\text{H-NMR}$ of mPEG-propargyl (A), RPCL- N_3 (B), poly(RCL-b-mEG) block copolymer (E-2 in Table 1) (C) (solvent: dimethyl sulfoxide- d_6).

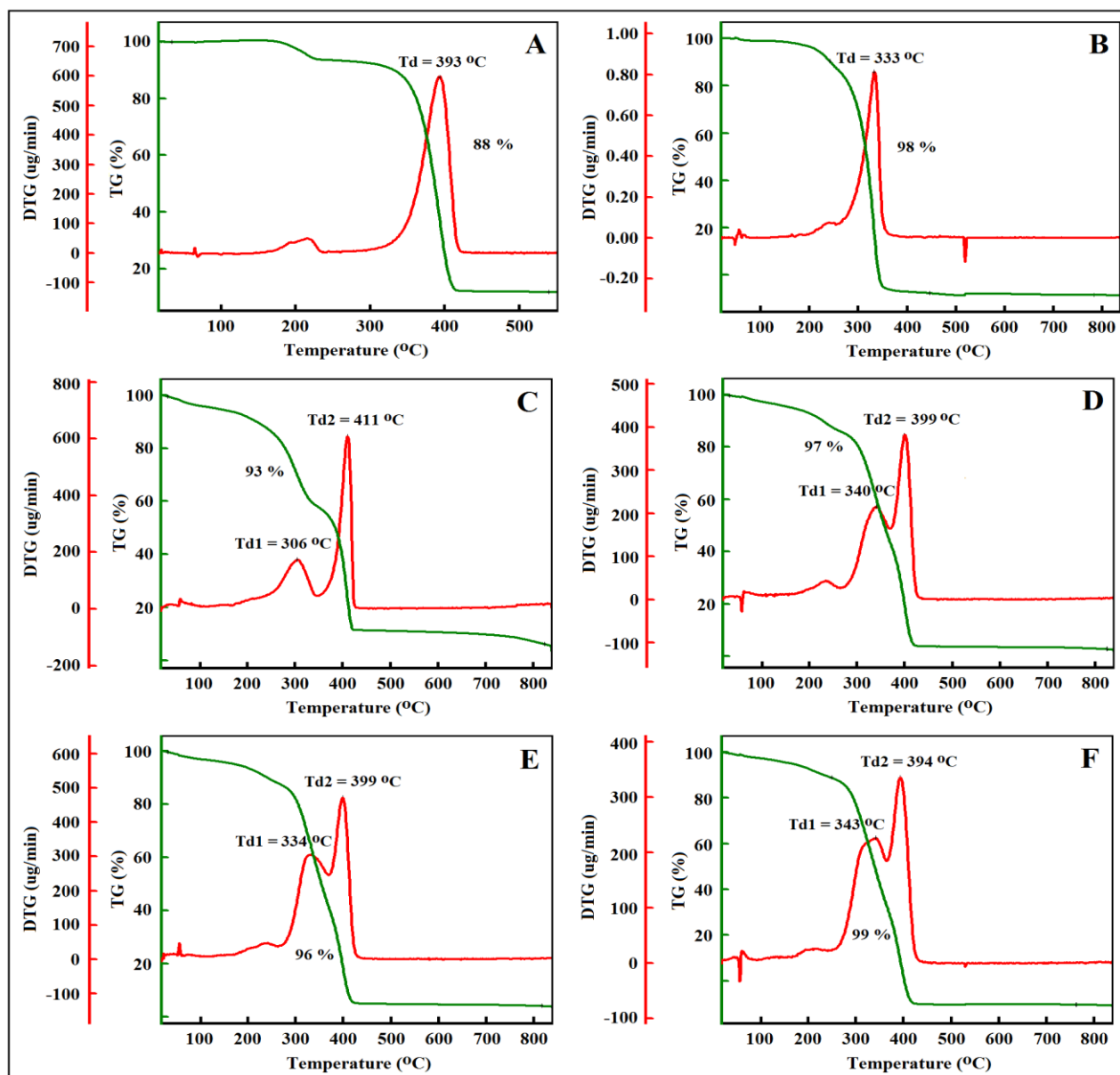


Figure 3. TGA curves of mPEG-propargyl (A), RPCL-N₃ (B), poly(RCL-b-mEG) block copolymer (E-1 in Table 1) (C), poly(RCL-b-mEG) block copolymer (E-2 in Table 1) (D), poly(RCL-b-mEG) block copolymer (E-3 in Table 1) (E), and poly(RCL-b-mEG) block copolymer (E-4 in Table 1) (F).

Synthesis of N₃ol

N₃ol as a colorless liquid was synthesized through reaction of 2-[2-(2-chloroethoxy)ethoxy]ethanol and NaN₃ (Baker et al., 2013). The reaction outline for N₃ol is shown in Scheme 1 (second line). FT-IR of N₃ol in Figure 1.B presented distinctive signals at 3414 cm⁻¹ for -OH, 2872 cm⁻¹ for aliphatic -CH₂, 2106 cm⁻¹ for -N₃, 1122 cm⁻¹ for -OC. Creation of specific -N₃ stretching band at about 2100 cm⁻¹ shows effective azidation of 2-[2-(2-chloroethoxy)ethoxy]ethanol.

Synthesis of RPCL-N₃ by ROP

RPCL-N₃ was synthesized by starting from N₃ol by ROP technique. The reaction pathway is included in Scheme 1 (third line) for RPCL-N₃. FT-IR of RPCL-N₃ as shown in Figure 1.C presented distinctive signals at 3440 cm⁻¹ for -OH, 2945 cm⁻¹ for aliphatic -CH₂, 1726 cm⁻¹ for -C=O. Figure 1.C shows small band feature at about 2099 cm⁻¹ specific for stretching vibration of azide. ¹H-NMR of

RPCL-N₃ (Figure 2.B) displayed peaks at 4.0 ppm for -NCH₂, 3.4 ppm for -OCH₂, 1.5 and 1.3 ppm for aliphatic -CH₂. Td value of RPCL-N₃ obtained from TGA was 333 °C as shown Figure 3.B. GPC curves of RPCL-N₃ were shown in Figure 4. Mw value of RPCL-N₃ was 2,264 Da. Dispersity index of RPCL-N₃ was 1.43. The value was relatively narrow.

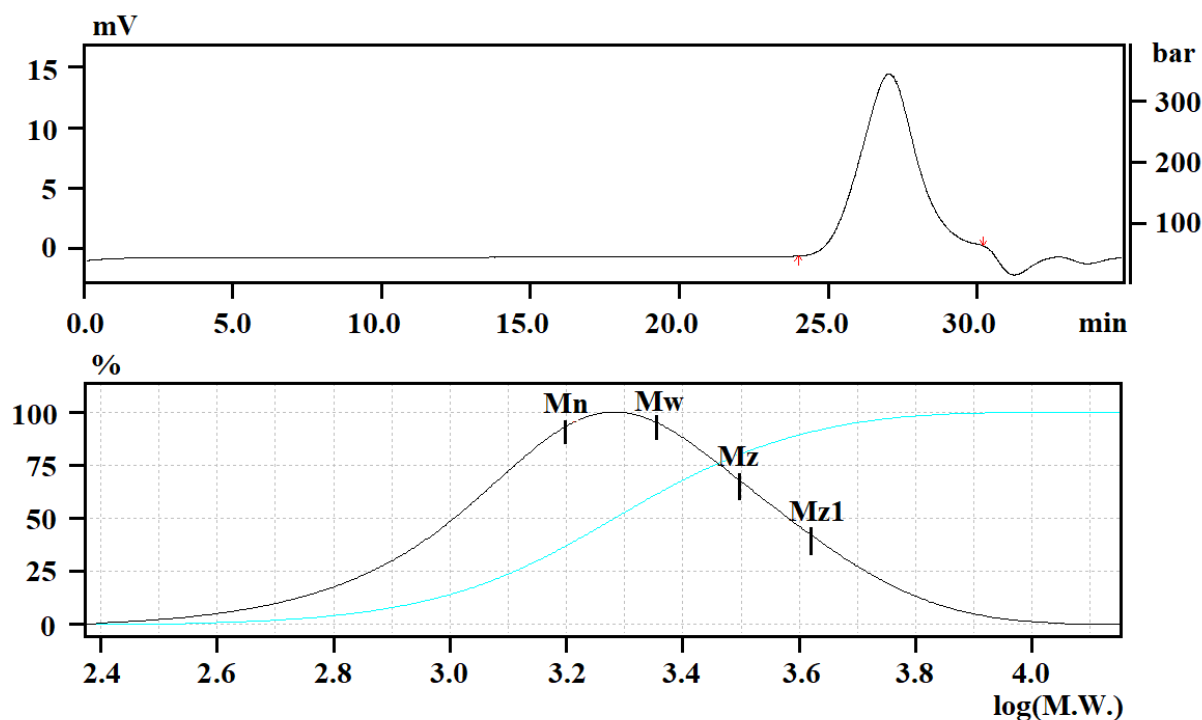


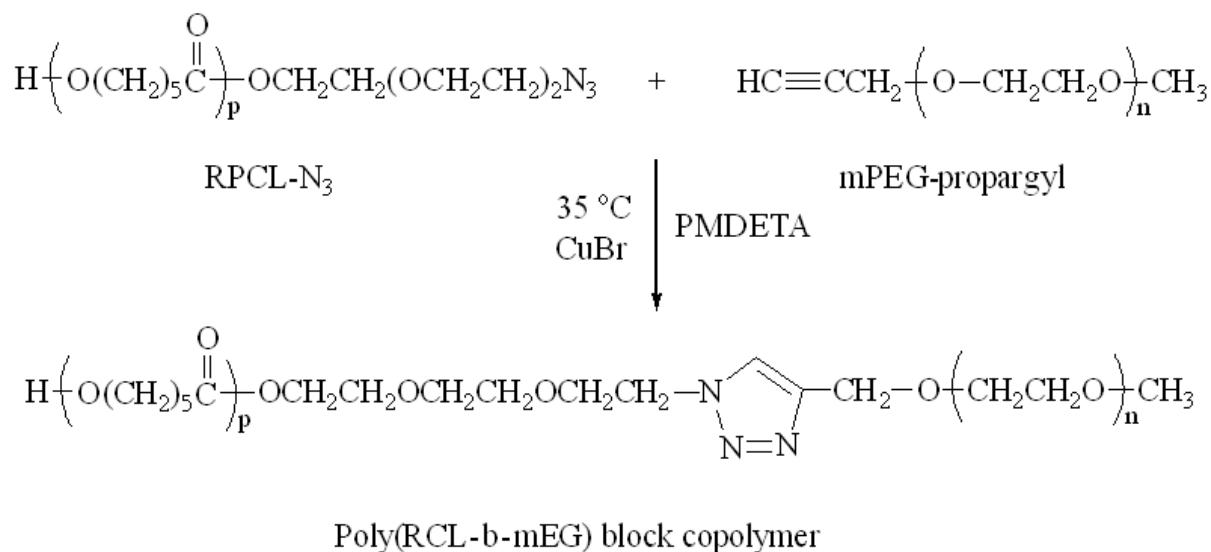
Figure 4. GPC curves of RPCL-N₃.

Synthesis of poly(RCL-b-mEG) by "click" chemistry

Poly(RCL-b-mEG) copolymers were obtained at 35 °C through "click" chemistry of mPEG-propargyl and RPCL-N₃. Pathway of reaction is included in Scheme 2 for the block copolymers. The yield was between 75.25 wt% and 93.72 wt%. The FT-IR of poly(RCL-b-mEG) as presented in Figure 1.D presents distinctive signals which belong to the PCL and mPEG-5000 units. Furthermore, the missing of azide (2106 cm⁻¹) and propargyl (3150 cm⁻¹) can be appropriate for "click" reaction between the homopolymers. Records of ¹H-NMR of poly(RCL-b-mEG) block copolymer in Figure 2.C were obtained. ¹H-NMR of poly(RCL-b-mEG) block copolymer displayed peaks at 8.4 ppm for aromatic -CH of triazole, 4.0 ppm for -NCH₂, 3.5 ppm for -OCH₂, 1.5 ppm and 1.2 ppm for aliphatic -CH₂. The signal at 8.4 ppm in the spectrum was regarded as a great evidence for aromatic -CH of triazole (Lakouraj et al., 2013; Rukmanikrishnan and Muthusamy, 2018; Çatıker, Meyvacı et al., 2019; Öztürk, Meyvacı et al., 2020).

Table 1 shows Td of poly(RCL-b-mEG) block copolymers which were obtained from TGA Figure 3 presents the TGA curves for all block copolymers. In the case of poly(RCL-b-mEG), PCL and PmEG include individual Td. As stated for many copolymers (Jamshid, 2008; Thanomsilp and Phetthianchai, 2012; Çatıker, et al., 2020; Savaş et al., 2020), units in a copolymer show Td as though units are alone. TGA demonstrated fascinating characteristics of copolymer such as continuous weight loss starting from about 200 °C to nearly 420 °C with derivatives at 306 °C and 411 °C (Figure 3.C). The glass temperature (Tg) value of poly(RCL-b-mEG) block copolymer (E-2 in Table 1) was determined by DSC. Tg value

was measured as 3 °C as shown in Figure 5. One main individual Tg of poly(RCL-b-mEG) block copolymer may be relied on high miscibility of mPEG polyether and PCL polyester units of copolymers. Mw of the block copolymers obtained from dynamic light scattering (DLS) instrument were between 6,510 Da and 10,400 Da. As the amounts of RPCL-N₃ have changed, Mw values of the block copolymers have interestingly also changed (Table 1). The relationship between Mw values of the block copolymers and the amounts of RPCL-N₃ could not be observed. The molecular weights of poly(RCL-b-mEG) block copolymers more than the molecular weight values of mPEG-propargyl and RPCL-N₃ could prove the formation of poly(RCL-b-mEG).



Scheme 2. Reaction outline for poly(RCL-b-mEG) copolymer.

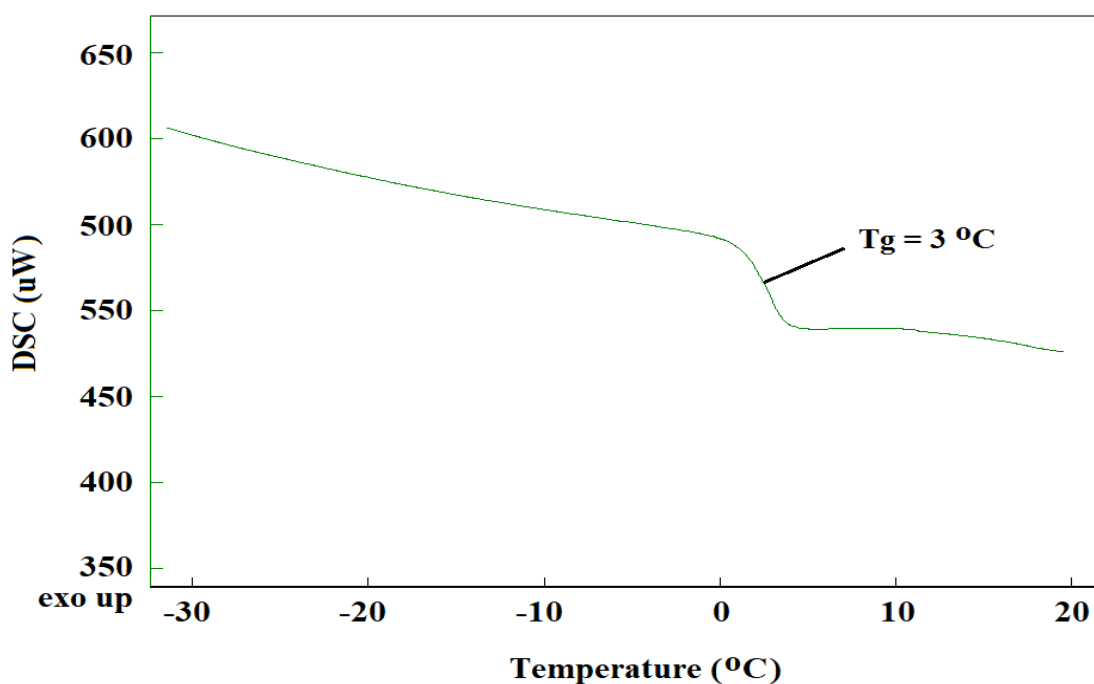


Figure 5. DSC diagram of poly(RCL-b-mEG) (E-2 in Table 1).

To examine the morphological properties of poly(RCL-b-mEG) block copolymer, SEM device was used. The polymer was coated with a thin layer of gold on its surface. The images were received from different views. The surface morphologies of poly(RCL-b-mEG) block copolymer (E-1 in Table 1) was shown in Figure 6. According to the SEM images of copolymer, homogenization of copolymer was great. By a morphology consisting platelets with channels, the polymer sample was characterized. The rough surfaces which form a continuous phase were recognized.

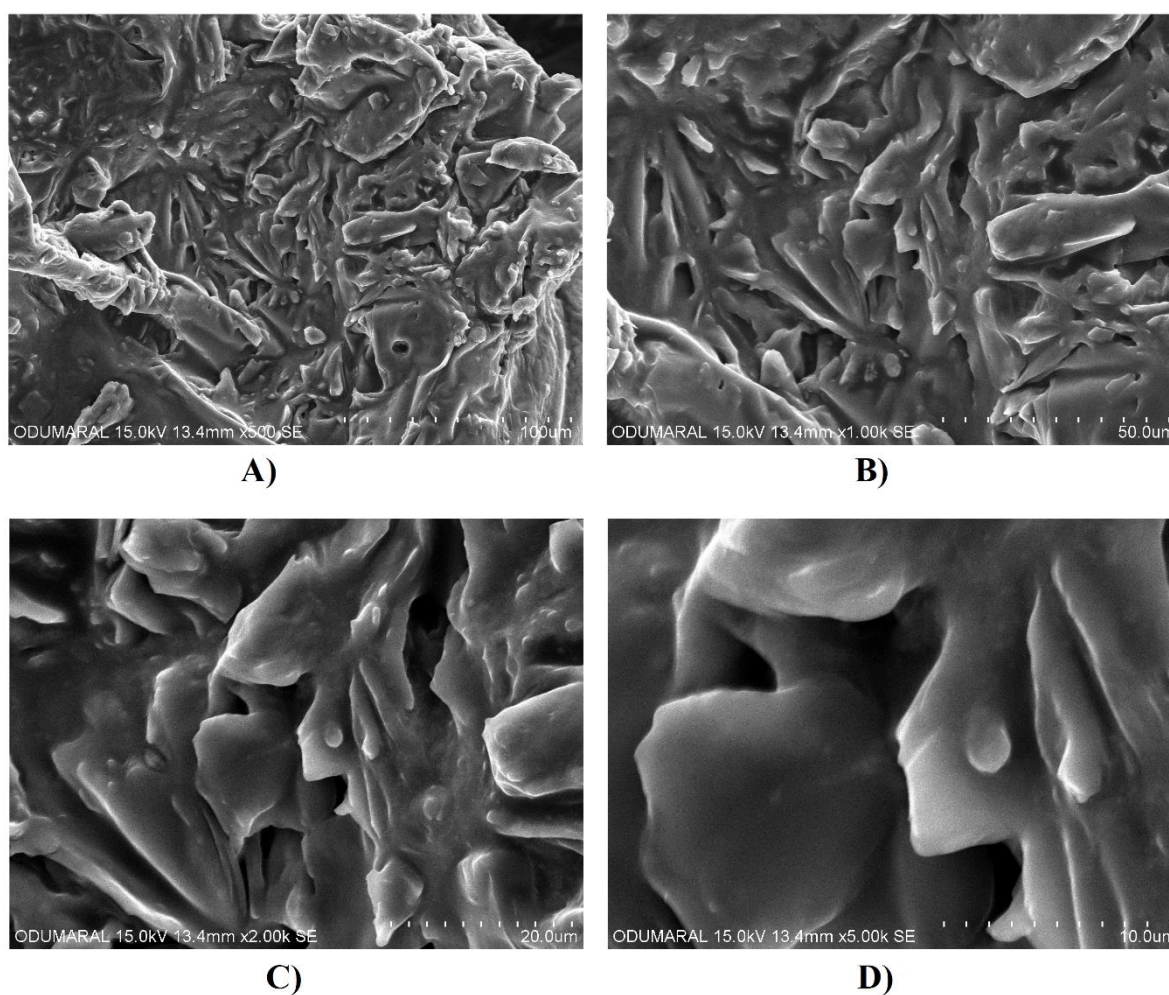


Figure 6. SEM displays of poly(RCL-b-mEG) (coded E-1); 500 X (A), 1000 X (B), 2000 X (C), 5000 X (D).

CONCLUSION

This work shows synthesis of poly(RCL-b-mEG). This procedure used to synthesize block copolymer is easy and effective. This work can lead the way for further and well-conceived materials used for many applications by means of combination of PCL and mPEG. Product characterization was obtained through $^1\text{H-NMR}$, SEM, FT-IR, TGA, DSC, DLS, GPC analyses.

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Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author's Contributions

The authors declare that they have contributed equally to the article.

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