



Synthesis and Characterization of Poly (Epichlorohydrin-Graft-Ethylene Glycol) Graft Copolymers by “Click” Chemistry

“Click” Kimyası ile Poli (Epiklorhidrin–G–Etilen Glikol) Graft Kopolimerlerin Sentezi ve Karakterizasyonu

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Abstract

Synthesis of poly (epichlorohydrin-g-ethylene glycol) [poly (ECH-g-EG)] graft copolymer was reported by means of “click” chemistry. For this purpose, epichlorohydrin (ECH) was polymerized by using H_2SO_4 via cationic ring-opening mechanism. Propargyl polyethylene glycol-1000 (propargyl PEG-1000) was synthesized by the reaction of polyethylene glycol (PEG) with 1000 Da and propargyl chloride. Terminally azide polyepichlorohydrin (PECH- N_3) was obtained by reaction of poly (epichlorohydrin) (PECH) and sodium azide. By using PECH- N_3 and propargyl PEG-1000, poly (ECH-g-EG) graft copolymers were synthesized. The graft copolymers were relatively obtained in high yield. The characterization of products was accomplished by using multi instruments and methods such as nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, gel permeation chromatography, elemental analysis, thermogravimetric analysis, and fractional precipitation [solvent (THF, mL)/non-solvent (petroleum ether, mL)] techniques. This method which is used for polymer synthesis is simple, effective, eco-friendly and has low energy consumption.

Keywords: “Click” chemistry, Fractional precipitation, Graft copolymer, Polyepichlorohydrin, Polyethylene glycol

Öz

Poli (epiklorhidrin-g-polietilen glikol) [poli (ECH-g-EG)] graft kopolimerlerin sentezi “click” kimyası metodu ile rapor edilmektedir. Bu amaçla, epiklorhidrin (ECH), H_2SO_4 ile katyonik halka-açılması polimerizasyonu üzerinden polimerleştirildi. Propargil polietilen glikol-1000 (propargil PEG-1000), propargil klorür ve 1000 Da molekül ağırlığına sahip polietilen glikolün (PEG) reaksiyonu ile sentezlendi. Poliepioklorhidrin azit (PECH- N_3), poliepioklorhidrin ve sodyum azidin reaksiyonu ile elde edildi. PECH- N_3 ve propargil PEG-1000 kullanılarak poli (ECH-g-EG) graft kopolimerler nispeten yüksek verimle sentezlendi. Ürünler, fraksiyonlu çöktürme [çözücü (THF, mL)/çöktürücü (petrol eteri, mL)] ile saflaştırıldı; nükleer manyetik rezonans spektroskopisi, Fourier transform infrared spektroskopisi, gel geçirgenlik kromatografisi, elemental analiz ve termogravimetric analiz cihazları kullanılarak karakterize edildi. Polimer sentezi için kullanılan bu metot basit, etkili, çevre dostu ve düşük enerji tüketimine sahiptir.

Anahtar Kelimeler: “Click” kimyası, Fraksiyonlu çöktürme, Graft kopolimer, Poliepioklorhidrin, Polietilen glikol

1. Introduction

“Click” chemistry, a technique presented by Sharpless et al. (2001), comprised a set of simple strong linking reactions which have high conversions, take minimum purification, and are skilled in participation different structures without the prerequisite (Wang et al. 2008). “Click” chemistry applications have been extensively carried out lately (Tu et al.

2012, Zhang et al. 2015, Scott et al. 2012, Liu et al. 2007). Ring-opening polymerization (ROP) technique has been performed to many monomers with a lot of initiators and catalyst systems (Dubois et al. 2006, Öztürk et al. 2014). The recent described synthesis of graft copolymers is a significant subject in polymer chemistry (Nuyken et al. 2002). Graft copolymers that supply particular compositions of physical properties are the most appropriate substances for different goals (Öztürk et al. 2013). Block and/or graft copolymers, having polyethylene glycol (PEG) blocks, are very appealing matters for chemicals, industrial and biomedical experien-

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ces, as PEG has matchless features such great hydrophilicity, flexibility, ion absorbability, and biocompatibility (Pitsikalis et al. 2006, Schue et al.2010, Carlo et al. 1999, Velichkova and Christova 1995, Riess 2003, Luo et al. 2008, Huang et al. 2008, Öztürk and Hazer 2010, Hazer 2010). Poly (epichlorohydrin) (PECH), an interesting commercially available polymer, is presented in a lot of synthesis of block/graft copolymer (Yagci et al. 2002, Al-Kaabi and van Reene 2008, Feng et al. 2015).

In this work, the synthesis of propargyl polyethylene glycol-1000 (propargyl PEG-1000) obtained by reaction of PEG (1000 Da) with propargyl chloride were introduced in the present study. Epichlorohydrin (ECH) was polymerized by using H_2SO_4 via cationic ring-opening mechanism. Terminally azide polyepichlorohydrin (PECH- N_3) was synthesized by using the reaction of PECH with sodium azide (NaN_3). Propargyl PEG-1000 and PECH- N_3 were used to obtain poly (epichlorohydrin-g-ethylene glycol) [poly (ECH-g-EG)] graft copolymers via “click” chemistry. Characterizations of the products were discussed in detail.

2. Material and Methods

Copper (I) bromide (CuBr), ECH, N,N-dimethylformamide (DMF), NaN_3 , 2,2'-bipyridyl (bpy), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA), copper (I) chloride (CuCl), propargyl chloride, chloroform, and dichloromethane were received from Sigma-Aldrich, tetrahydrofuran (THF), PEG with 1000 Da, methanol, triethylamine, and H_2SO_4 were supplied by Merck Millipore and all used as received. Diethyl ether and petroleum ether were received from Carlo Erba Reagent and all used without further purification. The other chemicals were reagent grade and used as supplied.

The molecular weights were determined by Malvern Viscotek RI-UV-GPC max gel permeation chromatography (GPC) with THF as solvent. A calibration curve was composed by using three polystyrene standards: 2,960, 50,400, and 696,500 Da, of low polydispersity. Fourier transform infrared (FTIR) spectra were detected using an Agilent Technologies Cary 660 model FTIR spectrometer. 1H -nuclear magnetic resonance (1H -NMR) spectra of the products in deuterated chloroform as the solvent, with tetra methylsilane as internal standard, were detected using a Bruker AVANCE III, ultra-long hold time 400 MHz NMR spectrometer. The elemental analyses of the samples were performed on a Costech ECS 4010 instrument. Thermal analysis measurements of the polymers were carried

out under nitrogen using a Setaram Labsys Evo (TG/DSC 1600) to determine thermal degradation.

2.1. Synthesis of PECH by Cationic Ring-Opening Polymerization

The similar procedure described in the cited literatures was applied for synthesize PECH (Öztürk et al. 2013, Öztürk et al. 2016). 25 mL of dichloromethane and 2.5 mL of 96 % H_2SO_4 were placed into a flask equipped with a magnetic stirrer, and subsequently argon was purged into the tube through a needle. To this system, 21 mL (24.843 g) of ECH was added over 4 h periods. After this time, the flask was opened and the sample was poured into 1 L of distilled water to remove the inorganic materials. Then the organic phase was separated. After the organic phase was dried with Na_2SO_4 , the solvent was removed by using a rotary evaporator. A viscous liquid, PECH, was obtained. The yield of polymer was determined gravimetrically.

2.2. Synthesis of Terminally Azide PECH- N_3 (PECH- N_3)

15.04 gram of PECH, 0.75 gram of NaN_3 , and 30 mL of DMF were placed into a flask. The flask was immersed in an oil bath fixed at 70 °C on a magnetic stirrer, and afterwards nitrogen gas was introduced in the tube by injection with a needle. After 59 hours, the flask was opened, and the content was filtered. The sample was poured into 1 L of water to remove unreacted NaN_3 and then the organic phase was separated. The solvent was evaporated by using a rotary evaporator. The mixture was drained into excess cold diethyl ether and kept in the refrigerator overnight. After decantation of cold diethyl ether, the product was dried under vacuum at room temperature for two days. Yield of PECH- N_3 was defined gravimetrically.

2.3. Synthesis of Propargyl Polyethylene Glycol-1000 (Propargyl PEG-1000)

The similar procedure reported in the cited literature (Bakker et al. 2013, Asan and Öztürk 2016) was used for synthesis of propargyl PEGs by using PEG. 15 g (15 mmol) of PEG with 1000 Da in 40 mL of THF was mixed with 0.21 mL (15 mmol) of triethylamine. The solution was transported into a 250 mL schlenk flask with a magnet and a nitrogen gas input. The flask was cooled down to below 0 °C and nitrogen gas was injected into the flask. This solution was added 1.12 gram (1.2 mL, 15 mmol) of propargyl chloride in 5 mL of THF via a dropping funnel for the duration of half an hour. The solution was stirred for two hours at down to below 0 °C. Afterwards, the mixture was slowly warmed

to room temperature. After 48 hours, the reaction was terminated. Solvent was partially evaporated and the residue precipitated in cold diethyl ether. The product was kept in a refrigerator overnight. After decantation, the product was dried at room temperature under vacuum for two days. The yield of propargyl PEG-1000 was defined gravimetrically.

2.4. Synthesis of Poly (ECH-g-EG) Graft Copolymers by “Click” Chemistry

Poly (ECH-g-EG) was synthesized by “click” chemistry in the present study. Specified amounts of PECH-N₃, propargyl PEG-1000, CuBr (or CuCl), bpy (or PMTEDA), and chloroform (or THF) as solvent were charged separately into a 250 mL schlenk flask in according to “click” chemistry mechanism, then, nitrogen gas was injected in the tube for five minutes. The flask was immersed in an oil bath thermostated at 45 °C for specific times. After the polymerization, the flask content was filtered. Solvent was partly moved away by using a rotary evaporator. The mixture was drained into excess methanol to separate poly (ECH-g-EG) graft copolymer. The polymers were dried at room temperature under vacuum for two days. The conversion of graft copolymer was defined gravimetrically.

2.5. Fractional Precipitation of the Graft Copolymers

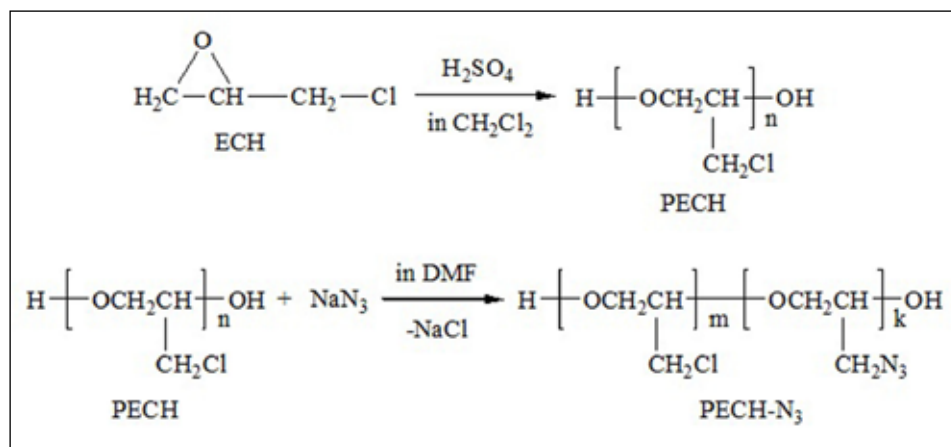
Fractional precipitations (γ) of the polymers were determined by following to the process stated in the literatures (Öztürk et al. 2014, Hazer et al. 1994, Hazer et al. 2016, Öztürk et al. 2011, Öztürk et al. 2014). Vacuum dried polymer sample (about 0.1 g) was dissolved in 10 mL THF. Petroleum ether was added as drop wise to 5 mL of the solution with mixing until turbidity forms, and then 1-2 mL petroleum ether was added to complete the precipitation. The precipitate was removed by filtration. In this solvent–nonsolvent system, the γ values were found from the following equation.

$$\gamma \text{ value} = \frac{\text{Volume of Nonsolvent, mL (petroleum ether)}}{\text{Volume of solvent, mL (THF)}}$$

3. Results and Discussion

Poly (ECH-g-EG) graft copolymer was reported by means of “click” chemistry method. This method which is used for polymer synthesis is simple, effective, eco-friendly and has low energy consumption. PECH with hydroxyl groups in the chain end was prepared by cationic ring-opening polymerization of ECH using H₂SO₄ as catalyst. Cationic ring-opening polymerization of ECH was carried out by a slow addition of a solution of H₂SO₄ to ECH. Growing PECH chain was terminated with water to yield -OH terminated PECH. The yield of the product was 91.05 wt%. The first line in Scheme 1 contains the basic outline for the synthesis of PECH. The ¹H-NMR spectrum of PECH in Figure 1(a) shows 4.3 ppm for -OCH₂ protons, 3.6 ppm for -OCH₂ and -ClCH₂ protons, 3.4 ppm for -OCH protons, and 2.5 ppm for -OH protons.

PECH-N₃ was synthesized by using synthesized PECH. The second line in Scheme 1 includes the reaction pathway for synthesis of PECH-N₃. PECH-N₃ yield was 48.95 wt%. The FTIR spectrum of PECH-N₃ in Figure 2(a) shows 3480 cm⁻¹ for -OH groups, 2880 cm⁻¹ for aliphatic -CH₂ groups, 2280 cm⁻¹ for -N₃ groups and 1100 cm⁻¹ for -OC groups. The ¹H-NMR spectrum of PECH-N₃ in Figure 1(b) shows 4.4 ppm for -OCH₂ protons, 3.6 ppm for -OCH₂ and -ClCH₂ protons, 3.4 ppm for -OCH protons, 3.0 ppm for -NCH₂ protons, and 2.2 ppm for -OH protons. Elemental analysis showed 6.72 wt% of nitrogen related to azide content. By using 6.72 wt% N and molecular weight of PECH-N₃, we found that the number of the xanthogenate groups was approximately 3 per chain.



Scheme 1. Reaction pathways in the synthesis of PECH and PECH-N₃.

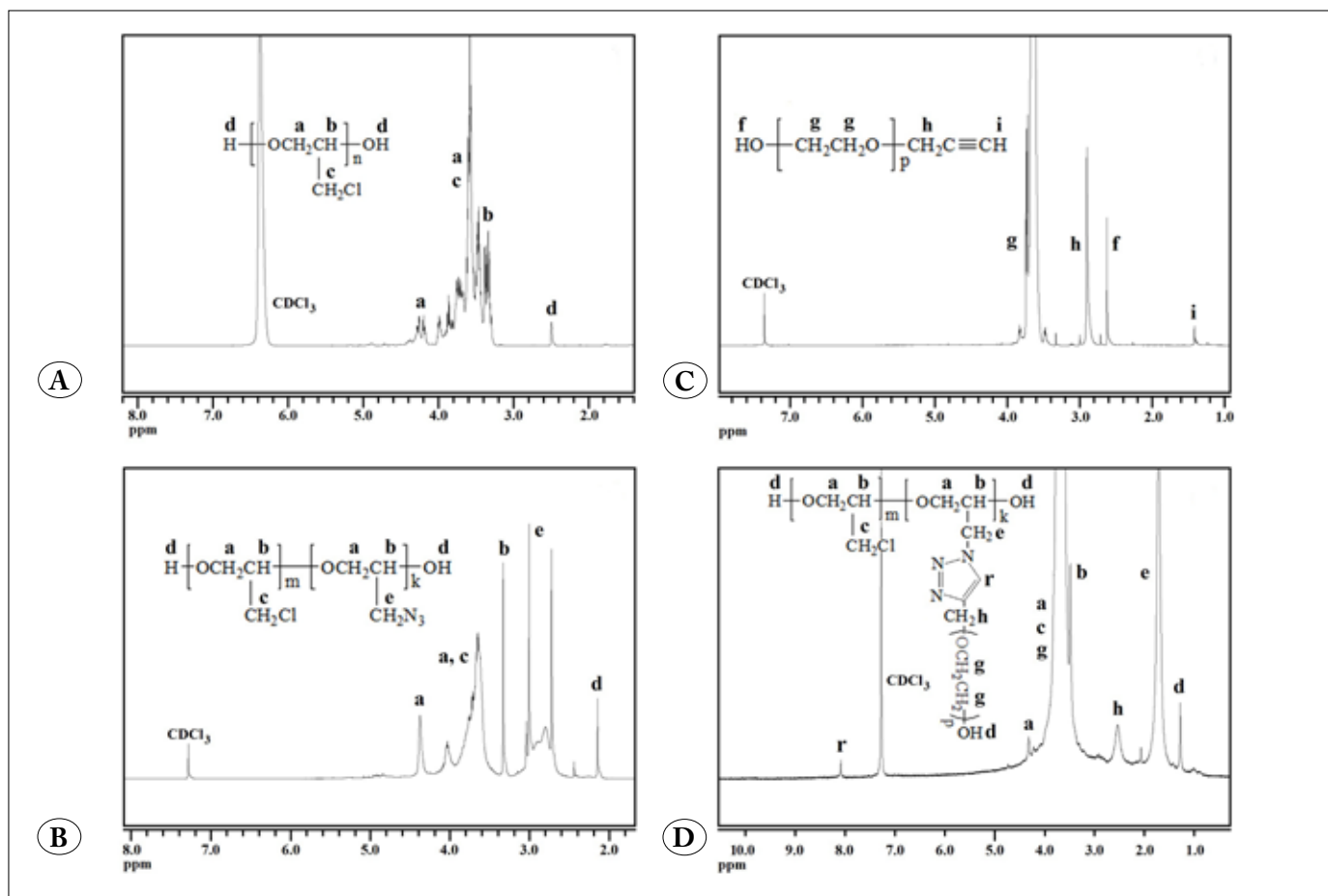


Figure 1. $^1\text{H-NMR}$ spectra of (A) PECH; (B) PECH- N_3 ; (C) propargyl PEG-1000; and (D) poly (ECH-g-EG).

Propargyl PEG-1000 was synthesized by using PEG with 1000 Da. The first line in Scheme 2 includes the reaction pathway for synthesis of propargyl PEG-1000. The FTIR spectrum of propargyl PEG-1000 in Figure 2(b) indicates the characteristic signals at 3400 cm^{-1} for $-\text{OH}$ groups, 1880 cm^{-1} for aliphatic $-\text{CH}_2$ groups, 2750 cm^{-1} for $\text{C}\equiv\text{C}$ groups, and 1100 cm^{-1} for $-\text{OC}$ groups. The $^1\text{H-NMR}$ spectrum of the product in Figure 1(c) also shows 1.4 ppm for $-\text{CH}$ protons, 2.6 ppm for $-\text{OH}$ protons, 3.0 ppm for $-\text{OCH}_2$ protons linked PEG block, 3.7 ppm for $-\text{OCH}_2$ protons of PEG block. It is more probably that there will be a population of three types of PEG which possess zero, one, and two propargyl end groups. As we used [propargyl chloride]/[PEG] = 1/1 (mol/mol) in the reaction, we think that there could be zero and two propargyl end groups at very little amounts. To the best of our knowledge, the large quantity propargyl PEG has been obtained with a propargyl group in the chain end as we are used 1/1 (mol/mol) ratio to synthesize propargyl PEG. The other propargyl PEG possessed two propargyl functions could be acquired at the

little quantities in the chain end. We are taking into account of propargyl PEG having a hydroxyl function and propargyl function for synthesis of the graft copolymer.

A set of synthesis, “click” chemistry conditions of the graft copolymers, were achieved. The graft copolymers were relatively acquired in high yield. The proposed procedure for the synthesis of graft copolymers is simple and efficient. The characterization of graft copolymers was accomplished by using $^1\text{H-NMR}$ spectroscopy, FTIR spectroscopy, GPC, and fractional precipitation techniques. Poly (ECH-g-EG) graft copolymers were synthesized at $45\text{ }^\circ\text{C}$ temperature by using “click” chemistry of propargyl PEG with 1000 Da and PECH- N_3 . The results of graft polymerization were shown in Table 1. The conversion obtained from weight of copolymer was between 45.65 wt% and 77.36 wt%. High conversions were relatively obtained by “click” chemistry of propargyl PEG and PECH- N_3 . The outline for synthesis of poly (ECH-g-EG) graft copolymer was shown in Scheme 2. The FTIR spectrum of poly (ECH-g-EG) graft copoly-

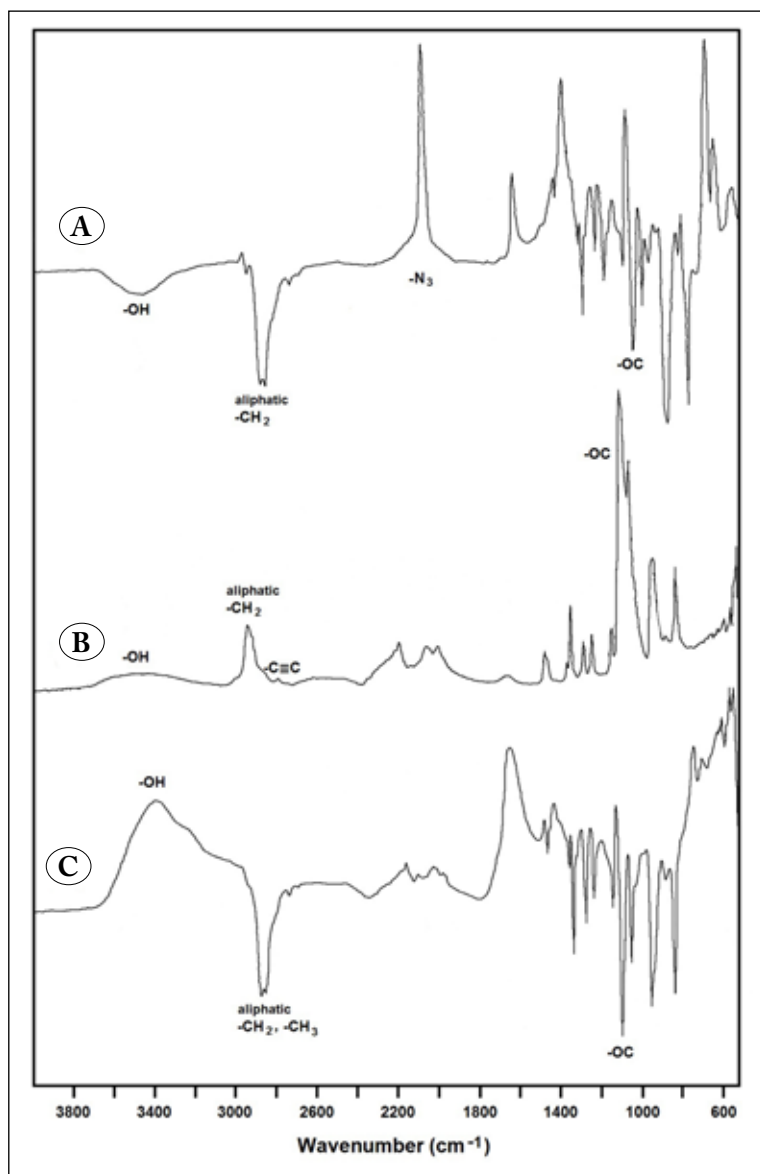


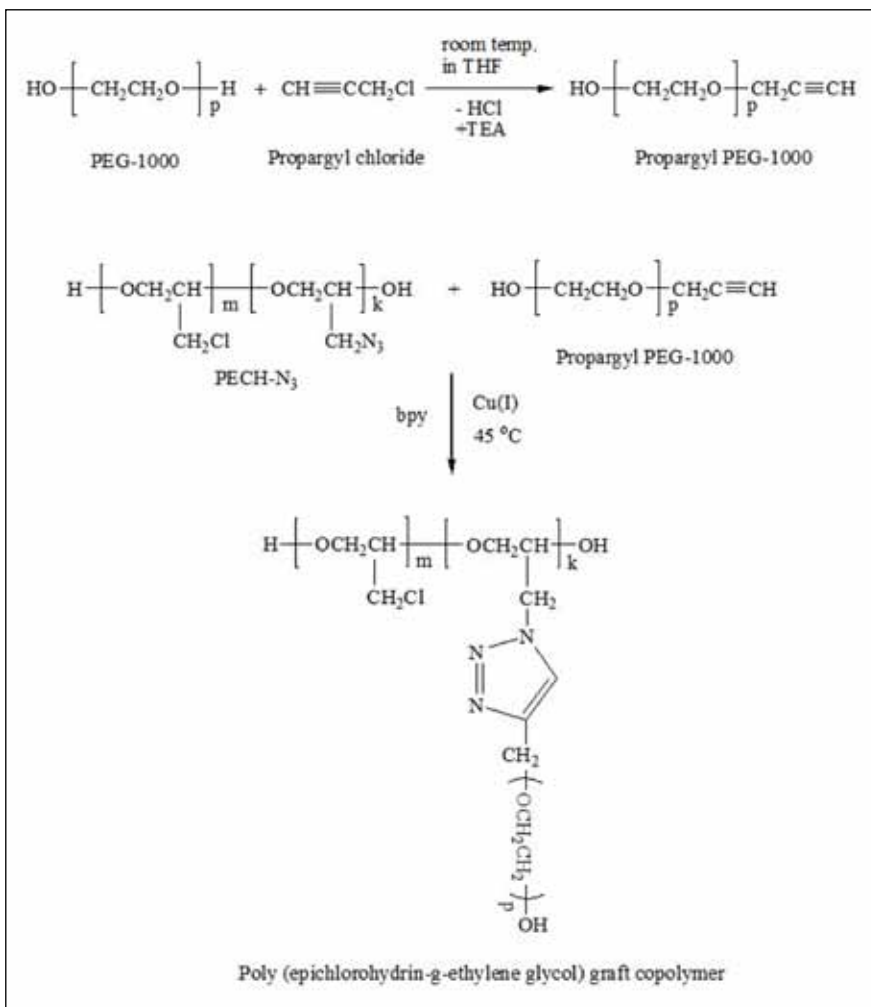
Figure 2. FTIR spectrum of (A) PECH-N₃; (B) propargyl PEG-1000; and (C) poly (ECH-g-EG).

mer in Figure 2(c) shows the signals at 3400 cm⁻¹ for -OH groups, 2880 cm⁻¹ and 2840 cm⁻¹ for aliphatic -CH and -CH₂ groups, 1100 cm⁻¹ for -OC groups. Typical ¹H-NMR spectra of the graft copolymers in Figure 1(d) shows 8.0 ppm for aromatic -CH proton of triazole group, 4.3 ppm for -OCH₂ protons of PECH-N₃ group, 3.8 ppm for -OCH₂ and -ClCH₂ protons of PECH-N₃ group and for -OCH₂ of PEG group, 2.5 ppm for -OCH₂ protons linked PEG block and triazole group, 1.8 ppm for -NCH₂ protons linked PECH and triazole group, and 1.3 ppm for -OH protons. The observed peak at 8.0 ppm for aromatic -CH proton of triazole group was evidence which the graft copolymer was obtained. Mn value of the graft copolymer (HA-1 in Table 1) is 2,569 gmol⁻¹. Polydispersity index of the copolymer is

1.03. This value of the graft copolymer is very low. Figure 3 shows the GPC curve of graft copolymer.

Thermal analysis of the graft copolymers was carried out by taking TGA curves. Decomposition temperatures (T_d) of the graft copolymers are shown in Table 1. The only one decomposition temperature value for the graft copolymer (HA-1 in Table 1) can show the miscible nature of the related polymers. TGA has showed interesting properties of the copolymers indicating continuous weight loss starting from 180 °C to nearly 660 °C (Figure 4).

Fractional precipitation experiments provide definite evidence for the formation of block or graft copolymers (Wu et al 1999). The γ values of poly (ECH-g-EG) graft copoly-



Scheme 2. Reaction pathways in the synthesis of propargyl PEG-1000 and poly (ECH-g-EG) graft copolymer.

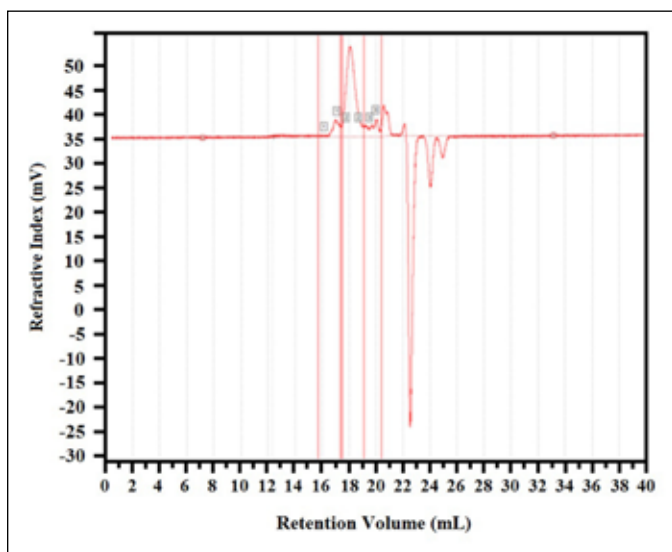


Figure 3. GPC curve of poly (ECH-g-EG) graft copolymer (HA-1 in Table 1).

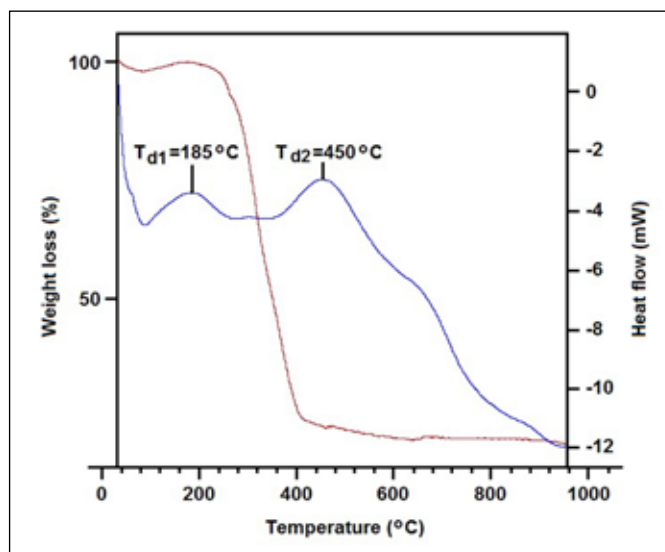


Figure 4. TGA curve of poly (ECH-g-EG) graft copolymer (HA-5 in Table 1).

Table 1. Synthesis of poly (epichlorohydrin-g-ethylene glycol) graft copolymers by “click” chemistry. Reaction temperature: 45 °C, solvent (THF-mL)/non-solvent (petroleum ether-mL).

Code	Propargyl PEG-1000 (g)	PECH-N ₃ (g)	CuCl (g)	CuBr (g)	bpy (g)	PMDETA (g)	THF (mL)	Chloroform (mL)	Time (hour)	γ	Yield (g)	Conver. (wt %)	Decomp. temp. (°C)	
													T _{d1}	T _{d2}
HA-1	5.001	3.022	0.470	-	0.750	-	24	-	94	0.62	5.070	63.19	-	415
HA-2	0.337	0.537	-	0.051	-	0.062	-	50	48	0.63	0.399	45.65	195	420
HA-3	0.527	0.511	-	0.070	-	0.085	-	50	48	0.60	0.479	46.15	310	425
HA-4	0.804	0.592	-	0.093	-	0.129	-	50	48	0.65	1.080	77.36	315	660
HA-5	1.174	0.568	-	0.143	-	0.191	-	50	48	0.62	1.156	66.36	185	450

mers were between 0.60 and 0.65. In the solvent-nonsolvent method, γ values were obtained 0.64-0.68 for homo-PECH (Öztürk et al. 2013), and 0.30 for homo-PEG. The γ values of graft copolymers are varied from those of homo-PECH and homo-PEG.

4. Conclusions

A set of synthesis, “click” chemistry conditions of the graft copolymers, were achieved. The graft copolymers were relatively acquired in high yield and molar weight. The proposed procedure for the synthesis of graft copolymers is simple and efficient. The characterization of graft copolymers was accomplished by using ¹H-NMR spectroscopy, FTIR spectroscopy, GPC, elemental analysis, and fractional precipitation techniques.

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