

Synthesis and Characterization of Poly(epichlorohydrin-g- ϵ -caprolactone) Graft Copolymers by “Click” Chemistry

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ABSTRACT

The synthesis of poly(epichlorohydrin-g- ϵ -caprolactone) [poly(ECH-g-CL)] graft copolymers were carried out by use of a “click” chemistry reaction to graft poly(ϵ -caprolactone) propargyl (PCL-propargyl) to poly(epichlorohydrin) azido (PECH-N₃). For this purpose, PECH-N₃ was synthesized by the reaction of poly(epichlorohydrin) and sodium azide. Then PCL-propargyl was obtained by the reaction of poly(ϵ -caprolactone) [PCL] and propargyl chloride. By reacting PECH-N₃ and PCL-propargyl, graft copolymers were obtained. The primary parameters, such as time and concentration, that influenced the reactions were assessed. The characterization of products was accomplished by using multiple instruments and methods including ¹H-NMR, ¹³C-NMR, FT-IR, GPC, DSC, TGA, and fractional precipitation [non-solvent (petroleum ether, mL) / solvent (THF, mL)] techniques.

KEYWORDS : “Click” chemistry, Graft copolymer, poly(epichlorohydrin), poly(ϵ -caprolactone), Fractional precipitation

1. INTRODUCTION

“Click” chemistry was described by Sharpless et al.^[1] in 2001 to include a set of simple strong linking reactions which have high yields, require minimum purification, and proceed in the presence of various functional groups without the need for protection chemistry^[2]. “Click” chemistry applications have been widely studied recently^[3-15]. Although block and graft

copolymers have many similar characteristics, such as the ability to microphase separate, graft copolymers have a branched chain structure, which may be easier to synthesize in some cases^[16,17]. The recently described syntheses of graft copolymers is an important field in the polymer science^[18-20]. Poly(epichlorohydrin) (PECH), an interesting commercially available polymer, is present in many syntheses of copolymers^[21-24]. Poly(ϵ -caprolactone) (PCL) is a semi-crystalline biodegradable polyester with a low melting point and glass transition temperature and is also used for many copolymer syntheses^[25-32]. The hydrophilic PCL copolymers can be appropriate for implantable appliances and injectable systems for controlled release and as coatings for metallic stents^[33].

This paper demonstrates the synthesis of graft copolymers of poly(epichlorohydrin-g- ϵ -caprolactone) [poly(ECH-g-CL)] using click chemistry. First, the synthesis of poly(ϵ -caprolactone) propargyl (PCL-propargyl) obtained by the reaction of PCL with propargyl chloride is presented. Poly(epichlorohydrin) azido (PECH-N₃) was synthesized by the chemical reaction of PECH with sodium azide (NaN₃). Lastly, PCL-propargyl and PECH-N₃ were used to obtain poly(ECH-g-CL) graft copolymers via “click” chemistry. Characterizations of the products are discussed in detail.

2. EXPERIMENTAL

2.1 Materials

PECH, propargyl chloride, copper(I) bromide (CuBr), NaN₃, chloroform, *N*, *N*, *N*₂, *N*₂, *N*₂ 2-pentamethyldiethylenetriamine (PMDETA), methanol, PCL (Mn ~10,000 g/mol) and *N,N*-dimethylformamide (DMF) were supplied by Sigma-Aldrich. Tetrahydrofuran

(THF) and triethylamine (TEA) were received from Merck Millipore. Diethyl ether and petroleum ether were bought from Carlo Erba Reagent. All the chemicals were used as supplied and used without further purification.

2.2. Instrumentation

Differential scanning calorimetry (DSC) measurement was conducted using a Perkin Elmer DSC 8500 series instrument. The sample was heated at a rate of 5 °C/min from -80 °C to 100 °C under N₂. Mn, Mw, and dispersities were examined with Tosoh HLC-8320GPC gel permeation chromatography (GPC) instrument with THF mobile phase (KT series) or DMF mobile phase (OC series) as the solvent 40 °C. Nuclear magnetic resonance (NMR) spectra were detected using Bruker Avance III 500 and Bruker Avance 400 NMR spectrometers. Fourier-transform infrared (FT-IR) spectra were detected using Thermo Scientific Nicolet 380 model FT-IR using ATR mode. Thermogravimetric analysis (TGA) measurements were conducted using a Seiko II Exstar 6000 model instrument. The sample was heated at a rate of 10 °C/min from 25 °C to 900 °C under N₂.

2.3. Synthesis of Poly(epichlorohydrin) azido (PECH-N₃)

A fixed quantity of PECH, NaN₃, and DMF (as solvent) were placed into a 500 mL flask ([PECH]/[NaN₃] = 1/100, mol/mol). The flask was immersed in an oil bath fixed at 70 °C on a magnetic stirplate, and nitrogen gas was introduced by injection with a needle. After a fixed time, the contents were filtered. The solvent was evaporated. The residue was drained into excess methanol to separate PECH-N₃. After decantation, the product was dried at 25 °C under vacuum for two days. PECH-N₃ yield was defined gravimetrically. The gravimetric conversion obtained from the weight of PECH-N₃ was between 92.86 wt% and 90.36 wt% as shown in Table 1.

The ¹H-NMR spectrum of PECH (Figure 1(a)) displayed peaks at 3.7 ppm for -OCH₂ protons and -ClCH₂ protons, 3.5 ppm for -OCH protons, 2.2 ppm for -OH protons. The ¹³C-NMR spectrum of PECH (Figure 2(a)) indicates 77 ppm for -OCH, 69 ppm for -OCH₂, and 44 ppm for -ClCH₂. The ¹H-NMR spectrum of PECH-N₃ (TK-2 in Table 1) in Figure 1(b) displayed peaks at 3.8 ppm for -OCH₂

TABLE 1. Synthesis of PECH-N₃.

Code	Reaction temperature: 70 °C.					
	PECH) (g)	NaN ₃ (g)	DMF (mL)	Time (hour)	Yield (g)	Conversion (wt %)
TK-1	10.2	0.0951	250	43	9.48	92.9
TK-2	5.48	0.0512	200	48	4.95	90.4
TK-3	2.53	0.0241	150	26	2.29	90.5

protons and -ClCH₂ protons, 3.6 ppm for -OCH protons, 3.4 ppm for -CH₂N₃ protons, 2.5 ppm for -OH protons. The ¹³C-NMR spectrum of PECH-N₃ (TK-2 in Table 1) in

Figure 2(b) displayed peaks at 77 ppm for -OCH linked -CH₂Cl group, 69 ppm for -OCH₂, 53 ppm for -CH₂Cl, 44 ppm for -CH₂N₃, and 41 ppm for -OCH linked -CH₂N group.

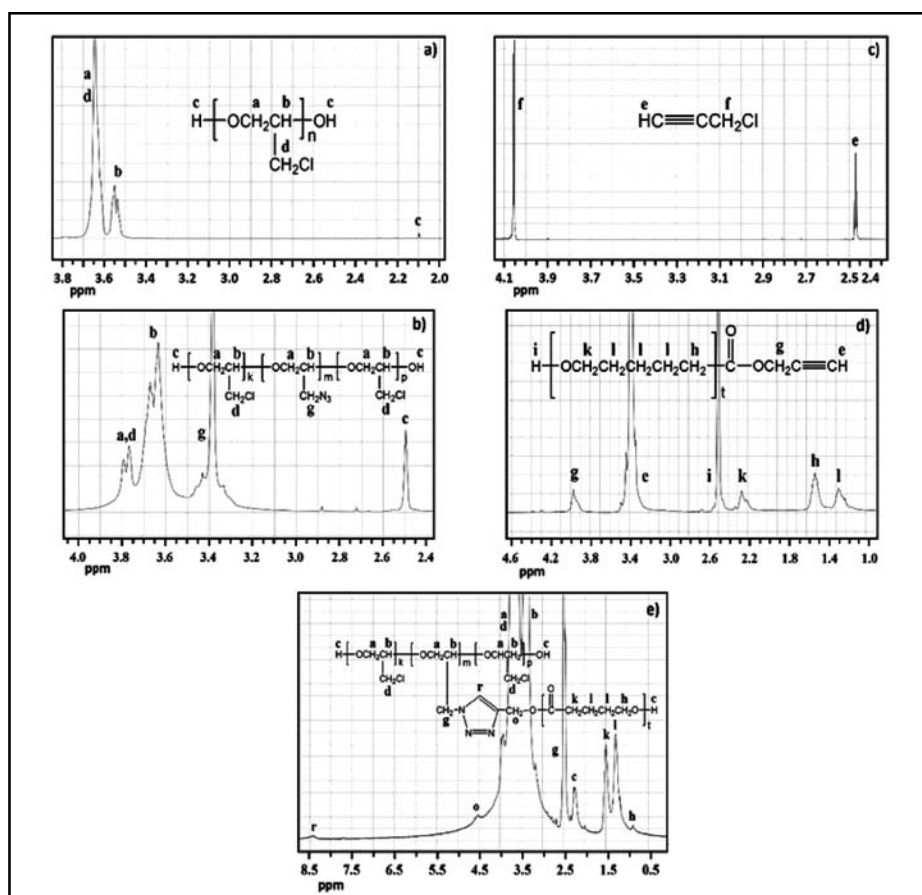


Fig. 1. ¹H-NMR spectra of (a) PECH; (b) PECH-N₃ (TK-2 in Table 1); (c) propargyl chloride; (d) PCL-propargyl (KT-3 in Table 2); (e) poly (ECH-g-CL) graft copolymer (OC-2 in Table 3).

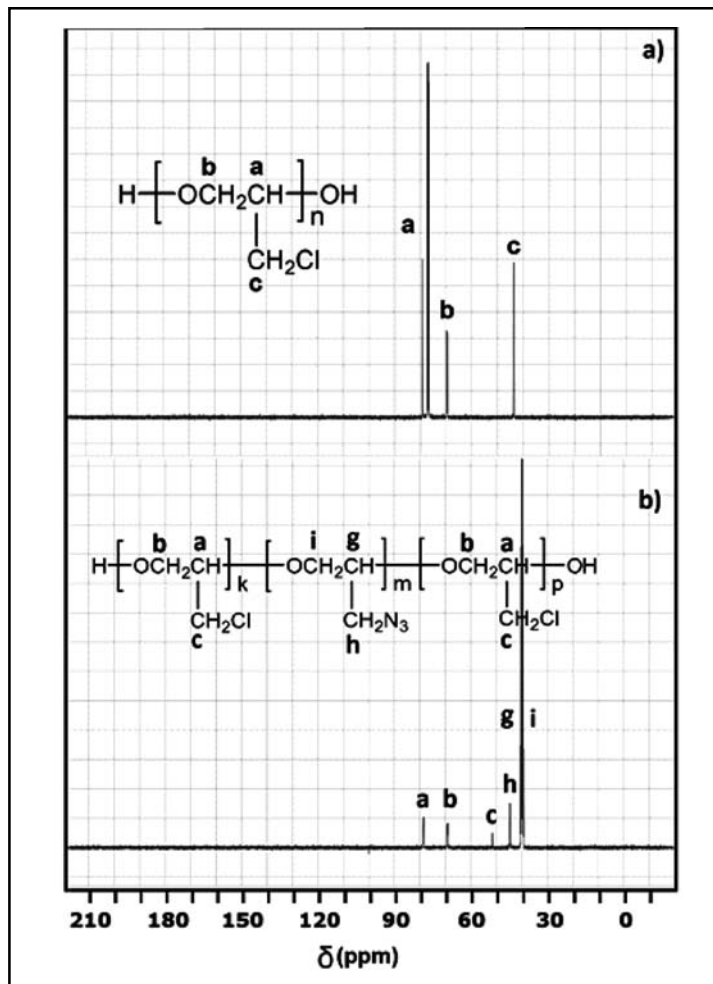


Fig. 2. ^{13}C -NMR spectra of (a) PECH; (b) PECH- N_3 (TK-2 in Table 1).

The FT-IR spectrum of PECH- N_3 (TK-2 in Table 1) in Figure 3(a) showed characteristic signals at 2950 cm^{-1} and 2850 cm^{-1} for aliphatic $-\text{CH}$ and $-\text{CH}_2$ groups, 2100 cm^{-1} for $-\text{N}_3$ groups, 1100 cm^{-1} for $-\text{OC}$ groups, 700 cm^{-1} for $-\text{Cl}$.

2.4. Synthesis of Poly(ϵ -caprolactone) Propargyl (PCL-propargyl)

A specified amount of PCL in a fixed amount of chloroform was mixed with a certain amount of TEA. The solution was transferred into a 150 mL flask with a

nitrogen gas input. The flask was cooled down to below $0\text{ }^\circ\text{C}$ and nitrogen was injected into the flask. To this solution certain amounts of propargyl chloride ([PCL]/[propargyl chloride] = 1/20, mol/mol) in 5 mL of chloroform was added via a dropping funnel over a duration of 60 minutes. The solution was mixed for 60 minutes below $0\text{ }^\circ\text{C}$. Afterwards, the contents were slowly warmed to $25\text{ }^\circ\text{C}$. After fixed time, the solvent was partially evaporated and the residue precipitated in diethyl ether. The sample was kept in a refrigerator overnight. After decantation, the product was dried at $25\text{ }^\circ\text{C}$ under

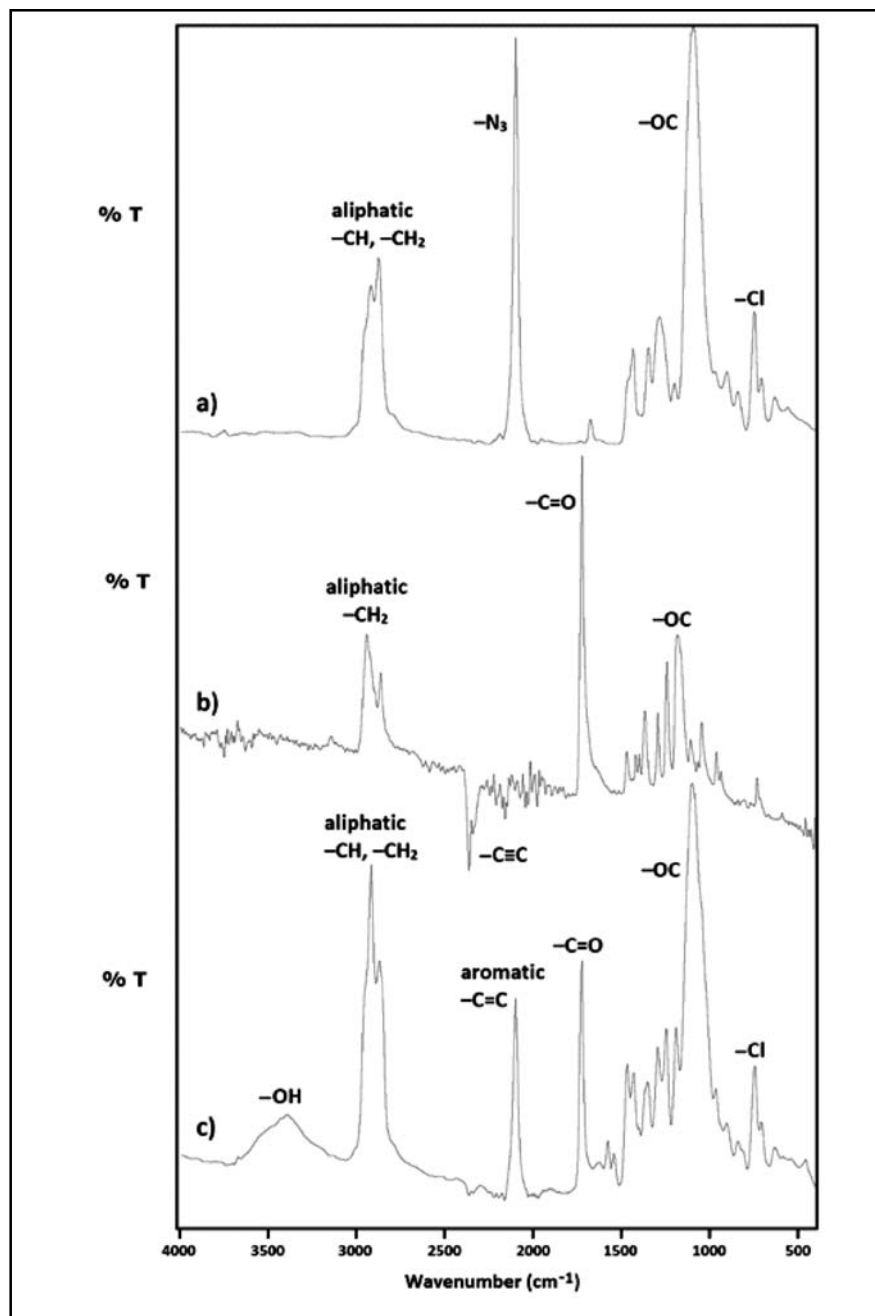


Fig. 3. FT-IR spectrum of (a) PECH-N₃ (TK-2 in Table 1); (b) PCL-propargyl (KT-3 in Table 2); (c) poly (ECH-g-CL) graft copolymer (OC-2 in Table 3).

vacuum for two days. PCL-propargyl yield was defined gravimetrically. The gravimetric conversion obtained from the weight of PCL-propargyl was between 87.38 wt% and 76.77 wt% as shown in Table 2.

TABLE 2. Synthesis of PCL-propargyl.

Code	Reaction temperature: 25 °C, TEA = 0.02 mL.							
	PCL (g)	Propargyl (g)	Chloroform (mL)	Time (hour)	Yield (g)	Conversion (wt %)	M _{n,GPC} (g.mol ⁻¹)	M _w /M _n
KT-1	0.51	0.078	35	48	0.44	87	-	-
KT-2	0.41	0.063	30	32	0.35	84	15,800	1.68
KT-3	0.30	0.046	25	27	0.26	84	16,000	1.67
KT-4	0.21	0.031	20	24	0.17	81	14,500	1.50
KT-5	0.16	0.024	15	22	0.12	77	14,700	1.50
KT-6	0.10	0.016	13	18	0.08	82	14,900	1.46

The ¹H-NMR spectrum of propargyl chloride (Figure 1(c)) indicates 4.1 ppm for -CH₂Cl protons, and 2.5 ppm for -CH protons. The ¹H-NMR spectrum of PCL-propargyl (KT-3 in Table 2) in Figure 1(d) displayed peaks at 4.0 ppm for -CH₂O protons linked C ≡ CH group, 3.4 ppm for -CH₂ protons of CL linked -OH group, 2.3 ppm for ≡ CH protons, 2.5 ppm for -OH proton, 1.5 ppm for -CH₂ protons of CL linked carbonyl group, 1.3 ppm for -CH₂ protons of CL. The FT-IR spectrum of PCL-propargyl (KT-3 in Table 2) in Figure 3(b) shows the characteristic signals at 3600 cm⁻¹ for -OH groups, 2900 cm⁻¹ for aliphatic -CH₂ groups, 2300 cm⁻¹ for -C≡C groups, 1700 cm⁻¹ for -C=O groups, 1100 cm⁻¹ for -OC groups. Mn values of PCL-propargyl were between 14,486 g.mol⁻¹ and 15,801 g.mol⁻¹ as shown Table 2. Mw/Mn of PCL-propargyl were between 1.46 and 1.68 (Table 2).

2.5. Synthesis of Poly(ECH-g-CL) Graft Copolymers by "Click" Chemistry

Poly(ECH-g-CL) was synthesized by "click" chemistry in this study. Specified amounts of PECH-N₃, PCL-propargyl, CuBr, PMDETA, and chloroform were put separately into a 250 mL Schlenk flask followed by injecting nitrogen gas in the tube for five minutes. The flask was immersed in an oil bath at 35 °C for specific times. After the polymerization, the flask contents were filtered. The solvent was partially removed by using a rotary evaporator. The mixture was drained into excess

methanol to separate precipitated poly(ECH-g-CL) graft copolymer. A small alumina column was used to remove the remaining copper catalyst from the copolymer. The copolymer was dried at 25 °C under vacuum for two days. The conversion of the graft copolymer was defined gravimetrically. The gravimetric conversion obtained from the weight of copolymer was between 93.72 wt% and 78.42 wt%. A typical ¹H-NMR spectrum of poly (ECH-g-CL) graft copolymers (OC-2 in Table 3) shown in Figure 1(e) displayed peaks at 8.4 ppm for aromatic -CH proton of triazole group, 4.0 ppm for -OCH₂ protons linked carbonyl group, 3.8 ppm for -OCH₂ protons of PECH group, 3.4 ppm for -OCH₂ protons linked triazole group and -OCH₂ protons of PCL group, 2.6 ppm for -ClCH₂ protons of PECH group, 2.5 ppm for -ClCH protons of PECH group, 2.2 ppm for -OH protons of PECH group and PCL group, 1.6 ppm for -CH₂ protons linked carbonyl group, and 1.5 ppm, and 1.3 ppm for -CH₂ protons of PCL group. The observed peak at 8.4 ppm for aromatic -CH proton of triazole group was evidence that the graft copolymer was obtained.

The FT-IR spectrum of the copolymer (OC-2 in Table 3) in Figure 3(c) indicates the characteristic signals at 3400 cm⁻¹ for -OH groups, 2950 cm⁻¹ and 2850 cm⁻¹ for aliphatic -CH and -CH₂ groups, 2100 cm⁻¹ for aromatic -C=C group of triazole group, 1700 cm⁻¹ for -C=O groups, 1100 cm⁻¹ for -OC groups, 700 cm⁻¹ for -Cl. Mn value of the copolymers were between 152,215 g.mol⁻¹

TABLE 3. Synthesis of poly(ECH-g-CL) graft copolymers by "click" chemistry.

Polymerization temperature : 35 °C, non-solvent (petroleum ether-mL) / solvent (THF-mL) CuBr = 0.001-0.002 g, PMTEDA= 0.011-0.022 g.

Code	PECH-N ₃ (g)	PCL- propargyl (g)	Chloroform (mL)	React. (hour)	γ	Yield (g)	Conversion (wt %)	M _{n,GPC} (g.mol ⁻¹)	M _w /M _n	Td (°C)
OC-1	1.00 (TK-1 in Table 1)	0.154 (TK-1 in Table 2)	50	72	0.80	1.01	87.0	187,600	3.15	286
OC-2	0.500 (TK-2 in Table 1)	0.111 (TK-3 in Table 2)	30	48	0.90	0.505	82.7	152,200	2.55	297
OC-3	0.305 (TK-3 in Table 1)	0.0751 (TK-4 in Table 2)	30	24	0.80	0.298	78.4	168,700	4.60	305
OC-4	0.202 (TK-2 in Table 1)	0.101 (TK-2 in Table 2)	20	17	0.70	0.284	93.7	-	-	385

and 187,586 g.mol⁻¹ as shown in Table 3. Thermal analysis of the products was carried out by DSC and TGA. The Tg and Tm values of the graft copolymer

(OC-2 in Table 3) were -39 °C, and 40 °C, respectively (Figure 4).

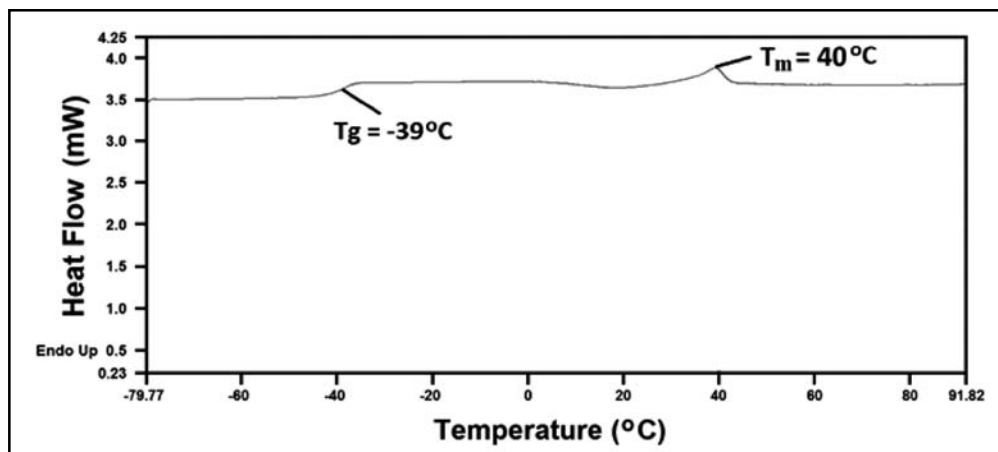


Fig. 4. DSC curve of poly (ECH-g-CL) graft copolymer (OC-2 in Table 3).

Decomposition temperatures (Td) of the copolymers are shown in Table 3. In the case of poly(ECH-g-CL) graft copolymer, poly-ECH and poly-CL units have not the individual Td as shown in Figure 5.

2.6. Fractional Precipitation of the Graft Copolymers

Fractional precipitations (γ) of the copolymers were determined by following to the process stated in the

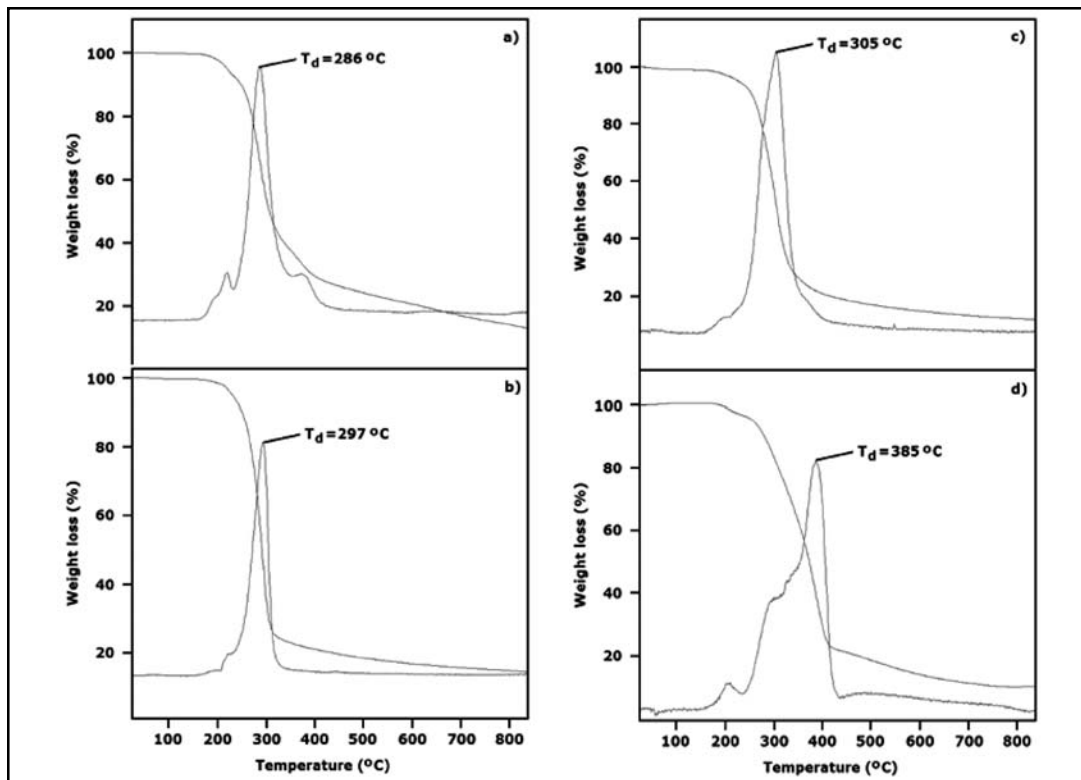


Fig. 5. TGA curves of poly (ECH-g-CL) graft copolymer: (a) OC-1 in Table 3; (b) OC-2 in Table 3; c) OC-3 in Table 3; d) OC-4 in Table 3.

literatures^[34,35]. Vacuum dried polymer sample (about 0.1 g) was dissolved in 10 mL THF, a good solvent for the polymer. Petroleum ether was added 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 γ values were determined as the ratios of total volume of non-solvent used for the first fraction to volume of good solvent used.

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

3. RESULTS AND DISCUSSION

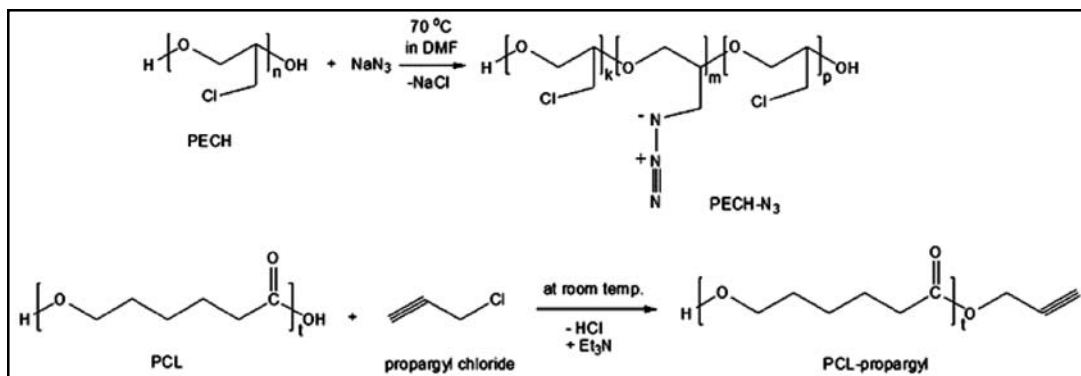
3.1. Synthesis of PECH-N₃

PECH-N₃ was synthesized starting from PECH. Scheme 1 (first line) includes the reaction

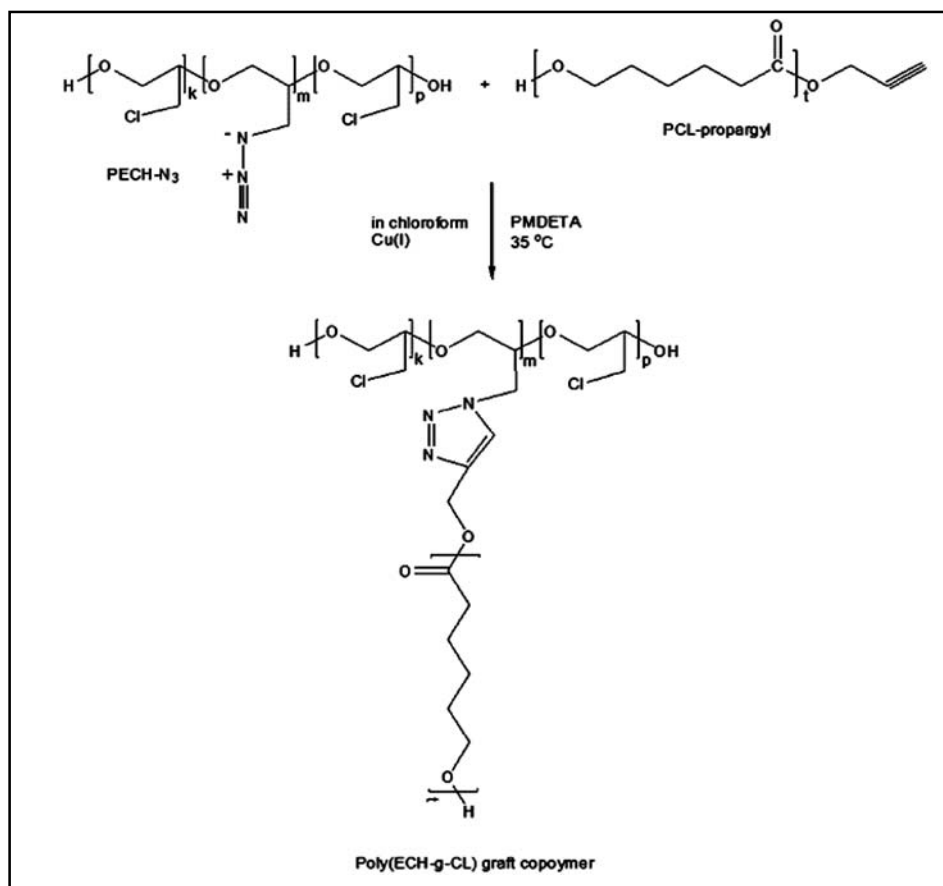
pathway for the synthesis of PECH-N₃. The observed peak at 44 ppm for $-\text{CH}_2\text{N}_3$ in ¹³C-NMR spectrum of PECH-N₃ was evidence that PECH-N₃ was obtained. Furthermore, the observed peak at 3.4 ppm for $-\text{CH}_2\text{N}_3$ protons in the ¹H-NMR spectrum of PECH-N₃ was further evidence that PECH-N₃ was obtained.

3.2. Synthesis of PCL-propargyl

PCL-propargyl was synthesized by reacting PCL and propargyl chloride for different times. Mw/Mn values of PCL-propargyl were relatively low. The second line in Scheme 1 shows the reaction pathway for PCL-propargyl. The maximum yield of PCL-propargyl was obtained



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



Scheme 2. Reaction outline for synthesis of poly (ECH-g-CL) graft copolymer.

at 48 hours. The minimum yield of PCL-propargyl was obtained at 22 hours. To the best of our knowledge, a great quantity of PCL-propargyl was obtained with a single propargyl group at one chain end. This semi-telechelic structure is useful for the synthesis of the graft copolymer.

3.3. Synthesis of Poly(ECH-g-CL) Graft Copolymers

Poly(ECH-g-CL) graft copolymers were synthesized at 35 °C by the “click” chemistry of PECH-N₃ and PCL-propargyl. Scheme 2 shows the reaction pathway for synthesis of the graft copolymer.

The results of the graft copolymerization are demonstrated in Table 3. The maximum yield of the graft copolymer was obtained by using PECH-N₃ (TK-2 in Table 1) and PCL-propargyl (KT-2 in Table 2). The minimum yield of the graft copolymer was obtained by using PECH-N₃ (TK-3 in Table 1) and PCL-propargyl (KT-4 in Table 2). Because of use of PECH, Mw/Mn values of the copolymers are larger. Increases in the molecular weights of the copolymers as

compared with the molecular weights of the reactants is consistent with the formation of graft copolymer.

Tg values were reported for homo PCL, and homo PECH as -72 °C^[35-37], and -22 °C³⁸, respectively. The Tg value observed by DSC appears between Tg of the PECH homopolymer and Tg of the PCL homopolymer. The presence of only one Tg value for the product in between that of the two constituent polymers is consistent with compatibility of the PECH and PCL in the amorphous region of the copolymer. The same situation can also be seen in our previous articles^[34,35,39-41]. Thermogravimetric analysis has showed interesting properties of the copolymers indicating continuous weight loss starting from 170 °C to nearly 415 °C with a derivative at 305 °C (Figure 5(c)). Figure 6 indicates the unimodal GPC curves of PCL-propargyl (KT-5 in Table 2), the graft copolymers (OC-2 in Table 3, and OC-3 in Table 3). Increases in the molecular weights of the copolymers as compared with molecular weights of reactants prove the formation of graft copolymer.

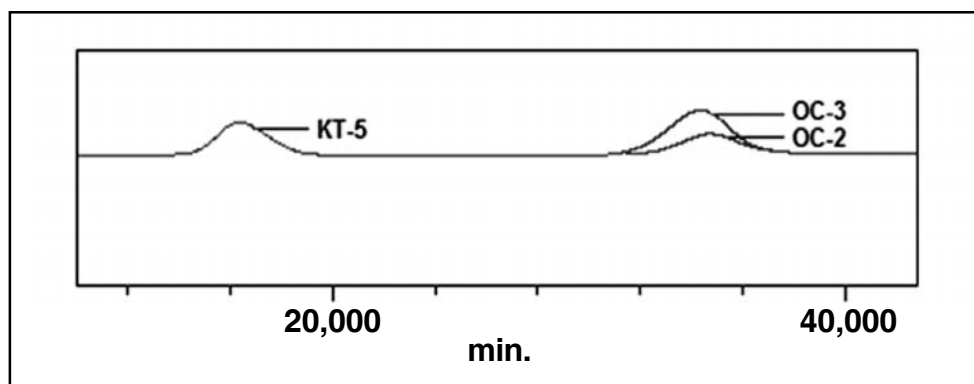


Fig. 6. GPC curves of PCL-propargyl (KT-5 in Table 2, THF mobile phase) and poly (ECH-g-CL) graft copolymers (OC-2 in Table 3, and OC-3 in Table 3, DMF mobile phase).

3.4. Fractional Precipitation

The γ values of poly (ECH-g-CL) graft copolymers were between 0.70 and 0.90, as shown in Table 3. The γ values were determined to be 0.64–0.68 for homo PECH, and 1.02–1.20 for homo PCL^[39]. The γ values of poly (ECH-g-CL) graft copolymers were generally between the γ values of homo PECH and the $\bar{\alpha}$ values of homo PCL. It can also be deduced that homopolymer formation is not available because polymer precipitation is not acquired at the γ values of related homopolymers.

4. CONCLUSIONS

The "click" chemistry synthesis of poly (ECH-g-CL) graft copolymers from the two constituent homopolymers was achieved. The graft copolymers were acquired in high yield and high molecular weight. The proposed method for the synthesis of copolymer is simple and efficient. The characterization of products was accomplished by using multi instruments and fractional techniques. This study can provide new, well-characterized materials with wide application potential through the synergistic combination of the soft PECH and crystalline PCL.

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