Research Article

Synthesis and characterization of comb-type graft copolymers by redox polymerization and "click" chemistry method

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Abstract
The synthesis of poly(epichlorohydrin-g-methyl methacrylate) [poly(ECH-g-MMA)] comb-type graft copolymers were carried out by use of a "click" chemistry to graft terminally propargyl poly(methyl methacrylate) (PMMA-propargyl) to poly(epichlorohydrin) azido (PECH-N_3). For this purpose, PECH-N_3 was synthesized by using poly(epichlorohydrin) and sodium azide. PMMA-propargyl was obtained by reaction of methyl methacrylate and propargyl alcohol via redox polymerization technique. By using PECH-N_3 and PMMA-propargyl, the comb-type graft copolymers were obtained. Characterization of the modified homopolymers and the comb-type graft copolymers was performed by using FT-IR, ^{1}H-NMR, SEM, GPC, and elemental analysis techniques. Thermal transitions and degradation features of the comb-type graft copolymers were investigated by using DSC and TGA methods. Spectroscopic and thermal analyses revealed that both group modifications and coupling reactions were successfully achieved.

Keywords "Click" chemistry · Redox polymerization · Comb-type graft copolymer · Poly(epichlorohydrin) · Poly(methyl methacrylate)

1 Introduction

After Sharpless et al. [1] described "click" chemistry method in 2001, applications of the methods have been widely studied [2–17]. Polyepichlorohydrin (PECH) is present in many syntheses of copolymers [18–22]. Poly(methyl methacrylate) (PMMA) is frequently used in sheet form as an alternative to glass. Copolymers have important interest for their mechanical properties and practical applications [9]. Block or graft copolymers are used in scientific applications and research [23–31]. One of the most important of these regularly branched polymers is the brush type copolymers. Brush type polymers usually consist of three categories considering the type and number of side chain, and the formation of framework. The first group includes one linear branch of homopolymer or diblock copolymer as the side chains deployed on each unit of the polymer backbone created by homopolymerization of one monomer [32].

This paper demonstrates the synthesis of poly(epichlorohydrin-g-methyl methacrylate) [poly(ECH-g-MMA)] comb-type graft copolymers by using "click" chemistry. In our previous work, we synthesized poly(epichlorohydrin) azido (PECH-N_3) [14]. Terminally propargyl poly(methyl methacrylate) (PMMA-propargyl) was obtained by reaction of MMA with propargyl alcohol via redox polymerization technique as shown the literature [33]. In this study, the synthesis of poly(ECH-g-MMA) comb-type graft copolymers obtained by "click" chemistry reaction of PECH-N_3 and PMMA-propargyl were introduced. Characterization of the comb-type graft

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copolymers was performed by using FT-IR, ^{1}H-NMR, SEM, GPC, TGA, and DSC.

2 Experimental

2.1 Materials

Propargyl alcohol, *N,N*-dimethylformamide (DMF), nitric acid (HNO_3), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), PECH, copper(I) bromide (CuBr), sodium azide (NaN_3), and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), ammonium cerium (IV) nitrate [$Ce(NH_4)_2(NO_3)_6$] were received from Sigma-Aldrich. MMA and methanol were supplied by Merck. An alumina column was used to remove the inhibitor from MMA.

2.2 Instrumentation

^{1}H-NMR spectra were recorded using Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometers. FT-IR spectra were detected using Jasco FT/IR 6600 FT-IR spectrometer in the range of 600–4000 cm^{-1}. Mw, Mn, and dispersities were examined with HPLC/GPC-Shimadzu RID-10A GPC instrument with DMF mobile phase as the solvent 40 °C using Refractive Index Detector (RID-10A). Polystyrene standards: 1490 Da (Mw), 2500 Da (Mw), 5480 Da (Mw), 9500 Da (Mw), 20,800 Da (Mw), 53,500 Da (Mw) 171,000 Da (Mw), 295,900 Da (Mw), 410,000 Da (Mw), and 566,200 of low polydispersity. Scanning Electron Microscopy (SEM) images was taken on a Zeiss EVO LS 10 electron microscope. The elemental analyses of the products were performed by a Costech ECS 4010. Thermogravimetric analysis (TGA) measurements were conducted using a Seiko II Exstar 6000 model instrument. The samples were heated at a rate of 10 °C/min from 25 °C to 800 °C under N_2. Differential scanning calorimetry (DSC) measurements were conducted at a rate of 10 °C/min from − 80 °C to 150 °C under N_2 atmosphere using a Perkin Elmer DSC 8500 series instrument.

2.3 Synthesis of poly(epichlorohydrin) azido (PECH-N_3)

PECH-N_3 were obtained as in our previous work [14]. Briefly, 1.43×10^{-5} mol of PECH, 3.08×10^{-2} mol of NaN_3, and 100 mL of DMF (as the solvent) were placed into a 250 mL flask. The flask was immersed in an oil bath fixed at 70 °C on a magnetic stir plate, and N_2 gas was introduced by injection with a needle. After 48 h, the flask was opened, and the contents were filtered. The sample washed with 30 wt% $NaHCO_3$ then dried over Na_2SO_4 to remove unreacted NaN_3 and then the organic phase was separated. The solvent was evaporated by using a rotary evaporator. The residue was drained into excess methanol to separate PECH-N_3. After decantation, the product was dried at 25 °C under vacuum for two days. PECH-N_3 yield was defined gravimetrically. The gravimetric conversion obtained from the weight of PECH-N_3 was 97.0 wt%. FT-IR spectrum of PECH-N_3 in Fig. 1a shows the signals at 3664 cm^{-1} for –OH, 2920 cm^{-1} for aliphatic –CH, –CH_2, 2094 cm^{-1} for –N_3 and 1084 cm^{-1} for –OC. The ^{1}H–NMR spectrum of PECH [Fig. 2a] displayed peaks at 3.7 ppm for –OCH_2 and for –OCH, 3.4 ppm for –NCH_2, and 1.7 ppm for –OH. Mn value of PECH–N_3 was 20,750 g mol^{-1}. Dispersity value of PECH-N_3 was 2.78. The result of the elemental analysis of PECH–N_3 shows 24.36 N wt%.

2.4 Synthesis of terminally propargyl poly(methyl methacrylate) (PMMA-propargyl) by redox polymerization

PMMA-propargyl were obtained as the literature [33]. Briefly, 9.99×10^{-2} mol of MMA, 3.21×10^{-2} mol of propargyl alcohol, 2.92×10^{-3} mol of ammonium cerium (IV) nitrate, and 30 mL of 1 molar nitric acid solution were placed into a 250 mL flask around closed with aluminum

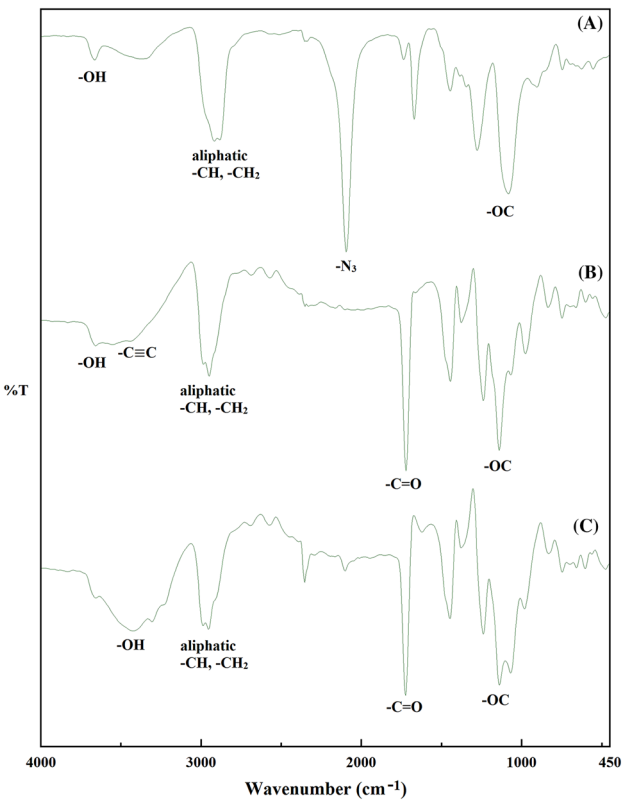


Fig. 1 FT-IR spectrum of **a** PECH-N_3; **b** PMMA-propargyl; **c** poly (ECH-g-MMA) comb-type graft copolymer (R2M2-3 in Table 1)

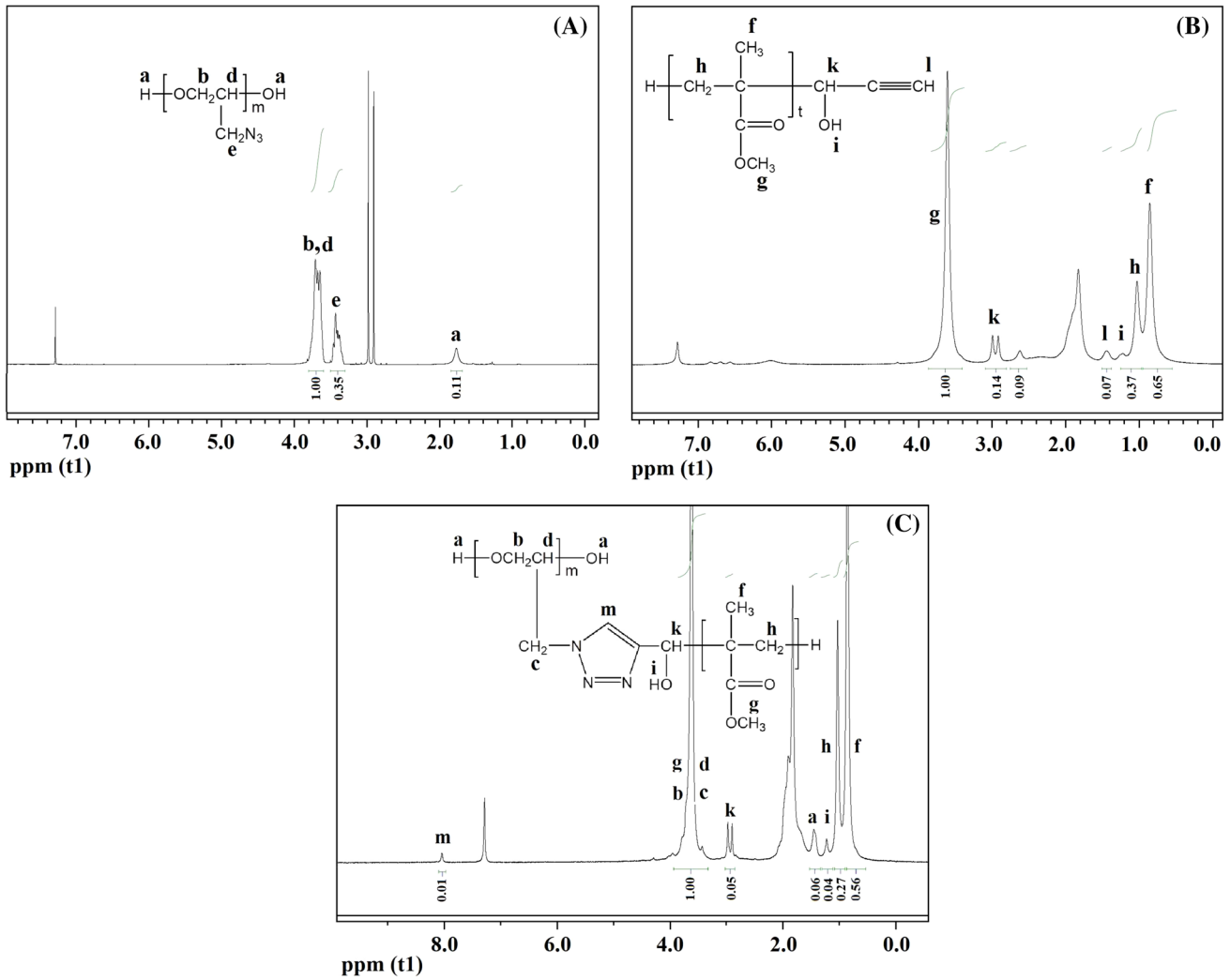


Fig. 2. ^{1}H-NMR spectra of **a** PECH-N_3; **b** PMMA-propargyl; **c** poly (ECH-g-MMA) comb-type graft copolymer (R2M2-3 in Table 1)

foil followed by N_2 gas inert atmosphere. The mixture was stirred at 30 °C for 24 h. The resulting product was precipitated in methanol. After decantation, the product was dried at 25 °C under vacuum for two days. The gravimetric conversion was 8.0 wt%. FT-IR spectrum of PMMA-propargyl in Fig. 1b shows the signals at 3660 cm^{-1} for –OH, 2950 cm^{-1} for aliphatic –CH, –CH_2, 3350 cm^{-1} for –C≡C, 1724 cm^{-1} for –C=O, and 1142 cm^{-1} for –OC. The ^{1}H-NMR spectrum PMMA-propargyl in Fig. 2b displayed peaks at 3.6 ppm for –OCH_3, 3.0 ppm for –OCH linked PMMA unit, 1.2 ppm for –OH, 1.1 ppm for –C≡CH, 1.0 ppm for aliphatic –CH_2, and 0.9 ppm for aliphatic –CH_3. Mn value of PMMA-propargyl was 13,322 g mol^{-1}. Dispersity value of PMMA-propargyl was 1.11.

2.5 Synthesis of poly(epichlorohydrin-g-methyl methacrylate) comb-type graft copolymers by "click" chemistry

Poly(ECH-g-MMA) comb-type graft copolymers was synthesized by "click" chemistry in this study. The amounts of chemicals used in the copolymerization are shown in Table 1. PMMA-propargyl, PECH-N_3, CuBr, PMDETA, and DMF were put separately into a Schlenk tube followed by nitrogen gas for two min. The tube was put in an oil bath at 35 °C on a magnetic stirrer. After 48 h, the flask contents were filtered. The mixture was drained into methanol to separate precipitated poly(ECH-g-MMA) comb-type graft copolymers. Small alumina column was used to remove remaining copper catalyst from the comb-type graft

Table 1 Synthesis of poly(ECH-g-MMA) comb-type graft copolymers by "click" chemistry

Code	PMMA-propargyl (mol × 10^{-6})	PECH-N_3 (mol × 10^{-5})	CuBr (mol × 10^{-4})	PMDETA (mol × 10^{-4})	Yield (g)	Eff	Mn, GPC (g mol^{-1})	Mw/Mn	Decomp. temp. (°C)	
									Td1	Td2
R2M2-1	7.73	1.00	3.62	2.42	0.239	0.75	31,460	2.01	215	395
R2M2-2	7.65	2.08	5.16	3.52	0.457	0.78	25,717	2.10	227	415
R2M2-3	8.03	3.18	6.41	4.90	0.715	0.80	39,128	1.97	230	414
R2M2-4	7.58	4.01	8.50	5.94	0.886	0.84	30,004	2.07	232	417

Reaction temperature: 35 °C; polymerization time: 48 h; DMF: 20 mL
eff.: efficiency of "click" chemistry

copolymer. The copolymer was dried at 25 °C for two days in vacuum oven. Vacuum dried copolymer sample was dissolved in chloroform, a good solvent for the copolymer. Methanol was added drop wise to the solution with mixing until turbidity forms, and then 1–3 mL methanol was added to complete the precipitation. After decantation, the dried copolymer sample was defined gravimetrically. The efficiency of click coupling was included in Table 1. There was not significant unreacted PECH-N_3 in poly (ECH-g-MMA) comb-type graft copolymer. The gravimetric conversion was between 94.87 wt% and 76.71 wt%. The FT-IR spectrum of poly(ECH-g-MMA) comb-type graft copolymers in Fig. 1c shows the signals at 3425 cm^{-1} for –OH, 2950 cm^{-1} for aliphatic –CH, $-CH_2$, 1724 cm^{-1} for –C=O, and 1138 cm^{-1} for –OC. The ^{1}H-NMR spectrum of the comb-type graft copolymers shown in Fig. 2c displayed peaks at 8.0 ppm for aromatic –CH of triazole ring, 3.6 ppm for $-OCH_3$ of PMMA unit and –OCH, $-OCH_2$ of PECH unit, 3.0 ppm for –OCH linked PMMA unit, 1.5 ppm for –OH of PECH unit, 1.2 ppm for –OH linked PMMA unit, 1.0 ppm for aliphatic $-CH_2$ of PMMA unit, and 0.9 ppm for aliphatic $-CH_3$ of PMMA unit.

3 Results and discussion

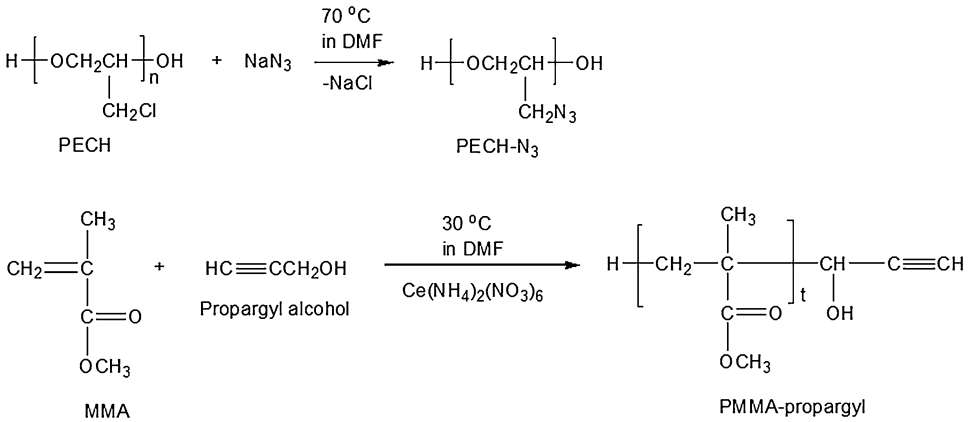
3.1 Synthesis of PECH-N_3

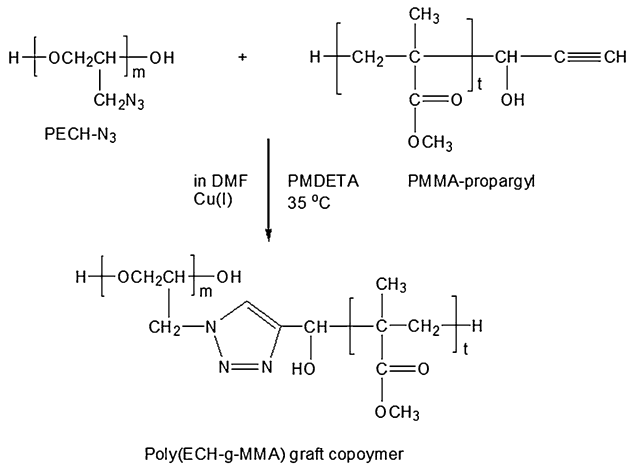
PECH-N_3 was synthesized starting from PECH. Scheme 1 (first line) includes the reaction pathway for the synthesis of PECH-N_3. The observed peaks at 2.9 ppm for $-CH_2N_3$ protons in the ^{1}H–NMR and 2094 cm^{-1} for $-N_3$ groups in the FT–IR spectrum of PECH–N_3 were further evidences that PECH–N_3 was successfully obtained.

3.2 Synthesis of PMMA-propargyl by redox polymerization

PMMA-propargyl was synthesized at 30 °C by redox polymerization [33]. Scheme 1 (second line) includes the reaction pathway for the synthesis of PMMA-propargyl. The formation of the specific acetylenic C–H stretching band at about 3350 cm^{-1} proves the propargylation of PMMA. Furthermore, the observed peak at 1.1 ppm for –C≡CH protons was the other evidence that PMMA-propargyl was obtained.

Scheme 1. Reaction pathways in the synthesis of PECH-N_3, and PMMA-propargyl





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

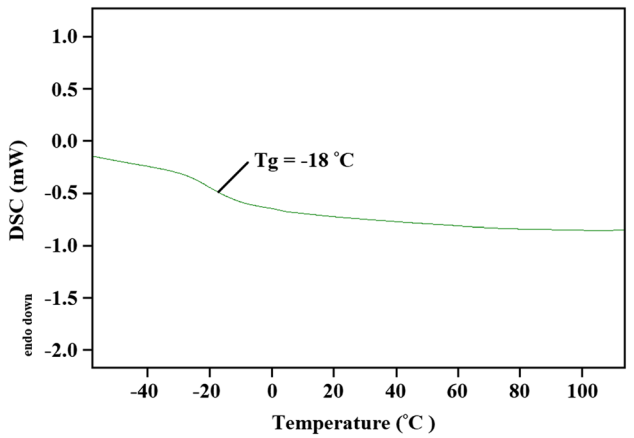


Fig. 3 DSC curve of poly(ECH-g-MMA) comb-type graft copolymer (R2M2-2 in Table 1)

3.3 Synthesis of poly(ECH-G-MMA) comb-type graft copolymers by "click" chemistry

Poly(ECH-g-MMA) comb-type graft copolymers were synthesized at 35 °C via the "click" chemistry of PECH-N_3 and PMMA-propargyl. Scheme 2 shows the reaction outline for synthesis of the comb-type graft copolymer. The signal at about 8.0 ppm in the ^{1}H–NMR spectrum is an indisputable evidence of aromatic –CH proton of triazole [34, 35].

Thermal analysis of poly(ECH-g-EG) comb-type graft copolymers was carried out by DSC and TGA. Tg value of the comb-type graft copolymer (R2M2-2 in Table 1) was – 18 °C (Fig. 3). Tg values were reported in the literatures for homo PECH and homo PMMA as – 43 °C [36] and 105 °C [37], respectively. Tg value of the comb-type graft copolymer changed to the value which was less than the value of

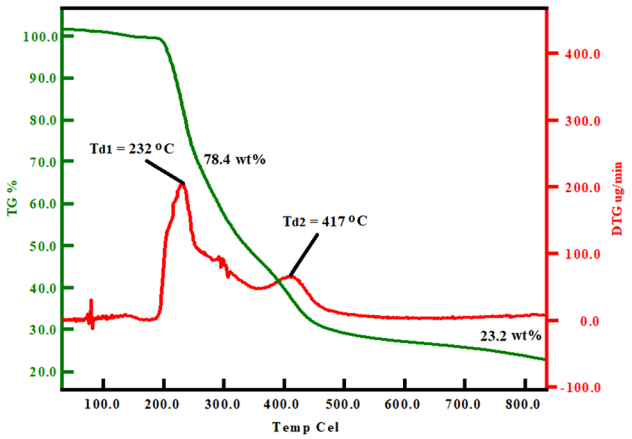


Fig. 4 TGA curves of poly(ECH-g-MMA) comb-type graft copolymer (R2M2-4 in Table 1)

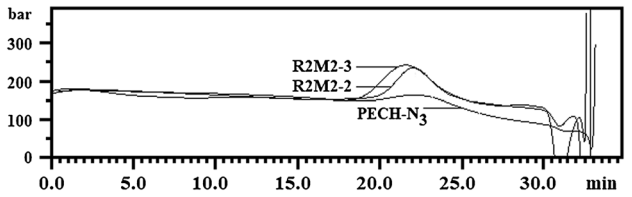


Fig. 5 GPC curves of poly(ECH-g-MMA) comb-type graft copolymers (R2M2-2 and R2M2-3 in Table 1) and PECH-N_3

PMMA because of PECH segment. The only one glass transition temperature value for the comb-type graft copolymers shows the miscible nature of the related polymers. Decomposition temperatures (Td) of the comb-type graft copolymers obtained from TGA were shown in Table 1. In the case of poly(ECH-g-MMA) comb-type graft copolymer, PECH and PMMA units have the individual Td as shown in Fig. 4. As reported for many copolymers [38–41], moieties in a copolymer exhibit decomposition curves as if they are alone. TGA has showed interesting properties of the copolymers indicating continuous weight loss starting from 180 °C to nearly 510 °C with derivatives at 232 °C and 417 °C through two steps (Fig. 4). Figure 5 indicates the unimodal GPC curves of the comb-type graft copolymers. Mn values of the comb-type graft copolymers were between 39,128 g mol^{-1} and 25,717 g mol^{-1}. Dispersity values of the copolymers are between 2.10 and 1.97. Increases in the molecular weights of the copolymers as compared with these of reactants is consistent with the formation of the comb-type graft copolymer.

SEM images of the copolymers were taken for the surface morphology characterization of the copolymers. The polymers were coated with a thin layer of gold on their surfaces. The images were received from different views. The surface morphologies of poly(ECH-g-MMA) comb-type

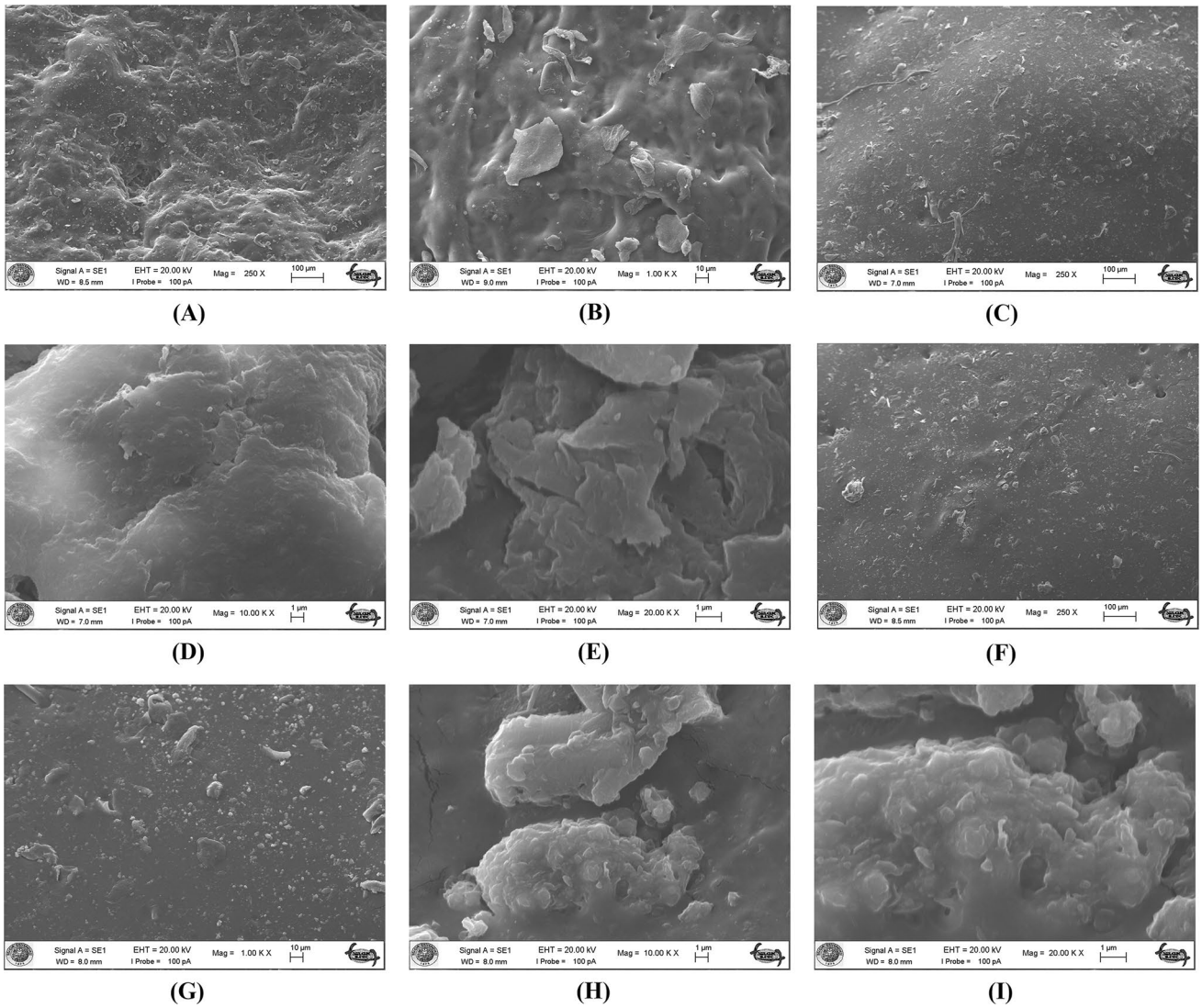


Fig. 6 SEM images of poly(ECH-g-MMA) comb-type graft copolymer; ×250 (**a**), and ×1000 (**b**) (R2M2-1 in Table 1); ×250 (**c**), ×10,000 (**d**), and ×20,000 (**e**) (R2M2-2 in Table 1); ×250 (**f**), ×1000 (**g**), ×10,000 (**h**), and ×20,000 (**i**) (R2M2-3 in Table 1)

graft copolymers was shown in Fig. 6 (R2M2-1, R2M2-2, and R2M2-3 in Table 1). According to the SEM images of poly(ECH-g-MMA) comb-type graft copolymers, homogenization of the copolymers was good. The copolymer samples were characterized by a morphology consisting platelets with channels. The SEM images of the comb-type graft copolymers show a rough surface and form a continuous phase.

4 Conclusions

The "click" chemistry synthesis of the comb-type graft copolymers from the two constituent homopolymers was acquired. This method for synthesis of the comb-type graft copolymers including triazole rings is simple and efficient. Products characterization was done using multi instruments. This study can provide well-characterized materials with wide biomedical application potential through the polymers including PECH and PMMA units.

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Compliance with Ethical Standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest. The authors declare that we have no conflict of interest.

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