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Synthesis and characterization of amphiphilic graft copolymer poly(ethylene oxide)-*graft*-poly(methyl acrylate)

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Abstract

A novel well-defined amphiphilic graft copolymer of poly(ethylene oxide) as main chain and poly(methyl acrylate) as graft chains is successfully prepared by combination of anionic copolymerization with atom transfer radical polymerization (ATRP). The glycidol is protected by ethyl vinyl ether first, then obtained 2,3-epoxypropyl-1-ethoxyethyl ether (EPEE) is copolymerized with EO by initiation of mixture of diphenylmethyl potassium and triethylene glycol to give the well-defined poly(EO-*co*-EPEE), the latter is deprotected in the acidic conditions, then the recovered copolymer [(poly(EO-*co*-Gly)] with multi-pending hydroxyls is esterified with 2-bromoisobutyryl bromide to produce the ATRP macroinitiator with multi-pending activated bromides [poly(EO-*co*-Gly)$_{(ATRP)}$] to initiate the polymerization of methyl acrylate (MA). The object products and intermediates are characterized by NMR, MALDI-TOF-MS, FT-IR, and SEC in detail. In solution polymerization, the molecular weight distribution of the graft copolymers is rather narrow ($M_w/M_n < 1.2$), and the linear dependence of Ln [M_0]/[M] on time demonstrates that the MA polymerization is well controlled.

Keywords: Amphiphilic graft copolymer; Poly(ethylene oxide); Poly(methyl acrylate)

1. Introduction

The graft copolymers have received much attention recently [1–6], among them, the amphiphilic graft copolymers are investigated widely because of their special physical and chemical properties and self-assembly morphologies [7].

Graft copolymers containing polyethylene oxide and poly[alkyl (methyl)acrylate] segments have been reviewed by Xie and Xie [8] in 1999, in which, however, all the main chains are poly[alkyl (methyl)acrylate] and the pended graft polymers are PEO. There are three methods to prepare graft copolymers of poly[alkyl (methyl)acrylate] as main chain and PEO as side chains: (1) ''grafting through'' method [9,10]: macromonomers are synthesized first and then homo- or copolymerized with other monomers by atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP) or radical addition fragmentation chain transfer (RAFT); (2) ''grafting onto'' method [11,12]: the backbone with reactive sites and side chains with functional end groups are prepared separately, then the side chains are grafted onto a backbone via a coupling reaction between the reactive sites of the backbone and the end functional groups of grafts; (3) ''grafting from'' method [13,14]: the side chains are grown from the pended reactive sites of polymeric backbone by a variety of controlled polymerization methods such as ATRP, NMP and RAFT, the resulting graft polymers can be easily purified.

However, the graft copolymers with inversed architecture, for example, PEO as main chain and poly[alkyl (methyl)acrylate] as pended side chains, are not reported up to now because of the difficulty in synthesis.

Here, an efficient and universal method is introduced to synthesize the well-defined amphiphilic or double hydrophilic graft copolymers of PEO as main chain, such as amphiphilic PEO-*g*-PMA and double hydrophilic PEO-*g*-PAA (hydrolysis

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of PEO-*g*-PtBA). In the reaction process, the protected glycidol (EPEE) is copolymerized with EO by anionic mechanism first, then the hydroxyl groups are recovered by deprotection of EPEE units of copolymer chains in acidic conditions, it can be further modified to form di- or trithiolester for the reversible addition-fragmentation chain transfer (RAFT), nitroxide for nitroxide-mediated polymerization (NMP) and alkyl bromide for atom transfer radical polymerization (ATRP). This presentation is only centered on the preparation of the graft copolymer of PEO-*g*-PMA by ATRP.

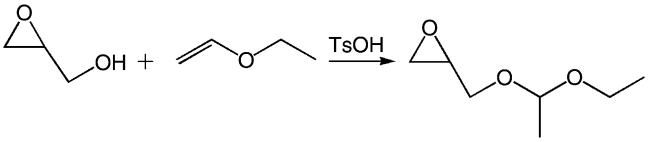
2. Experiment part

2.1. Materials

Glycidol (tech.) is purchased from Acros and dried over calcium hydride for 48 h, then distilled under reduced pressure just before use. 2-Bromoisobutyryl bromide (98%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) and *p*-toluene sulfonic acid (TsOH, >98%), ethyl vinyl ether (98%), pyridine (99.5%) are purchased from Aldrich and Sinopharm Chemical Reagent Co., Ltd. (SCR), respectively, and used as received. CuBr (95%) is stirred overnight in acetic acid and filtrated, then the solid is washed with ethanol and diethyl ether successively, and dried in vacuo. Methyl acrylate and acetonitrile are stirred over CaH_2 and distilled subsequently. Triethylene glycol is distilled from CaH_2 under reduced pressure and the fraction of 134 °C/90 Pa is collected. 1,1-Diphenylmethane (99%) is also distilled from CaH_2 under reduced pressure and the fraction of 105 °C/80 Pa is collected. THF (99%) is refluxed over sodium wire and distilled from sodium naphthalenide solution. EO (SCR, 98%) is dried over calcium hydride for 48 h and then distilled under N_2 before use. All other reagents are purified by common purification procedures.

2.2. Synthesis of 2,3-epoxypropyl-1-ethoxyethyl ether (EPEE)

Glycidol is protected with ethyl vinyl ether according to previous literature [15] as shown in Scheme 1; the product (b.p. 152–154 °C) is a colorless liquid with a yield of 84%. Element Anal.: Calcd. for $C_7H_{14}O_3$: C, 57.58; H, 9.66, found 57.77, 9.55; GC (99.6%), MS (70 Ev) *m/z* (%): 131 (33) $[M-CH_3]^+$, 101 (27) $[M-C_2H_5O]^+$, 73 (88) $[M-C_4H_9O]^+$; ^1H NMR ($CDCl_3$): $\delta = 4.76$ [−O−*CH*(CH_3)−O−], 3.35–3.90 (−O−C*H*$_2$CH$_3$ and −O−C*H*$_2$−C_2H_4O), 3.15 (methine C*H* of oxirane ring), 2.61–2.91 (methylene CH_2 of oxirane ring), 1.33 [−OCH(C*H*$_3$)−O−], 1.19 (−O−C*H*$_3$) ppm; FT-IR (film): $\upsilon = 1350$, 1254 cm^{-1} (acetal).



Scheme 1. Synthesis of 2,3-epoxypropyl-1-ethoxyethyl ether (EPEE).

2.3. Anionic copolymerization of EPEE with EO

The copolymerization of EPEE with EO is described in Scheme 2. Diphenylmethyl potassium (DPMK) is prepared as in literature [16]: to a 150 mL three-neck flask, about 100 mL dry THF and 7.7 g (0.06 mol) naphthalene are added, then 2.34 g (0.06 mol) potassium with fresh surface is added under bubbling of dry nitrogen, after stirring for 4 h, 11.1 g (0.066 mol) diphenylmethane is introduced by a syringe and the system is refluxed at 80 °C for 24 h, then filtered. The filtrate is titrated with 0.1 M HCl, the concentration of DPMK is 0.57 M.

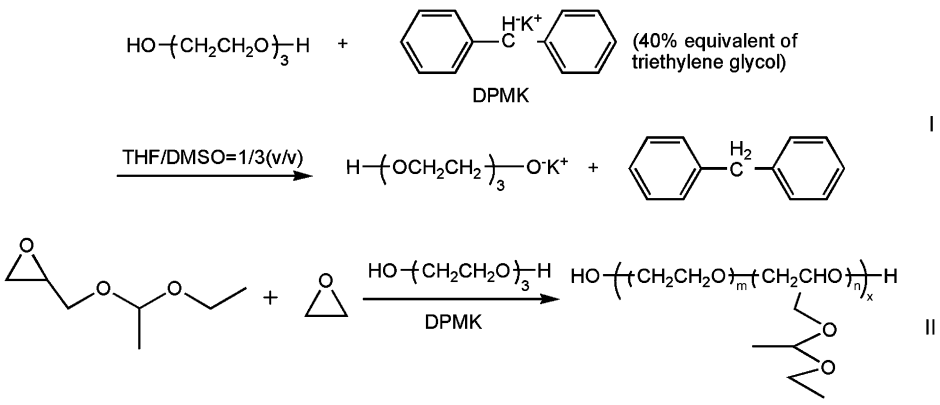
The copolymerization is carried out in the kettle, the typical procedure is showed as follows: a 150 mL kettle is vacuumed at 80 °C for 24 h, and cooled to room temperature and then to −20 °C, given volume of initiator solution [triethylene glycol (0.67 mL, 0.005 mol) mixed with DPMK (3.5 mL, 0.002 mol) in 50 mL THF], EPEE (16.0 g, 0.11 mol) and EO (44.0 g, 1.0 mol) are introduced successively into kettle under magnetic stirring. Subsequently, it is heated to 60 °C under stirring for 48 h. The reaction is terminated by a few drops of acidified methanol. After all the solvents are removed by reduced distillation, the crude product is dissolved in CH_2Cl_2, then filtrated and dried over anhydrous $MgSO_4$, the yellowy viscous wax-like product [poly(EO-*co*-EPEE)] is obtained in the yield of 94% after CH_2Cl_2 is removed.

2.4. Deprotection of EPEE units of copolymers

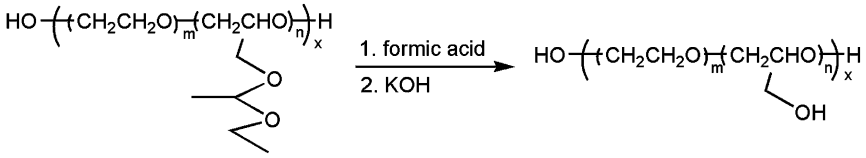
The deprotection of EPEE units of copolymer [17] may take place following the two steps shown in Scheme 3: (1) 10.0 g of poly(EO-*co*-EPEE) ($M_n = 12{,}700$; 0.855 mmol) is mixed with 160 mL of formic acid (0.266 mol), the solution is stirred at 20 °C for 30 min and then poured into methanol, the precipitate is separated and dried in vacuo at 50 °C; (2) the dried product is then dissolved in a mixture of dioxane (100 mL) and methanol (50 mL), and hydrolyzed by KOH methanol solution (1 N, 27 mL) under refluxing for 24 h, then neutralized with 5% HCl. After the solvents are removed under reduced pressure, the polymer is dissolved in water and purified by ultra filtration membrane, then the filtrated aqueous solution is concentrated to dryness, dissolved in CH_2Cl_2 and dried over anhydrous $MgSO_4$, then distillated in vacuum to remove CH_2Cl_2 and dried in vacuo at 50 °C. The pale yellow product poly(EO-*co*-Gly) is obtained in yield of 93%.

2.5. Esterification of poly(EO-co-Gly) with 2-bromoisobutyryl bromide

Esterification of hydroxyl groups of glycidol units of poly-(EO-*co*-Gly) with 2-bromoisobutyryl bromide [18] is carried out as shown in Scheme 4. A typical example is described as follows: 5 g (0.49 mmol) of poly(EO-*co*-Gly) ($M_n =$ 10,200; 12.8 mmol hydroxyl) is dissolved in 100 mL



Scheme 2. Anionic copolymerization of EPEE with EO.

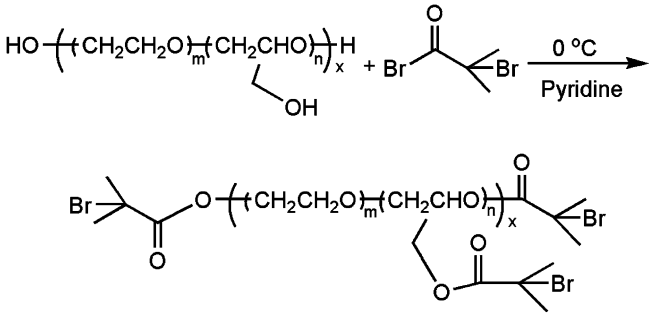


Scheme 3. Deprotection of EPEE segments of copolymers.

anhydrous pyridine under bubbling of dry nitrogen, 2.4 mL (19.2 mmol, 1.5 eq. of hydroxyl) of 2-bromoisobutyryl bromide is added dropwise at 0 °C for over 20 min under vigorous stirring, the initial yellow color disappeared immediately, and pyridinium bromide with red-brown color precipitated, then continuously stirred for another 15 min. The reaction process can be monitored by IR (KBr, ester-band at 1736 cm^{-1}). After that, to the system, 10 g (72.2 mmol) of K_2CO_3 is added at room temperature, the pyridine is removed by azeotropic distillation with dry toluene (6 × 40 mL). The residue is dissolved in water and separated by ultra filtration membrane. The aqueous solution is concentrated to dryness and dissolved in CH_2Cl_2, and then dried over anhydrous $MgSO_4$; after CH_2Cl_2 is removed by distillation in vacuum, the remains are dried in vacuo at 50 °C and the yellowy product with the yield of 95% is obtained.

2.6. Synthesis of graft copolymer PEO-g-PMA

The synthesis is conducted in bulk at 90 °C or in acetonitrile at 60 °C, as shown in Scheme 5. Here, the entries no. A_1–A_5 in Table 3 are exemplified: a group of ampoules

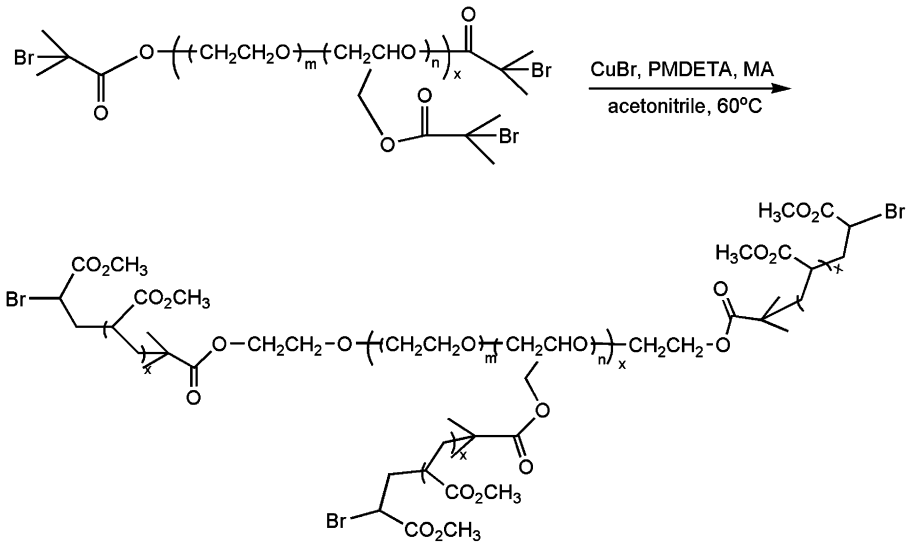


Scheme 4. Esterification of poly(EO-*co*-Gly) with 2-bromoisobutyryl bromide.

charged with poly(EO-*co*-Gly)$_{(ATRP)}$ (M_n = 13,800; 0.106 g, 0.0077 mmol; content of bromide end group: 0.202 mmol), CuBr (29.0 mg, 0.202 mmol, 1 eq.), PMDETA (31.5 mg, 0.202 mmol, 1 eq.), methyl acrylate (2.0 mL, 22.1 mmol, 109 eq.), and acetonitrile (2.0 mL) are vacuumed by three freeze-thaw cycles at the temperature of liquid nitrogen, then sealed and placed in an oil bath at 60 °C. The ampoules are taken out from the oil bath at different time intervals and are dipped in liquid nitrogen to stop the polymerization. The polymerized products are diluted by THF and passed through the silica gel column to remove the Cu^{2+} ions, then the colorless solution is concentrated to half of its original volume and precipitated in heptane. The product is dried at 40 °C under vacuum, a pale yellow polymer is obtained. It could be dissolved in THF, acetone, $CHCl_3$ and toluene.

2.7. Analysis

MALDI-TOF-MS is performed by a Bruker Reflex II MALDI-TOF (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometer equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm, α-cyano-4-hydroxycinnamic acid is used as matrix. ^1H NMR spectra are obtained on a DMX 500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. Size-exclusion chromatography (SEC) is performed on an Agilentl100 with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector using tetrahydrofuran (THF) as eluent at 35 °C with an elution rate of 1.0 mL/min. One 5 μm PL gel column (500 Å, molecular range 500–2 × 10^4 g/mol) and two 5 μm PL gel mixed bed column (molecular range 200–3 × 10^6 g/mol) are calibrated by polystyrene standard samples. For poly(EO-*g*-Gly), SEC is performed in distilled water at 40 °C with an elution



Scheme 5. Grafted polymerization of methyl acrylate by ATRP.

rate of 0.5 mL/min on same instrument except that the G1314A variable wavelength detector is substituted by a G1315A diode-array detector. Three TSK-gel PW columns in series (bead size: 6, 13, 13 μm; pore size: 200 Å, greater than 1000 Å, less than 100–1000 Å; molecular range: 0–5×10^4, 5×10^4–8×10^6, 5–8×10^6 g/mol) are calibrated by PEO standard samples. The injection volume is 20 μL, and the concentration is 5 mg/mL. IR spectra are obtained on a Magna-550 Fourier transform infrared spectrometer. Gas chromatographic–mass spectrometry analysis (GC/MS) of monomer EPEE is carried out using Finnigan Voyager system with mass selective detection operating in conjunction with electronic ionization (EI): a silica capillary column 30 m × 0.25 mm (I.D.) with 0.25 μm film thickness (DB-5 Restek) is used, the GC/MS parameters are as follows: ion source temperature: 200 °C, carrier gas: helium, column flow: 1 mL/min; temperature program: from 100 to 200 °C at 15 °C/min, splitless injection at 250 °C, the ionization is achieved at 70 eV. The Ultra Filtration Separator is purchased from Shanghai Institute of Nuclear Research, Chinese Academy of Science, the cut-off molecular weight of used poly(ether sulfone) film: $M_{n,\ \text{cut-off}} = 2000$ (calibrated by global protein). Conversions are determined by the gravimetric method.

3. Results and discussion

3.1. Characterization of parent copolymers poly(EO-co-EPEE) and EPEE units' hydrolysis

In the anionic copolymerization of EO and glycidol, the glycidol has to be protected because the exchanging reaction between hydroxyl groups of glycidol and DMPK would take place [19], so the side reaction is unavoidable. The glycidol (Gly) is protected with ethyl vinyl ether first, then is copolymerized with EO using the mixture solution of triethylene glycol and 20% DPMK as initiator, a linear α-hydroxyl-ω-hydroxyl poly(EO-*co*-EPEE) is produced. A series of parent copolymers with different contents of EPEE and with different molecular weights could be prepared by the variation of the monomer feed ratio and initiator volume as shown in Table 1 and Fig. 1 from which it could be observed that in all the cases the molecular weight distribution is much narrower, and with the increase of EPEE in the monomer feed ratio, the content of EPEE in the copolymer is also increased. Fig. 2(A) is a typical ^{1}H NMR spectrum of the copolymer poly(EO-*co*-EPEE). The quadruplets at $\delta = 4.63$–4.75 ppm are assigned to the methyl protons (H_a) of EPEE moiety, the doublets at $\delta =$ 1.30, 1.29 ppm and the triplet at $\delta = 1.21$, 1.19, 1.18 ppm are assigned to methyl protons of EPEE moiety (H_b, H_c), the chemical shift at $\delta = 3.53$–3.80 ppm is assigned to protons of main chain (H_f, H_g, H_h, H_i) and protons of lateral chains (H_c, H_e). The copolymer composition can be readily

Table 1
The data of the parent copolymers poly(EO-*co*-EPEE)

Sample[a]	R_f[b]	R_T[c]	M_n[d]	M_w/M_n[e]	M_n[f]	M_w/M_n[g]	N_{EPEE}[h]
A	1/9	1/8.4	12 700	1.06	11 600	1.01	24
B	1/9	1/9.5	6400	1.08	6210	1.05	13
C	1/5	1/5.3	5640	1.05	5340	1.04	17

[a] The molecular weight of poly(EO-*co*-EPEE) is designed by the formula: $M_n = W_{EO} + W_{EPEE} + W_{TEG}/N_{TEG}$, where W_{EO}, W_{EPEE} and W_{TEG} are the weights of ethylene oxide, EPEE and triethylene glycol, respectively, and N_{TEG} is the mole of triethylene glycol; the reaction is conducted at 60 °C.
[b] The feed ratio of EPEE to EO.
[c] The molar ratio of EPEE to EO in copolymer poly(EO-*co*-EPEE) measured by ^{1}H NMR.
[d] Number-average molecular weight determined by SEC, calibrated against PS standard.
[e] The polydispersity determined by SEC.
[f] Number-average molecular weight determined by MALDI-TOF-MS.
[g] The polydispersity determined by MALDI-TOF-MS.
[h] The number of EPEE units in poly(EO-*co*-EPEE), calculated by the formula: $N_{EPEE} = M_n^f/(146 + 44/R_T^c)$.

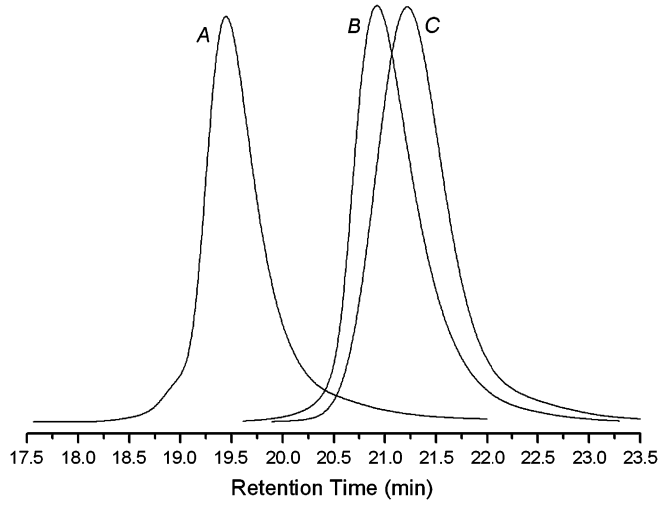


Fig. 1. SEC traces of poly(EO-*co*-EPEE) (A, B and C are prepared as shown in Table 1).

obtained by using the following formula based on the ^{1}H NMR spectrum:

$$R_T = \frac{4A_a}{A_{sum} - 7A_a} \quad (1)$$

where R_T is the molar ratio of EPEE to EO in copolymers; A_{sum} and A_a represent the peak area sum of the protons c, e, f, g, h and i and the peak areas of the methine protons of the EPEE moiety, respectively. The R_T values of copolymers A, B and C are 1/8.4, 1/9.5 and 1/5.3, respectively, which are nearly equivalent to the monomer feed ratio of EPEE to EO.

The protecting group acetal of EPEE units in poly(EO-*co*-EPEE) could be cleaved by formic acid, then hydroxymethyl is recovered after saponification as shown in Schemes 3 and 4. Table 2 listed the data of hydrolyzed products of poly-(EO-*co*-EPEE) samples, from which it could be observed that the molecular weight and molecular weight distribution before and after hydrolysis do not change obviously if the mass variation of EPEE before and after hydrolysis is considered, which means the main chain of copolymer was not cleaved, and the hydrolysis was successful. Fig. 2(B) is the ^{1}H NMR spectrum of the hydrolyzed product (EO-*co*-Gly). Comparing with Fig. 2(A), the peaks at $\delta = 4.71$ ppm [−O−*CH*(CH3)−O−], 1.33 ppm [−OCH(C*H*$_3$)−O−], 1.19 ppm (−O−C*H*$_3$) attributed to EPEE units of poly(EO-*co*-EPEE) disappeared, which means the hydrolysis of poly(EO-*co*-EPEE) is complete. The FTIR spectra before [Fig. 3(A)] and after hydrolysis [Fig. 3(B)] of poly(EO-*co*-EPEE) provided another evidence for complete hydrolysis, the peaks at 1379 cm^{-1} attributed to acetal in Fig. 3(A) disappeared and the new peaks at 3473 cm^{-1} in Fig. 3(B) attributed to hydroxymethyl appeared.

Table 2
The data of the hydrolyzed products of poly(EO-*co*-EPEE) and their esterified products poly(EO-*co*-Gly)$_{(ATRP)}$

Sample	M_n[a]	M_w/M_n[b]
Poly(EO-*co*-Gly)$_A$	10 200	1.14
Poly(EO-*co*-Gly)$_B$	5310	1.15
Poly(EO-*co*-Gly)$_{A(ATRP)}$	13 800	1.09
Poly(EO-*co*-Gly)$_{B(ATRP)}$	7680	1.08

[a] Number-average molecular weight determined by SEC, poly(EO-*co*-Gly) calibrated against PEO standard and poly(EO-*co*-Gly)$_{(ATRP)}$ calibrated against PS standard.
[b] The polydispersity determined by SEC.

3.2. Synthesis of polyethylene oxide with pending multi-activated isobutyryl bromides

The poly(EO-*co*-Gly) can be regarded as polyethylene oxide with pending multi-hydroxylmethyl groups, and the

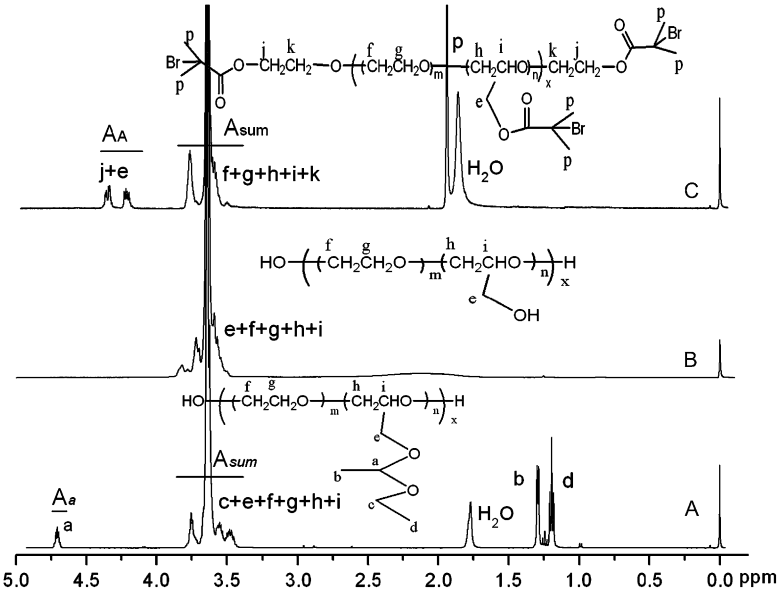


Fig. 2. (A) ^{1}H NMR spectrum of poly(EO-*co*-EPEE) (A: $M_n = 1.27 \times 10^4$; solvent: $CDCl_3$). (B) ^{1}H NMR spectrum of poly(EO-*co*-Gly) (A: $M_n = 1.02 \times 10^4$; solvent: $CDCl_3$). (C) ^{1}H NMR spectrum of poly(EO-*co*-Gly)$_{(ATRP)}$ (A: $M_n = 1.38 \times 10^4$; solvent: $CDCl_3$).

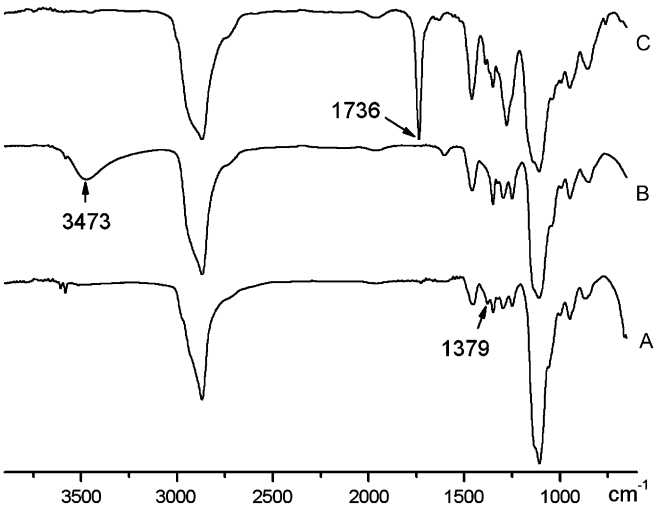


Fig. 3. FTIR spectra of copolymers (KBr) [(A): poly(EO-*co*-EPEE), $M_n = 1.27 \times 10^4$; (B): poly(EO-*co*-Gly), $M_n = 1.02 \times 10^4$; (C): poly(EO-*co*-Gly)$_{(ATRP)}$, $M_n = 1.38 \times 10^4$].

hydroxyl groups could be converted into alkyl bromides easily, which are used as effective initiators for ATRP. Fig. 2(C) shows the typical ^{1}H NMR spectrum of poly(EO-*co*-Gly) with pending multi-bromoisobutyryl groups [poly(EO-*co*-Gly)$_{(ATRP)}$], the hydroxyl group conversion can be calculated by the following formula:

$$E_T = \frac{\left(\frac{4}{R_T} + 3\right) \times N_{EPEE} \times A_A}{2A_{sum} \times (N_{EPEE} + 2)} \times 100\% \quad (2)$$

where E_T is the conversion efficiency of hydroxyl groups of poly(EO-*co*-Gly), A_{sum} and A_A represent the integral area of the protons of the PEO main chain (the peaks at $\delta = 3.35-3.90$ ppm) and the integral area of the methylene protons (H_e, H_j) linked to ester (the peaks at $\delta = 4.13-4.42$ ppm), respectively, N_{EPEE} is the number of EPEE units in poly(EO-*co*-EPEE) and R_T is the molar ratio of EPEE to EO in copolymer poly(EO-*co*-EPEE) measured by ^{1}H NMR (see Table 1). The E_T values for two samples are nearly 100%, it suggested that the conversion of hydroxyl groups to bromoisobutyryl is complete. The FTIR spectra before and after esterification of poly(EO-*co*-Gly) provided another evidence for complete esterification, the peaks at 3473 cm^{-1} attributed to hydroxymethyl in Fig. 3(B) disappeared and new peaks at 1736 cm^{-1} in Fig. 3(C) attributed to ester-band appeared.

3.3. Graft polymerization of MA using poly(EO-co-Gly)$_{(ATRP)}$ as initiator

Two poly(EO-*co*-Gly) samples with pending activated bromides are used as macroinitiators to initiate the polymerization of methyl acrylate by ATRP in bulk at 90 °C or in acetonitrile at 60 °C, respectively, the copolymerization data are listed in Table 3. The polymerization is conducted in bulk first, however, as Fig. 4 shows there appears a peak with low molecular weight at the large elution volume besides the main peak for products, it may be produced by the thermal polymerization of MA at 90 °C [18]. As the conversion of MA is increased, for example, to 35%, the gelation is found due to the coupling between macromolecular radicals. These observations are coincident with the previous results reported by Haddleton et al. [20] and Maier et al. [18]. In these cases, although the concentration of active radicals in the polymerization of MA is low due to the presence of the Cu(I/II) system, the gelation is still unavoidable. In order to suppress this process, the polymerization is carried out in acetonitrile at 60 °C. As we expected, the polymerization of MA in acetonitrile is better-controlled than in bulk, the molecular weight distribution of the product obtained in acetonitrile (about 1.15) is much narrower than that in bulk (about 1.37). It means in our system the

Table 3
The data of the amphiphilic graft copolymers PEO-*g*-PMA and their corresponding precursors

Initiator	Entry	Time (h)	Conv. (%)[a]	M_n[b] $\times 10^{-4}$	M_w/M_n[c]	M_n (calcd.)[d] $\times 10^{-4}$
A (*in acetonitrile*)	A_1	0.5	6.62	2.58	1.14	3.96
	A_2	1	11.8	3.37	1.15	4.75
	A_3	1.5	16.3	4.13	1.13	5.51
	A_4	2	21.1	4.91	1.11	6.29
	A_5	2.5	26.7	5.78	1.18	7.06
A (*in bulk*)	A_6	0.25	8.11	2.85	1.34	
	A_7	0.50	16.4	4.16	1.37	
	A_8	0.75	24.7	5.21	1.33	
	A_9	1	33.1	6.47	1.39	
	A_{10}	1.25		Gelation		
B (*in acetonitrile*)	B_1	0.5	3.59	1.23	1.16	
	B_2	1	6.41	1.70	1.15	
	B_3	1.5	8.84	2.19	1.13	
	B_4	2	11.6	2.63	1.16	
	B_5	2.5	14.8	3.14	1.19	

[a] The monomer conversion was determined by gravimetric method.
[b] Number-average molecular weight determined by SEC, calibrated against PS standard.
[c] The polydispersity determined by SEC.
[d] The average molecular weight of PEO-*g*-PMA is calculated from the ^{1}H NMR data on formula (3) in text.

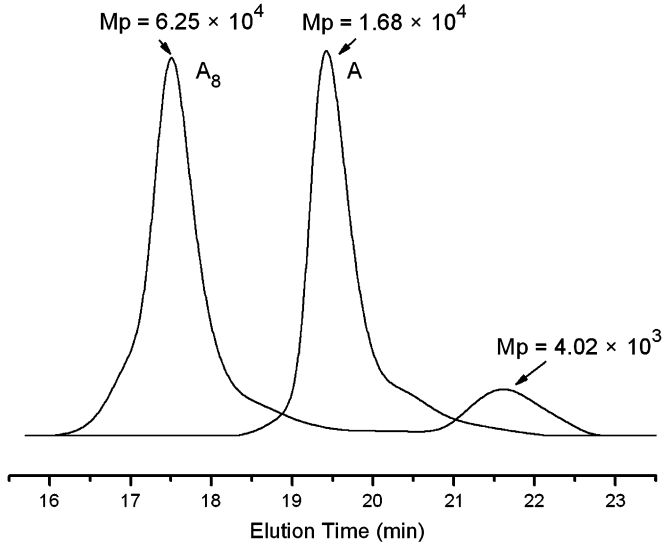


Fig. 4. SEC traces of the graft copolymer: PEO-*g*-PMA (sample A_8, $M_n = 5.21 \times 10^4$, $M_w/M_n = 1.33$) and the macroinitiator poly(EO-*co*-Gly)$_{(ATRP)}$ no. A ($M_n = 1.38 \times 10^4$, $M_w/M_n = 1.09$, EPEE/EO = 1:8.4).

inter-macromolecular coupling during the whole polymerization does not occur, and we also do not find the homopolymerization of methyl acrylate.

Fig. 5 is the ^{1}H NMR spectra of the resultant polymer (A_3, $M_n = 4.13 \times 10^4$), the appearance of a signal at $\delta = 4.20$–4.35 ppm attributed to the methylene protons (H_a, H_b) linked to ester (its integral area is defined as A_A), the signal at $\delta = 4.07$ ppm assigned to the secondary bromine end group ($-CH_2CH(CO_2CH_3)Br$) (its integral area is defined as A_C), and the signal at $\delta = 3.41$–3.86 ppm attributed to the protons of the PEO main chain and the protons of methyl acrylate ($-CO_2CH_3$) (the integral area for them are defined as A_{sum})

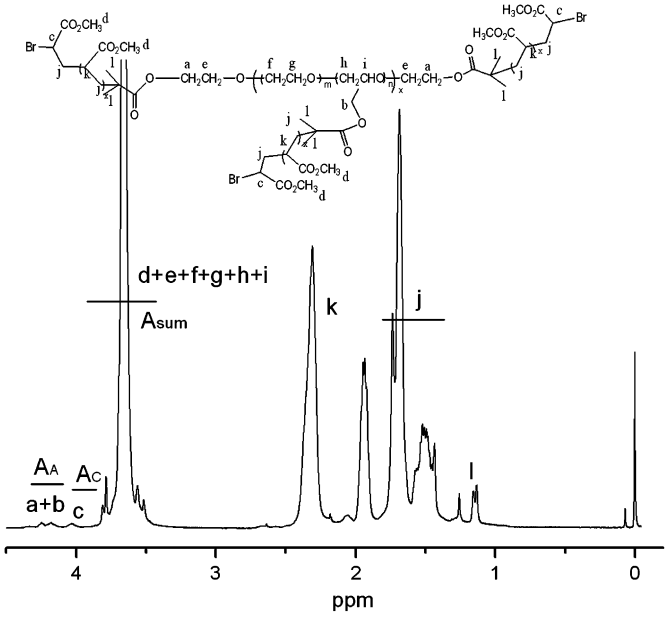


Fig. 5. ^{1}H NMR spectrum of PEO-*g*-PMA (A_3: $M_n = 4.13 \times 10^4$; solvent: $CDCl_3$).

confirmed that the graft copolymer PEO-*g*-PMA is successfully prepared. The calculated ratio of A_A/A_C is equal to 2/1, which means all the macroinitiator have took part in the polymerization of MA.

The total average molecular weight of the graft copolymer can be obtained by Eq. (3):

$$\overline{M_n} = \frac{A_{sum} - \left(\frac{4}{R_T} + 3\right) \times N_{EPEE} \times \frac{A_A}{2(N_{EPEE}+2)}}{3 \times \frac{A_A}{2(N_{EPEE}+2)}} \times M_{MA} + \overline{M_{n_I}} \quad (3)$$

where N_{EPEE} is the number of EPEE units in poly(EO-*co*-EPEE) and R_T is the molar ratio of EPEE to EO in copolymer poly(EO-*co*-EPEE) measured by ^{1}H NMR (see Table 1). M_{MA} is the mole mass of MA and Mn_I is the molecular weight of macroinitiator. The A_A and A_{sum} have the same meaning as before.

Table 3 lists the M_n data by calculation using formulae (3) and SEC, and the experimental value is lower than that of calculated value due to the sharp difference of hydrodynamic volume between the graft copolymer and linear polystyrene standard.

3.4. Controllability of grafting copolymerization of methyl acrylate

As illustrated in Fig. 6, the plot of Ln $[M_0]/[M]$ ($[M_0]$: initial MA concentration; [M]: MA concentration at certain time) versus time is linear for different macroinitiators either in bulk (conversion is less than 30%) or in acetonitrile, indicating that the apparent propagation rate constant is in first-order with the monomer concentration, which means the concentration of the

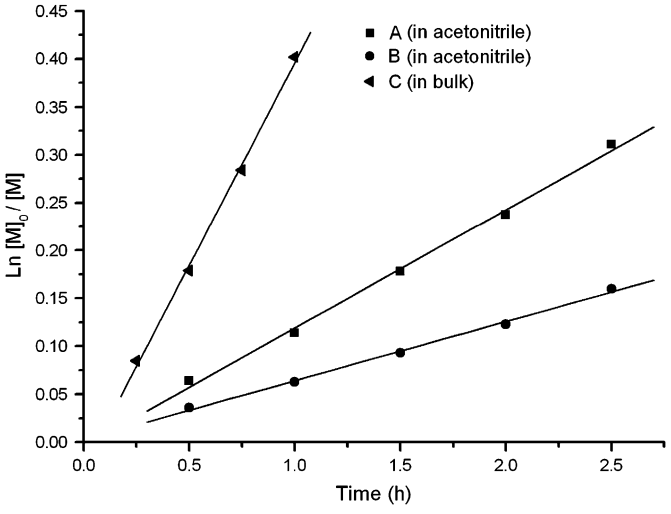


Fig. 6. Ln ($[M_0]/[M]$) versus time plots for the graft polymerization of methyl acrylate, which is polymerized via ATRP in bulk at 90 °C and in acetonitrile solution at 60 °C (macroinitiator poly(EO-*co*-Gly)$_{A(ATRP)}$: $M_n = 1.38 \times 10^4$, $M_w/M_n = 1.09$, EPEE/EO = 1:8.4 for linear A and linear C; macroinitiator poly(EO-*co*-Gly)$_{B(ATRP)}$: $M_n = 7.68 \times 10^3$, $M_w/M_n = 1.08$, EPEE/EO = 1:9.5 for linear B). In all the cases, the [M]/[I] = 109, [I]:[CuBr]:[PMDETA] = 1:1:1; [M]/[I] = concentration of monomer:concentration of initiating bromides.

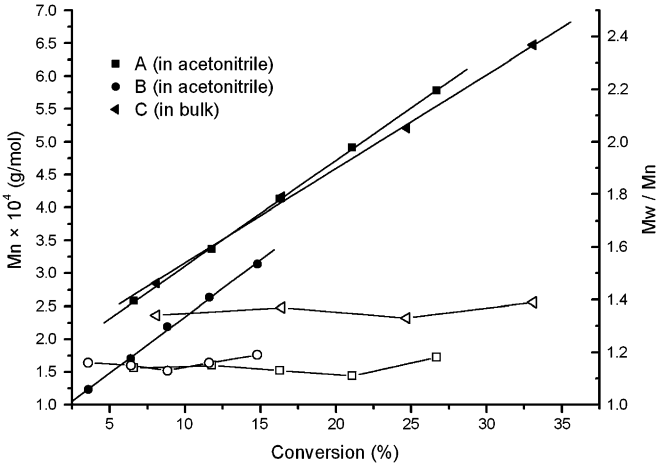


Fig. 7. M_n and M_w/M_n versus conversion plots for the graft polymerization of methyl acrylate, which polymerized via ATRP in bulk at 90 °C and in acetonitrile solution at 60 °C (macroinitiator poly(EO-*co*-Gly)$_{A(ATRP)}$: $M_n = 1.38 \times 10^4$, $M_w/M_n = 1.09$, EPEE/EO = 1:8.4 for linear A and linear C; macroinitiator poly(EO-*co*-Gly)$_{B(ATRP)}$: $M_n = 7.68 \times 10^3$, $M_w/M_n = 1.08$, EPEE/EO = 1:9.5 for linear B). In all the cases, the [M]/[I] = 109, [I]:[CuBr]:[PMDETA] = 1:1:1; [M]/[I] = concentration of monomer:concentration of initiating bromides. The open circle, open square and open triangle are the polydispersity index of the copolymers corresponding to solid circle, solid square and solid triangle.

growing radicals is constant during the polymerization regardless of the initial concentration of the initiator. The number-average molecular weight is increased linearly with conversion (Fig. 7) for the three groups of experiments, which is consistent with the common characteristics of ATRP. The copolymers in acetonitrile solution show the relatively narrow polydispersity because of the better-controlled processes. As Fig. 7 indicated for the same macroinitiator A, the slope derived from bulk is smaller than that from acetonitrile, which means in the same conversion of MA, the molecular weight of the graft copolymer obtained by bulk polymerization is smaller than that obtained by solution polymerization. It may be caused by homopolymerization of methyl acrylate in bulk polymerization leading to the decrease of efficient concentration of MA.

4. Conclusion

A novel amphiphilic graft copolymer of PEO as main chain and PMA as side chains is successfully synthesized by combination of anionic copolymerization with ATRP. The protected glycidol is copolymerized with EO first, then the hydroxyl of deprotected glycidol of copolymerized product is esterified by bromoisobutyryl bromide to form the macroinitiator poly(EO-*co*-Gly)$_{(ATRP)}$ to initiate the polymerization of MA. In solution polymerization of MA, the molecular weight distribution of the graft polymers is much narrower than in bulk, and the linear dependence of Ln [M_0]/[M] on time demonstrates that the MA polymerization is well controlled.

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