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Synthesis and characterization of comb-shaped poly(amido amine)-*g*-PEO via Michael addition polymerization

Ding Wang [a], Ye Liu [b], Chun-Yan Hong [a], Cai-Yuan Pan [a,*]

[a] *Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[b] *Institute of Materials Research and Engineer, 3 Research Link, Singapore 117602, Singapore*

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Abstract

Linear pH-sensitive poly(amido amine)s were synthesized via Michael addition polymerization of *N*-aminoethyl piperazine (AEPZ) or 4-aminomethyl piperidine (AMPD) with 1,12-dodecylene diacrylamide (DDA). Successive Michael addition reaction of acryl-terminated poly(ethylene oxide) (A-PEO) with the secondary amine of linear poly(DDA–AEPZ) that has one secondary amine in every repeating unit afforded PEO-grafted poly(amido amine). Variation of grafting degree could be obtained conveniently via tuning the feed molar ratio of acryl/secondary amine. When this ratio equals to 1.2, all the secondary amines on the backbone of poly(DDA–AEPZ) (or poly(DDA–AMPD)) were consumed and the comb-shaped polymers were formed. The amphiphilic comb-shaped poly(DDA–AEPZ)-*g*-PEO was molecularly dissolved in water at pH 2.0 (w/v = 0.25%), and micelles were formed when pH value of aqueous solution was adjusted to 6.5. ^{1}H NMR data verify the formation of micelles due to the disappearance of signals attributed to poly(DDA–AEPZ). The formation of micelles can be confirmed further by TEM photos, they show that all the particles are approximately spherical and their number-average diameter is around 95 nm.

Keywords: Comb-shaped polymer; Michael addition polymerization; Micelles

1. Introduction

The comb-shaped polymers with poly(ethylene oxide) (PEO) side-chains have received tremendous attention in recent decades, not only due to their rich morphological textures [1–3], but also due to their potential applications as compatibilizer in polymer blending [4], as surfactant [5,6], in high energy density lithium batteries [7,8] and especially in biomedical materials because PEO exhibits high protein resistance, biocompatibility, low toxicity and immunogenicity [9–14]. Poly(amido amine)s synthesized from Michael addition polymerization of diacrylamides and multifunctional amines have been widely developed for applications as biomedical materials and polymer therapeutics [15–17]. Both PEO and poly(amido amine)s have potential applications in biomedical field. Therefore, the preparation of poly(amido amine)s grafted with PEO chains will be interesting. One easy method for preparation of this comb-like copolymer is the synthesis of linear poly(amido amine)s with reactive secondary amines in their backbone, followed by Michael addition reaction with acryl-terminated PEO.

Generally, linear poly(amido amine)s are prepared by Michael addition polymerizations of diacrylamides with both primary mono(amine)s and secondary bis(amine)s [18,19]. However, these polymers are composed of tertiary amine, and do not contain reactive secondary amine. Under non-selective conditions, the reaction of primary bis(amine)s with bis(acrylamide)s gives usually cross-linked products [18,20]. However, under special conditions including low concentrations of reactant and low reaction temperatures, soluble branched poly(amido amine)s carrying secondary amine instead of tertiary amino groups in their backbone were formed [15].

In our previous work, linear poly(MDA–AEPZ), which is soluble in water, was obtained via the Michael addition polymerization of *N*,*N*′-methylene diacrylamide (MDA) with an equal molar trifunctional amine, *N*-aminoethyl piperazine (AEPZ) [21]. For synthesis of micelles by self-assembling of amphiphilic graft copolymers with PEO side chains, regulating the spacer length of diacrylamide is expected to produce the pH sensitive linear poly(amido amine)s containing one secondary amine in every repeat unit, following Michael addition reaction of those amines with acryl-terminated PEO will form

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* Corresponding author.
E-mail address: pcy@ustc.edu.cn (C.-Y. Pan).

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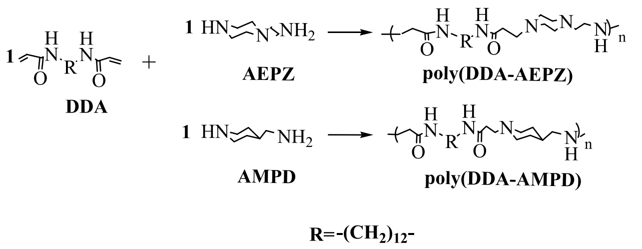


Scheme 1. Michael addition polymerizations of diacrylamide with equimolar trifunctional amine for preparation of linear polymers.

poly(amido amine)s grafted PEOs, which might have potential applications in drug deliver. In this report, we present the synthesis of a series of linear pH-sensitive poly(amido amine)s via Michael addition polymerization of AEPZ or (AMPD) with 1,12-dodecylene diacrylamide (DDA) as described in Scheme 1. Successive Michael addition reaction with acryl-terminated PEO afforded comb-shaped copolymers as described in Scheme 2. The micelles were obtained by self-assembly of the amphiphilic comb-shaped copolymer poly(DDA–AEPZ)-*g*-PEO in water at pH 6.5.

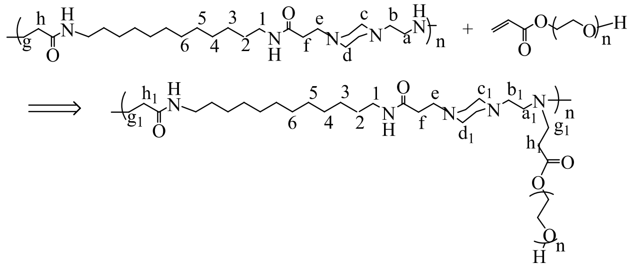
2. Experimental

2.1. Materials

Poly(ethylene glycol) acrylate (A-PEO)($M_n = 375$), 1-(2-aminoethyl) piperazine (AEPZ), 4-aminomethyl piperidine (AMPD) and 1,12-diaminododecane purchased from Aldrich were used as received. Acryloyl chloride (Fluka, 98%) was used as received. All other chemicals and solvents were purified according to the normal methods prior to use.

2.2. Characterization

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker DRX-300 nuclear magnetic resonance (NMR) spectrometer. ^{13}C NMR was performed using an inverse-gated broadband decoupled (INVGATE) program. Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC822 under nitrogen at a heating rate of 20 °C/min from −50 to 200 °C, and the results were obtained in the second scan. Gel permeation chromatography (GPC) was carried out on a Waters 2690 apparatus with two columns in series (Waters Ultrahydrogel 250, 200) and a Waters 410 refractive index detector using 0.5 M acetic acid/0.5 M sodium acetate as eluent and poly(ethylene oxide) standards. Thermal gravimetric analysis (TGA) was performed on a thermo-gravimetric analyzer DT-50 with a heating rate of 10 °C/min under a nitrogen flow rate of 20 mL/min. The size measurement and morphology observation of micelles were performed using a JEM-100SX transmission electron microscopy (TEM).



Scheme 2. Michael addition of secondary amine formed with acryl-terminated PEO.

2.3. Preparation of diacrylamide monomers

Diacrylamides were prepared according to a similar method reported [22], and synthetic procedure of dodecylene diacrylamide (DDA) is described as follows. Into a 250 mL round-bottom flask containing a solution of acryloyl chloride (9.0 mL, 112 mmol) in acetonitrile (40 mL), benzene (15 mL) and chloroform (15 mL) filled with dry nitrogen, a solution of 1,12-dodecylene diamine (7.998 g, 40 mmol) in benzene (20 mL) and chloroform (20 mL) was added dropwise at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 5 h, and then at 25 °C for an additional 4 h. A white solid product was obtained by filtration, and then washed with benzene (300 mL) and saturated sodium bicarbonate water solution (200 mL) successively. After dried in vacuum oven at room temperature for 36 h, a white powder was precipitated from methanol at −26 °C, and the target product (7.0 g) was obtained in 57% yield. ^{1}H NMR (300 MHz, D_2O) δ (ppm): 5.61–6.21 (m, 6H, $CH_2{=}CH$), 3.23 (m, 4H, CH_2–N), 1.53 (m, 4H, CH_2), 1.31 (s, 16H, CH_2 in the middle eight methylene).

2.4. Preparation of linear polymers

Poly(amido amine)s were prepared with a similar method reported [21]. A typical polymerization procedure is as follows: AEPZ (258 mg, 2 mmol) was added into a solution of DDA (616 mg, 2 mmol) in methanol (6 mL). The polymerization was performed at 50 °C. The conversion of DDA was monitored by measurement of their ^{1}H NMR spectra, and it was calculated based on Eq. (1)

$$\text{DDA\% (conversion)} = \{1 - [I_{5.7\text{–}6.3}/0.25(I_{1.3} + I_{1.5} + I_{3.3})]\}100\% \quad (1)$$

where $I_{5.7\text{–}6.3}$ is the integral value of signals at $\delta = 5.7$–6.3 ppm attributed to the vinyl protons, $I_{1.3}$, $I_{1.5}$ and $I_{3.3}$ are the integral values of signals at 1.31–1.35, 1.53–1.55 and 3.23–3.28 ppm attributed to the dodecylene protons in the DDA, respectively.

Once conversion reached to ~100%, the polymerization was stopped, and the solution was concentrated under reduced pressure, followed by precipitation from cold acetone. The product was purified by dissolving in methanol, and followed precipitated from cold acetone. After separation by filtration, the product was dried in a vacuum oven at 40 °C for 24 h.

Table 1
The results in Michael addition polymerization of diacrylamides with trifunctinal monomers

Entry	Feed molar ratio		CH_3OH (mL)	Yield (%)	M_n[a]	M_w/M_n[a]	T_g[b] (°C)	T_d[c] (°C)
	DDA	DA						
L1[d]	2	2	6	94	6200	4.2	14.3	309
L2[d]	2	2	6	93	4700	5.66	15.4	287

In all cases, the molar ratio of DDA to AEPZ (or AMPD) is 1; temperature, 50 °C.

[a] Obtained by GPC.

[b] Obtained by DSC.

[c] The temperature at which a 5% weight loss occurred.

[d] DA of L1 was AEPZ, and DA of L2 was AMPD.

2.5. Preparation of comb-shaped copolymers

A typical procedure is as follows. The acryl-terminated PEO (A-PEO) ($M_n = 375$, 155 mg, 0.41 mmol) was added into a solution of poly(DDA–AEPZ) (L1 in Table 1, 300 mg, 0.049 mmol) in 4 mL methanol (molar ratio of PEO/secondary amine = 0.6). The polymerization was performed at 60 °C. After 48 h, the polymerization was stopped and the solution was concentrated under reduced pressure, followed by precipitation from diethyl ether. The product was collected by filtration; and it was purified by pouring the polymer solution in methanol into diethyl ether. The target polymer (428 mg) was obtained in 94% yield after it was dried in a vacuum oven at 40 °C for 24 h. Through tuning the molar ratio of PEO/secondary amine, graft polymers with different grafting degree were obtained.

2.6. Preparation of micelles

The micelles were prepared according to a method reported [23]: the PEO grafted poly(DDA–AEPZ)s [P(DDA–AEPZ)-*g*-PEO] were dissolved in water at pH 2.0 (w/v = 0.25%), and the solution was adjusted to pH 6.5 to induce the formation of micelles.

3. Results and discussion

3.1. Preparation of linear polymers

The Michael addition polymerizations of trifunctional amines AEPZ or AMPD with an equimolar DDA were performed in methanol. When the monomer concentrations were ca. 11%, no gelation occurred up to almost complete conversion in all the polymerizations. The polymerization conditions and results are listed in Table 1. The molecular weight distributions of the linear polymers are broader ($M_w/M_n = 4.2$–5.66, in Table 1), and this may be due to very low branch of the polymers obtained that cannot be detected by NMR method.

Our previous results obtained from the Michael addition polymerization of diacrylamide with trifunctional amines AEPZ or AMPD [21,24] showed that the reactivity sequence of three types of amines in AEPZ and AMPD is as following: 2° amine (original) > 1° amine ≫ 2° amine (formed), and the 2° amine (formed) is kept out of the reaction at feed molar ratio of diacrylamide/trifunctional amine = 1:1 due to that the high steric hindrance of polymer chains leads to the lowest reactivity of the 2° amine (formed). However, steric hindrance of cyclic aliphatic rings in AEPZ and AMPD on the 2° amines (original) is much lower, and the inductive effect of aliphatic substituent on the nitrogen atoms increases the electron density, leading to a higher reactivity of the 2° amines (original) in comparison with the 1° amines. Therefore, linear poly(amido amine)s containing secondary and tertiary amines in the backbones are obtained in the Michael addition polymerizations of AEPZ and AMPD with an equimolar DDA, respectively (Scheme 1).

Fig. 1 is the quantitative ^{13}C NMR spectra of poly(DDA–AEPZ), and for comparison, the ^{13}C NMR spectrum of AEPZ is also shown in Fig. 1(a). The assignment of signals for the polymers obtained is based on the references reported [21,24] and the ^{13}C NMR spectrum of the diacrylamide monomers. In comparison with the ^{13}C NMR spectrum of AEPZ (Fig. 1(a)), it can be found that there are three types of carbons a, g and 1 attached to secondary amines with their peaks located at $\delta =$ 45.8, 45.8 and 39.5 ppm in poly(DDA–AEPZ), respectively. The polymerization has little effect on the peak positions of carbons 1–6 in DDA, so there are only two types of carbons a and g attached to secondary amine were formed in the polymerization with their peaks overlapped at $\delta = 45.8$ ppm (Fig. 1(b)). Fig. 1(b) also reflects that there are four carbon signals b, c, d and e attached to tertiary amines with their peaks located at $\delta = 57.4$, 53.2, 52.8 and 54.5 ppm, respectively, but no carbon signal is attached to primary amine, indicating almost complete reaction of the secondary (original) and primary amine of AEPZ with diacrylamide.

Similar to the polymerization of AEPZ with DDA, the Michael addition polymerization of AMPD with equimolar DDA yielded also linear poly(amido amine)s containing tertiary and secondary amines in their backbones. This can be confirmed by the ^{13}C NMR spectra of poly(DDA–AMPD) and AMPD in Fig. 2. In comparison with the ^{13}C NMR spectrum of AMPD (Fig. 2(a)), we can see that two signals a and g at $\delta = 55.4$ and 46.0 ppm, respectively, in Fig. 2(b) are assigned to those two carbons attached to secondary amine, which were formed in the polymerization. The vinyl carbon signals of DDA are shifted to $\delta = 54.8$ (e), 33.1 (f), 46.0 (g) and 35.9 ppm (h) in Fig. 2(b), and the carbon signals of AMPD at $\delta = 46.6$ (a_0), 37.8 (b_0), 29.3 (c_0) and 44.6 ppm (d_0) in Fig. 2(a) are shifted to new positions at $\delta = 55.4$ (a), 35.3 (b), 30.5 (c)

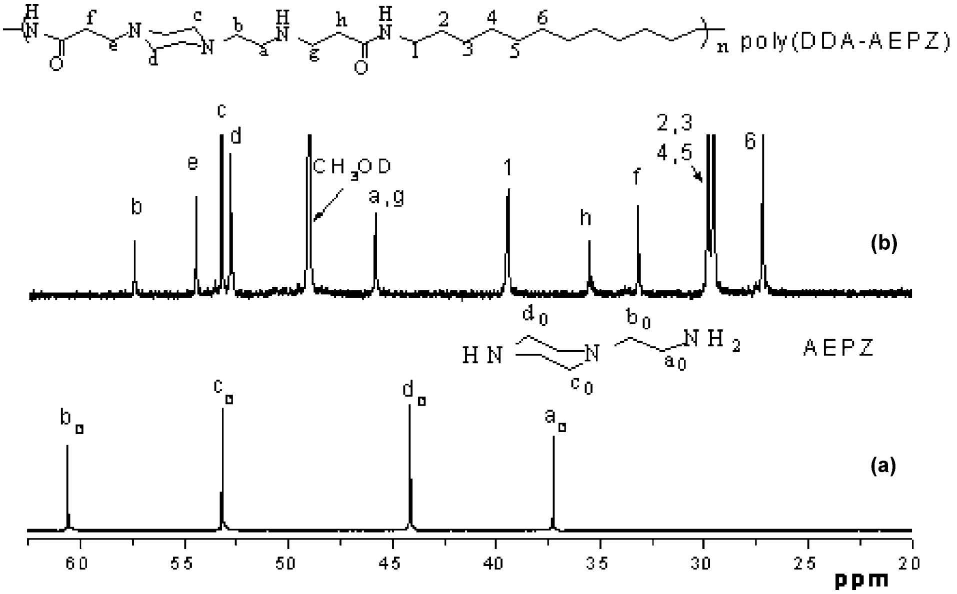


Fig. 1. The quantitative ^{13}C NMR spectra of (a) AEPZ; (b) linear poly(DDA–AEPZ) (L1 in Table 1).

and 53.4 ppm (d) in Fig. 2(b), respectively, due to the Michael addition reactions of secondary amine in AMPD ring and primary amine with vinyl groups of DDA. No signals of carbons formed by the Michael reaction of secondary amine formed in situ with vinyl group of DDA are observed, indicating the formation of linear poly(DDA–AMPD). Therefore, for Michael addition polymerization of AEPZ or AMPD with equimolar DDA, linear polymers were produced. These polymers containing lots of amide and amine groups can be dissolved in acidic but insoluble in neutral or alkaline water due to the long aliphatic spacer in DDA unit. So pH-sensitive poly(amido amine)s was obtained.

3.2. Polymerization of grafted polymers

Although the secondary amine formed in situ has lower reactivity, it can undergo Michael addition reaction. However, application of this amine in synthesis of graft polymers has not been reported based on our knowledge. Thus we studied this reaction for preparation of comb-like copolymer. The reactions

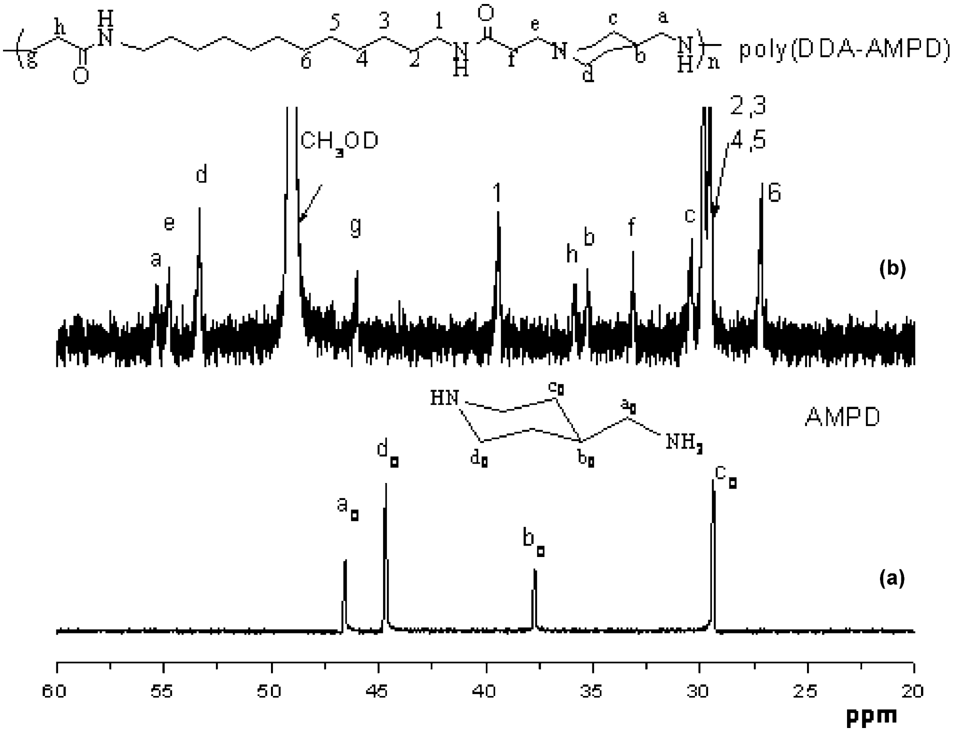


Fig. 2. The quantitative ^{13}C NMR spectra of (a) AMPD; (b) linear poly(DDA–AMPD) (L2 in Table 1).

Table 2
The synthetic conditions and results of graft copolymer obtained from the reaction of linear poly(amido amine)s with acryl-terminated PEO

Entry[a]	Temperature (°C)	Time (h)	Feed molar ratio[b]	Yield (%)	DG (%)[c]	M_n (NMR)[d]
G1	60	48	0.4	97	36.4	8500
G2	60	48	0.6	97	56.7	10,200
G3	60	48	1.2	98	~100	12,700
G4	60	48	1.2	98	~100	8900

[a] Obtained from poly(DDA–AEPZ)(G1–G3) and poly(DDA–AMPD)(G4).

[b] Molar ratio of acryl/secondary amine.

[c] DG, degree of grafting; $DG = I_{56.3}/(I_{57.2}+I_{56.3})100\%$.

[d] $M_n\ (\mathrm{NMR}) = [1.5 I_{4.35} M_{n,\mathrm{PEO}} + 0.15 I_{1.2\text{–}1.5} M]/I_{5.7\text{–}6.3}$.

of linear poly(DDA–AEPZ) and poly(DDA–AMPD) with acryl-terminated PEO (11.4% (w/v)) were carried out in methanol. The reaction conditions and results are listed in Table 2. Typical grafting reaction of poly(DDA–AEPZ) proceeds according to Scheme 2. Although the reactivity of the secondary amine formed in situ is low [21,24], the grafting degree via Michael addition reaction with acryl-terminated PEO (A-PEO) at 60 °C is not low (Table 2). For determination of grafting degree of the copolymers obtained, the reaction was followed by ^{13}C NMR measurements. The quantitative ^{13}C NMR spectra of three grafting copolymers, poly(DDA–AEPZ)-*g*-PEO obtained are shown in Fig. 3. Fig. 3(a)–(c) are the ^{13}C NMR spectra of the grafting copolymers obtained from reaction with the feed molar ratio of secondary amine (formed)/acryl group = 0.4 to 0.6 to 1.2. Except characteristic signals of poly(DDA–AEPZ), the signal at $\delta = 70.5$ ppm attributed to the carbons of PEO indicates the formation of grafting copolymers. According to Scheme 2, the carbons a and g should be affected significantly, but the carbons b and h, c and d are less affected by the Michael addition reaction of secondary amine with acryl group of A-PEO. We can observe that the signals of carbons a and g, b and h, c and d are shifted from $\delta = 45.8$ (a and g), 57.2 (b) and 35.4 (h), 53.1(c) and 52.7(d) to $\delta = 51.2(a_1)$ and $50.7(g_1)$, $56.3(b_1)$ and $33.8(h_1)$, $53.4(c_1)$ and $52.5(d_1)$ ppm, respectively. By comparison of Fig. 3(a)–(c), we will find that the carbons a and g, b and h, c and d signals decrease with the feed molar ratio increase of acryl in A-PEO/secondary amine. At the feed molar ratio = 1.2, carbons signals a and g, b and h, c and d disappear completely in Fig. 3(c). Hence the degree of grafting (DG) could be calculated based on ^{13}C NMR data according to Eq. (2)

$$DG = I_{56.3}/(I_{57.2} + I_{56.3})100\% \tag{2}$$

where $I_{57.2}$ and $I_{56.3}$ are the integral intensities of signals at $\delta =$ 57.2 and 56.3 ppm attributed to the carbon b and b1 in Fig. 3, respectively. The calculated results are listed in Table 2.

When the feed molar ratio of acryl/secondary amine increased from 0.4 to 0.6 to 1.2, the DG values of the

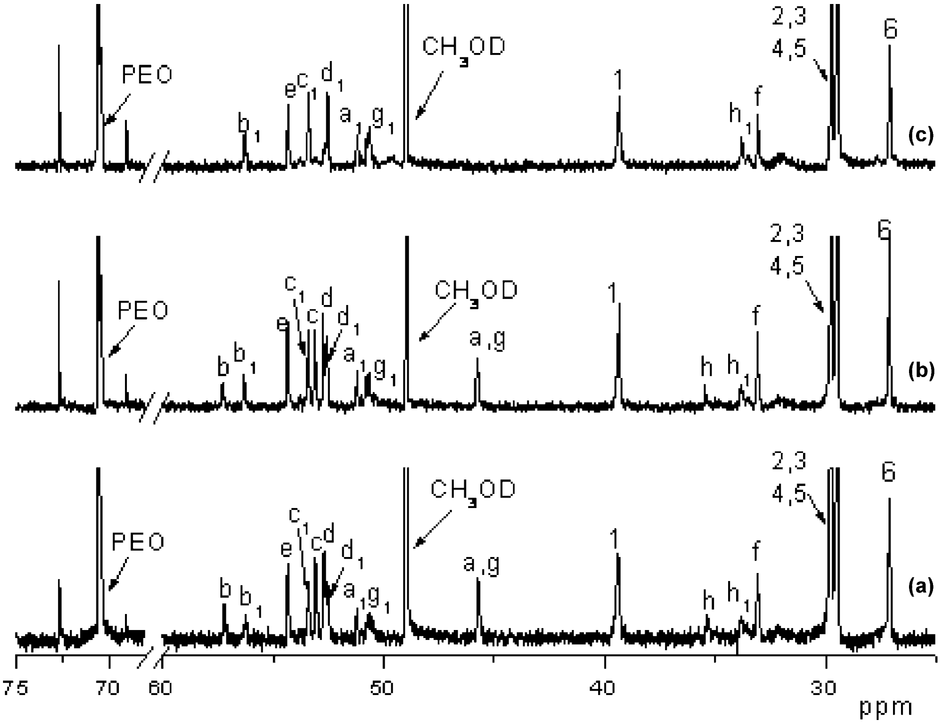


Fig. 3. The quantitative ^{13}C NMR spectra (INVGATE) of the grafted poly(DDA–AEPZ)-*g*-PEO obtained with the feed molar ratio of acryl/secondary amine: (a) 0.4; (b) 0.6 and (c) 1.2.

copolymers obtained increased from 36.4 to 56.7% to almost 100%. Therefore, the comb-like copolymers with one PEO chain in every unit were successfully prepared.

Similar to the grafting reaction of poly(DDA–AEPZ) with A-PEO, the Michael addition reaction of poly(DDA–AMPD)s with A-PEO yielded also comb-shaped poly(DDA–AMPD)-*g*-PEOs with the feed molar ratio of secondary amine (formed)/acryl group = 1.2. This can be confirmed by their ^{13}C NMR spectra of poly(DDA–AEPZ)-*g*-PEO in Fig. 4. Except characteristic signals of poly(DDA–AMPD), the signal at $\delta = 70.5$ ppm attributed to the carbons of PEO indicates the formation of grafting copolymers. Similarly, the carbons a and g should be affected significantly, but carbons b and h are less effected by the Michael addition of secondary amine with acryl group of A-PEO. By comparison of the ^{13}C NMR spectrum of poly(DDA–AMPD) in Fig. 2(b), we can observe that the signals of carbons a and g, b and h are shifted from $\delta = 55.4$ (a) and 46.0 (g), 35.3 (b) and 35.9 (h) ppm to $\delta = 59.9$ (a_1) and 50.9 (g_1), 34.9 (b_1) and 34.0 (h_1) ppm, respectively. At the feed molar ratio = 1.2, carbons signals a and g, b and h disappear completely in Fig. 4, which indicates almost 100% of the DG value and the formation of the comb-shaped poly(DDA–AMPD)-*g*-PEO.

After grafting reaction, one method for calculation of molecular weight of the comb-like copolymers obtained is based on their ^{1}H NMR data. Thus their ^{1}H NMR spectra were measured, and Fig. 5(a) shows a typical ^{1}H NMR spectrum of the grafted polymer G3. Since the 1:1 of feed molar ratio of DDA to AEPZ (or AMPD) was used in the Michael addition polymerization, the linear poly(DDA–AMPD) with one terminal acryl group should be formed. Thus the number-average molecular weight [M_n (NMR)] of the grafted copolymers could be calculated based on ^{1}H NMR data according to Eq. (3)

$$M_n(\mathrm{NMR}) = \frac{1.5 I_{4.35} M_{n,\mathrm{PEO}} + 0.15 I_{1.2\text{–}1.5} M}{I_{5.7\text{–}6.3}} \tag{3}$$

where $I_{4.35}$, $I_{1.2\text{–}1.5}$ and $I_{5.7\text{–}6.3}$ are the integral intensities of signals at $\delta = 4.35$, 1.2–1.5 and 5.7–6.3 ppm attributed to protons of the methylene next to ester of A-PEO, the dodecylene protons in the DDA and vinyl protons, respectively; $M_{n,\mathrm{PEO}}$ stands for the number-average molecular weight of A-PEO; $M(=437)$ is the molecular weight of repeating unit of poly(DDA–AEPZ). The data listed in Table 2 demonstrate that the molecular weights of the comb-like copolymers increase with the increase of feed molar ratio of acryl/secondary amine. This is consistent with the result of DG.

The ^{1}H NMR spectra of the grafted polymers poly(DDA–AMPD)-*g*-PEO is similar to that of poly(DDA–AEPZ)-*g*-PEO due to their almost same chemical environments. And the number-average molecular weight [M_n (NMR)] of the grafted copolymers poly(DDA–AMPD)-*g*-PEO could also be calculated based on Eq. (3), where the $M(=422)$ is the molecular weight of repeating unit of poly(DDA–AMPD).

3.3. Properties of micelles

The linear polymers, poly(DDA-AEPZ) and poly(DDA–AMPD) are insoluble in neutral water due to the long aliphatic spacer in DDA, but they would be dissoluble in acidic water due to lots of acrylamide and amine groups. The PEO is well-known water soluble polymer. The amphiphilic comb-like copolymer poly(DDA–AEPZ)-*g*-PEO is pH-sensitive, and by adjusting the pH values of water, the micelles should be formed in neutral or alkaline water. For confirmation this idea, the poly(DDA–AEPZ)-*g*-PEO with

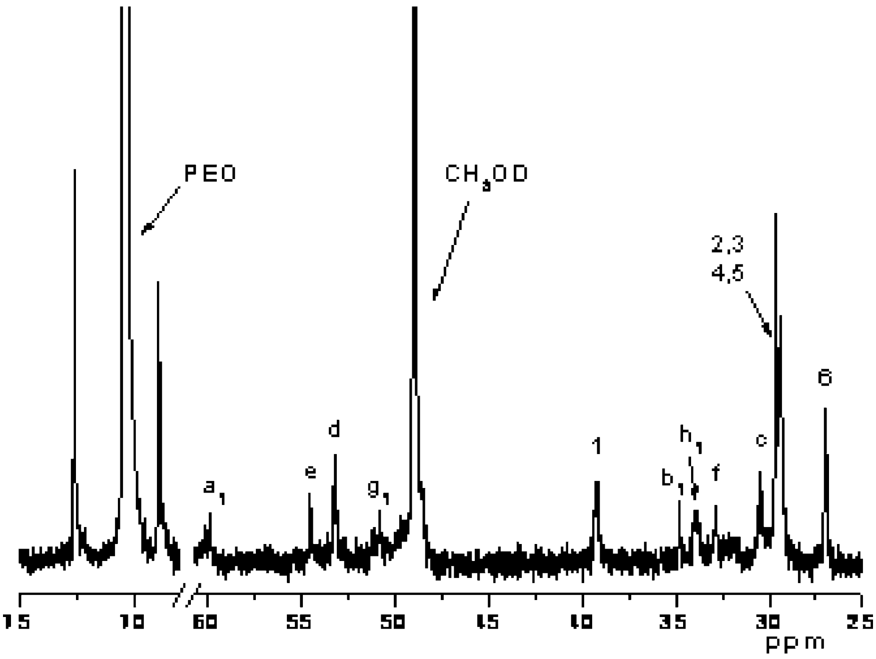


Fig. 4. The enlarged ^{13}C NMR spectrum of the grafted poly(DDA–AMPD)-*g*-PEO obtained with the feed molar ratio of acryl/secondary amine = 1.2.

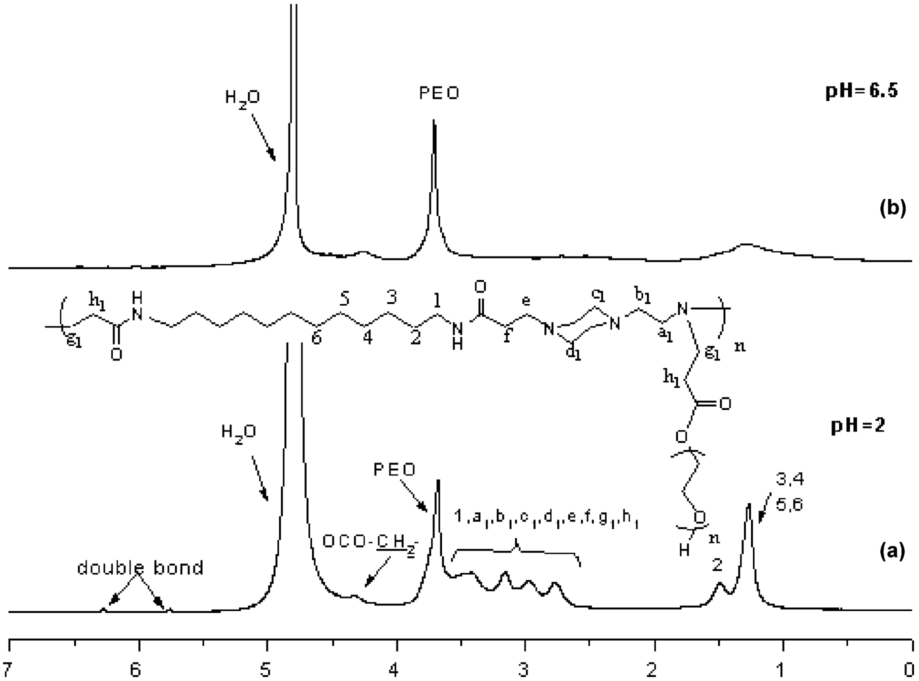


Fig. 5. The ^{1}H NMR spectra of the poly(DDA–AEPZ)-*g*-PEO in D_2O at (a) pH 2; (b) pH 6.5.

DG = 100% (G3) was dissolved in acidic water at pH 2.0. By addition of aqueous NH_3 solution, the aqueous polymer solution was adjusted to pH 6.5 until a lightly blue transparent solution was formed. For verifying formation of the micelles, the ^{1}H NMR spectra of aqueous polymer solution in D_2O were measured at different pH values. Fig. 5(a) shows ^{1}H NMR spectrum of the sample G3 at pH 2. The characteristic signals of PEO and poly(DDA–AEPZ) can be observed clearly, because linear poly(DDA–AEPZ) was dissolved molecularly in acidic water at pH 2. Fig. 5(b) shows ^{1}H NMR spectrum of the comb-like polymer in D_2O at pH 6.5. In comparison with Fig. 5(a), all the signals ascribed to linear poly(DDA–AEPZ) are disappeared completely, indicating the formation of micelles with relatively compact, hydrophobic poly(DDA–AEPZ) core. This can be confirmed further by their TEM photos. As shown in Fig. 6, the sizes of the micelles formed were determined by TEM, and all the particles are spherical approximately, the number-average diameter is around 95 nm.

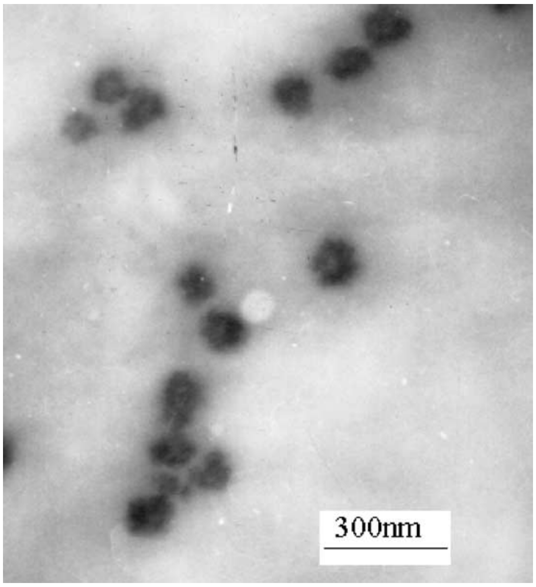


Fig. 6. TEM image of the sample G3 in Table 2.

4. Conclusion

Graft polymers with PEO as side chains have been successfully prepared by the Michael addition reaction of poly(DDA–AEPZ) with acryl-terminated PEO. The degree of grafting could be tuned easily with different feed molar ratio of acryl in A-PEO/secondary amine in poly(DDA–AEPZ), and comb-shaped polymers were obtained with 1.2 of feed molar ratio of the acryl/secondary amine. Poly(DDA–AEPZ) and poly(DDA–AMPD) are pH-sensitive, it can dissolve in acidic water, but it is insoluble in neutral and alkaline water. The amphiphilic comb-like poly(DDA–AEPZ)-*g*-PEO was molecularly dissolved in water at pH 2.0, and by adjusting pH value of water to 6.5, the macromolecules will be aggregated to form micelles. TEM photo of the micelles shows the particles are spherical and the number-average diameter is around 95 nm.

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