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Michael addition polymerizations of trifunctional amines with diacrylamides

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Abstract

With the aim to get a clear understanding of this category of polymerizations, the Michael addition polymerizations of trifunctional amines, i.e. 4-aminomethyl piperidine (AMPD), *N*-methyl ethylenediamine (MEDA), and 1-(2-aminoethyl) piperazine (AEPZ), with an equimolar diacrylamide, *N*,*N*′-methylene diacrylamide (MDA), were investigated. Similar to the polymerizations of these amines with an equimolar diacrylate, novel linear poly(amido amine)s containing secondary and tertiary amines in the backbones are obtained from these polymerizations as reflected by ^{13}C NMR (INVGATE). In situ monitoring the polymerization processes using NMR shows that the reactivity sequence of three types amines in the trifunctional amines is 2° amine (original) $>$ 1° amine $\gg$ 2° amine (formed), and the 2° amine (formed) is kept out of the reaction. But these results are different from those reported for the polymerizations of the similar amines with an equimolar divinyl sulfone and some diacrylates. The molecular weights and properties of poly(amindo amine)s obtained were characterized by GPC, DSC and TGA, respectively.

Keywords: Poly(amido amine)s; Multifunctional monomers; Michael addition polymerization

1. Introduction

The mechanisms of polymerizations of multifunctional monomers are more complicated in comparison with those of bisfunctional monomers [1–7]. When multifunctional monomers have equal reactivity, nonlinear polymers and infinite networks as manifested by gelation are formed with predictable gel points [1,2]. However, when the reactivity of multifunctional groups is unequal, many possible reaction routs exist [4,5]; the ratios of reaction kinetic constants of different functional groups are a key factor in determining the mechanisms of polymerizations and predicting the gel points, but these parameters usually are difficult to be determined [1–4]; when the reactivity of functional groups was sufficiently different, the polymerizations were suggested to be multistage processes [6,7]. Nevertheless, novel polymers can be produced via polymerizations of suitable multifunctional monomers on the basis of a clear understanding of the mechanisms of these polymerizations.

Recently, the approaches via A_2+B_3 monomers of unequal reactivity have been exploited to preparing hyperbranched polymers [8–15]. The advantages of these approaches lie in the availability of the monomers, ease of polymerization processes and novel hyperbranched polymers produced. In comparison, AB_m monomer approaches adopted specific AB_m monomers normally prepared by several steps [16–19], and stringent polymerization conditions needed to be followed for the approaches via A_2+B_3 monomers of equal reactivity [20–24].

In our previous work [25,26], we have found that the reactivity of trifunctional amines is unequal in the Michael addition polymerizations with diacrylates, and novel linear poly(amino ester)s applicable for safe and efficient delivery of gene are obtained. Nevertheless, the reactivity sequence of amines and the structures of polymers observed in our works are different from those reported for the polymerizations of trifunctional amines with divinyl sulfone or other diacrylates [27–29], so it is necessary to get understanding of the mechanisms of other polymerizations of this

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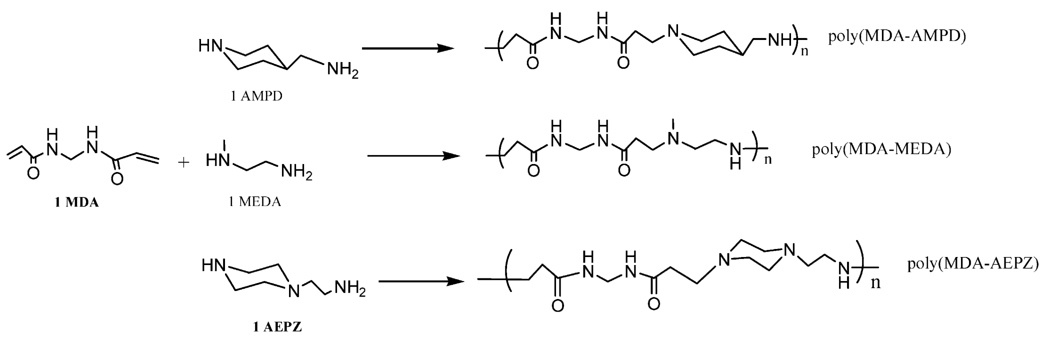


Scheme 1. Poly(amido amine)s obtained from the Michael addition polymerizations of trifunctional amines and an equimolar diacrylamide.

category. In this paper we investigate the Michael addition polymerizations of some trifunctional amines, i.e. 4-aminomethyl piperidine (AMPD), *N*-methyl ethylenediamine (MEDA), and 1-(2-aminoethyl) piperazine (AEPZ), with an equimolar diacrylamide. It is found that novel poly(amido amine)s containing secondary and tertiary amines in their backbones are formed as described in Scheme 1, similar to our results obtained for the Michael addition polymerizations of these trifunctional amines with an equimolar diacrylate [25,26]. These novel kinds of poly(amido amine)s are different from those poly(amido amine)s containing only tertiary amines in the backbones, on which Ferruti's group has carried out a systematic investigation [30]. In addition, Michael addition polymerization of diamines has been applied to prepared novel processable polyaspartimides containing phosphorus [31].

2. Experimental

2.1. Materials

N,N'-Methylene diacrylamide (MDA), 4-aminomethyl piperidine (AMPD), *N*-methyl ethylenediamine (MEDA), and 1-(2-aminoethyl) piperazine (AEPZ), were purchased from Aldrich and used as received. All other materials and solvents were used as received without further purification.

2.2. Characterization

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker DRX-300 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 with a heating rate of 20 °C/min from 0 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. TGA was performed on a thermal analyzer DT-50 with a heating rate of 10 °C/min under a nitrogen flow rate of 20 ml/min.

2.3. Polymerization processes

In a typical polymerization procedure, 258 mg (2 mmol) of AEPZ was added into a solution of 308 mg (2 mmol) of MDA in a 4.5 ml of mixture solvent of methanol and water (70:30, v/v). The polymerization was performed at 20 or 50 °C. The polymerization was monitored by the conversion of MDA determined by using ^{1}H NMR based on Eq. (1).

$$\text{MDA\%(conversion)} = (1 - I_{5.7\text{–}6.3}/3I_{4.5\text{–}4.7}) \times 100\% \qquad (1)$$

where $I_{5.7\text{–}6.3}$ and $I_{4.5\text{–}4.7}$ were the integral intensities of peaks at ca. 5.7–6.3 and 4.5–4.7 ppm attributed to the protons attached to the carbons in the vinyl groups and the methylene units in the MDA, respectively.

When MDA% got ca. 100%, the polymerization was stopped and the solution was concentrated under reduced pressure followed by precipitation into cold acetone. The product was purified by dissolving in water, precipitating in cold acetone, and drying under vacuum at 40 °C for 24 h.

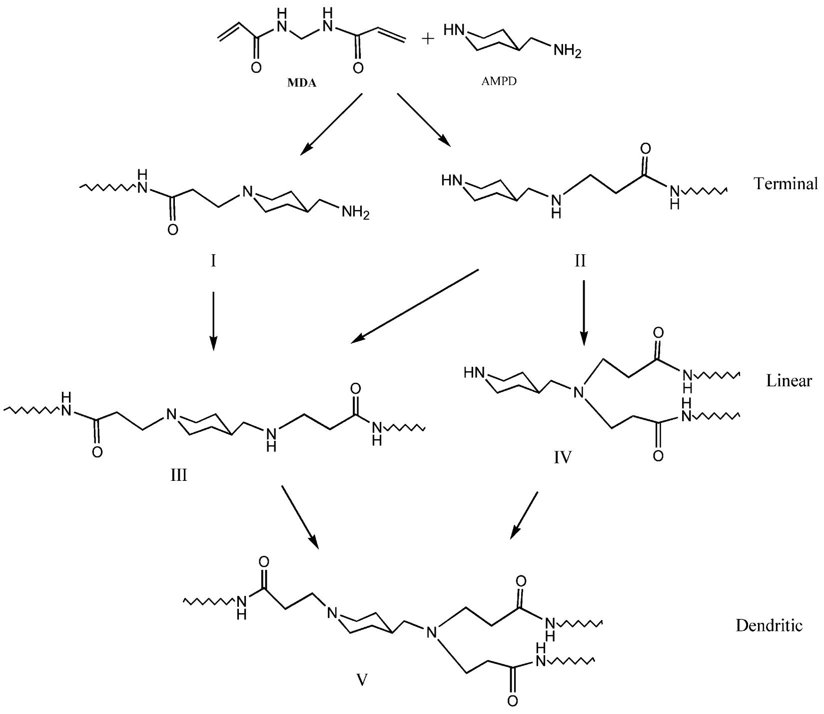
2.4. In situ monitoring polymerization processes using NMR

Typically, an equimolar MDA was added into a solution of AEPZ in deuterium water in a NMR tube. The polymerization was performed at 50 °C. ^{13}C NMR spectrum was recorded at different polymerization stages. Two-hundred times scan taking around 10 min was enough to get a good ^{13}C NMR spectrum. Meanwhile, the conversions of MDA were also measured by ^{1}H NMR based on Eq. (1).

3. Results and discussion

3.1. Polymerization

The Michael addition polymerizations of trifunctional amines, i.e. AMPD, MEDA, and AEPZ with an equimolar MDA were performed using a mixture solvent of methanol and water (70:30, v/v) due to poor solubility of MDA in pure water (2 g in 100 ml water at 40 °C). Addition of methanol



Scheme 2. The possible reaction routes in the polymerizations of AEPZ and MDA.

increased the solubility of MDA so the polymerizations could be performed with monomer concentrations of ca. 11% (w/v). The effect of temperature on the kinetics of polymerizations was significant. For the polymerization of MDA and AEPZ, it took ca. 94 min at 50 °C and ca. 1650 min at 20 °C to get 98% conversion of MDA. Nevertheless, at both temperatures, the conversions of MDA got ca. 50% quickly in several minutes, then the reactions rates slowed down. When the monomer conversions got ca. 100%, no gelation occurred in all the polymerizations. The polymers were collected by precipitating in cold acetone and purified by precipitation in acetone from aqueous solution followed by drying under vacuum.

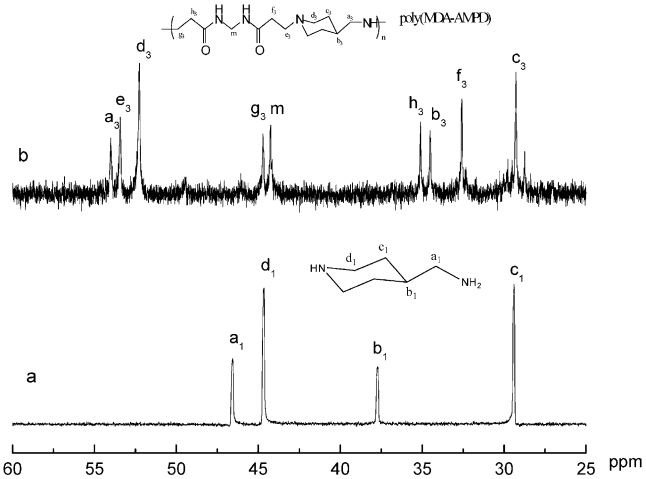


Fig. 1. A comparison of the enlarged ^{13}C NMR spectrum (INVGATE) of carbons adjacent to amines in (a) AMPD and (b) poly(MDA–AMPD).

3.2. Polymer structures

Linear poly(amido amine)s containing secondary and tertiary amines in the backbones are obtained from the Michael addition polymerization of AMPD with an equimolar MDA. Scheme 2 shows the possible structure units formed in the Michael addition polymerization of MDA and AMPD, and Fig. 1 is a comparison of the enlarged quantitative ^{13}C NMR spectra (INVGATE) of polymers, poly(MDA–AMPD), and that of AMPD. In ^{13}C NMR of poly(MDA–AMPD) (Fig. 1(b)), two peaks at ca. 44.3 and 44.7 ppm are attributed to carbon m and g_3 on the base of Fig. 1(b) due to their almost same chemical environments. As shown in Scheme 2, type I or II terminal units have carbon peaks near the peaks of carbon a_1 or d_1 shown in Fig. 1(a); nevertheless, no corresponding peaks can be found in this range in Fig. 1(b), so no type I and II terminal units and the coexisting type V dendritic units exist in poly(MDA–AMPD). Further type IV linear unit should also have a peak near carbon d_1, no such a peak in Fig. 1(b) indicates no formation of typer IV linear unit. Therefore, linear poly(MDA–AMPD) as illustrated in Fig. 1(b) is obtained.

Fig. 2 is a comparison of the enlarged ^{13}C NMR spectrum of poly(MDA–MEDA) and that of MEDA, and Scheme 3 shows the possible structure units formed in the Michael addition polymerization of MEDA and MDA. In ^{13}C NMR spectra, the peak position of methylene carbons attached to tertiary amines are higher than 50 ppm as shown in Fig. 1. In

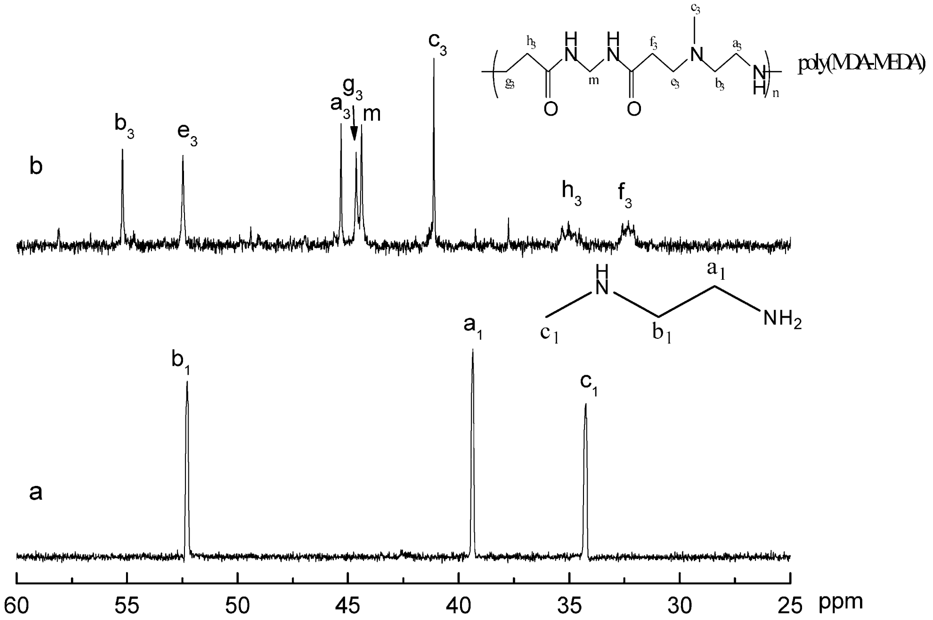
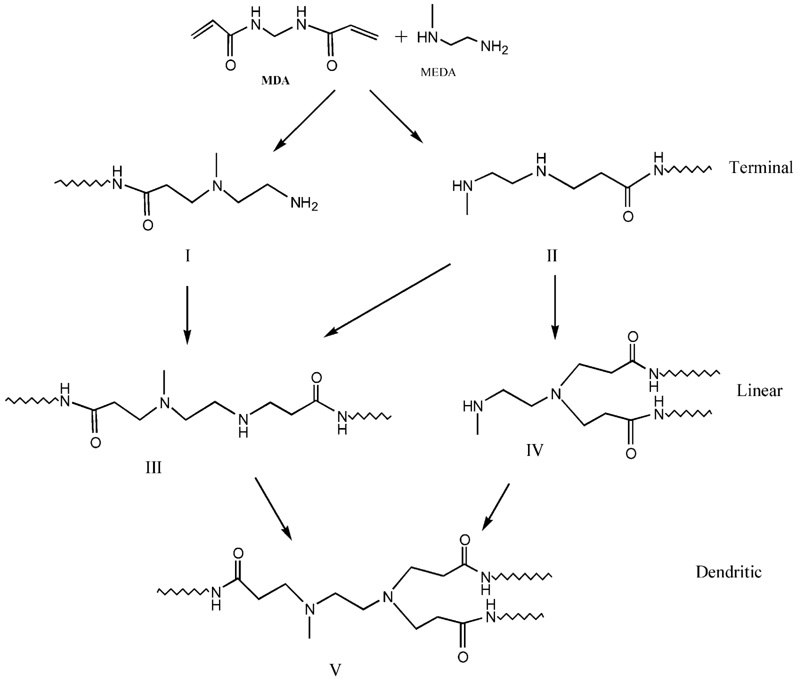


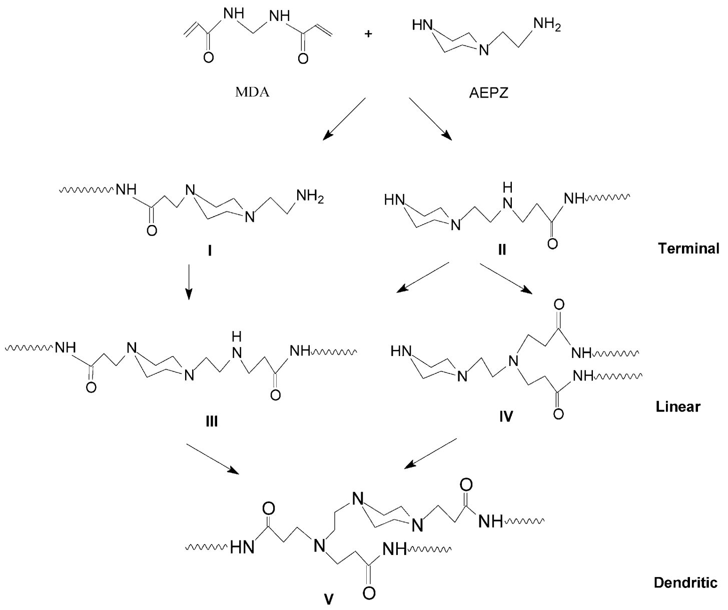
Fig. 2. A comparison of the enlarged ^{13}C NMR spectrum (INVGATE) of carbons adjacent to amines in (a) MEDA and (b) poly(MDA–MEDA).

Fig. 2(b), only two peaks appear in this range at ca. 52.5 and 55.2 ppm implying that at most two types of methylene carbon attached to tertiary amines are produced. Type V dendritic units as depicted in Scheme 3 have four types of methylene carbons linked to tertiary amines at least, so no type V dendritic units and the coexisting type I and II terminal units were formed. In Fig. 2(b), the ratio of integral intensities of the two peaks at ca. 52.5 and 55.2 ppm is close to 1:1, but type IV linear units have two peaks with a ratio of integral intensity of 1:2 in this range, so only type III linear units were formed Therefore, linear poly(MDA–MEDA) as described in Fig. 2 was obtained.

Scheme 4 shows the possible reaction routes and the structure units produced in the polymerization of AEPZ and MDA. Probably the polymer contains five types of structure units, i.e. terminal (I and II), linear (III and IV) and dendritic units (V). ^{13}C NMR was applied for the characterization of the polymers structures. Fig. 3 is a comparison of the enlarged quantitative ^{13}C NMR spectrum (using an inverse-gated broadband decoupled technique (INVGATE)) of the



Scheme 3. The possible reaction routes in the polymerizations of AMPD and MDA.



Scheme 4. The possible reaction routes in the polymerizations of MEDA and MDA.

polymer, poly(MDA–AEPZ), and that of the monomer AEPZ. Through comparing with the ^{13}C NMR spectrum of AEPZ (Fig. 3(a)), it could be found that there were three types of carbons attached to secondary amines with their peaks located at ca. 44.5, 44.8, and 45.0 ppm in poly(MDA–AEPZ). The polymerization had a little effect on the peak position of carbon *m* in MDA at 44.5 ppm, so only two types of carbons attached to secondary amines were formed. Fig. 3(b) also reflects that there are four types of carbons attached to tertiary amines with the peaks located at ca. 51.6, 52.1, 53.2 and 56.7 ppm, respectively, but no carbons attached to primary amines. As shown in Scheme 4, type I terminal units has one type of carbon attached to primary amines, and type II terminal units has at least three types of carbon linked to secondary amines, so no type I and II terminal units and coexisting type V dendritic units can be found in poly(MDA–AEPZ). The ratio of the integral intensity of the two peaks at 44.8 and 45.0 ppm attributed to carbons attached to secondary amines is close to 1, so only type III linear units were formed in the reaction without type IV linear units because the two types of carbons attached to secondary amines in type IV units are identical and only one peak corresponding to these two carbons should appear. So linear poly(MDA–AEPZ) as listed in Fig. 3(b) was formed in the polymerization. In Figs. 2 and 3, the peaks ascribed to carbon h_3 and f_3 got broaden, which probably is due to restricted motion (relaxation time effects).

Novel liner poly(amido amine)s containing secondary

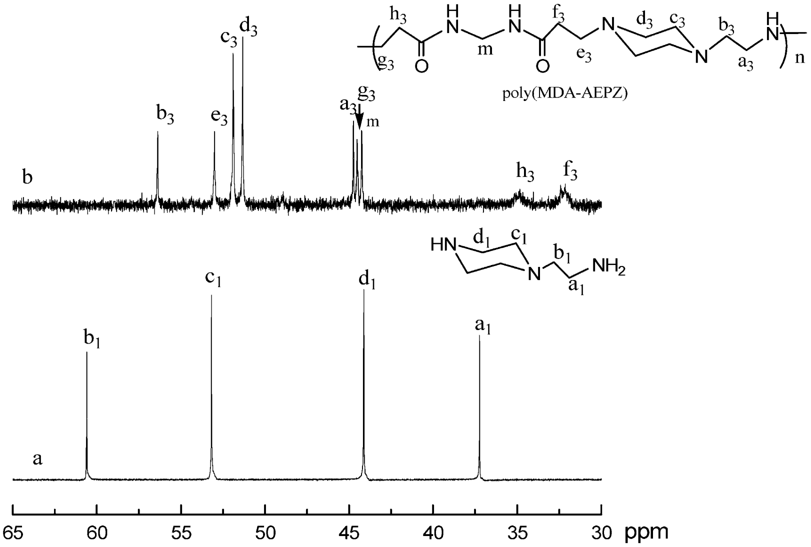


Fig. 3. A comparison of the enlarged ^{13}C NMR spectrum (INVGATE) of carbons adjacent to amines in (a) AEPZ and (b) poly(MDA–AEPZ).

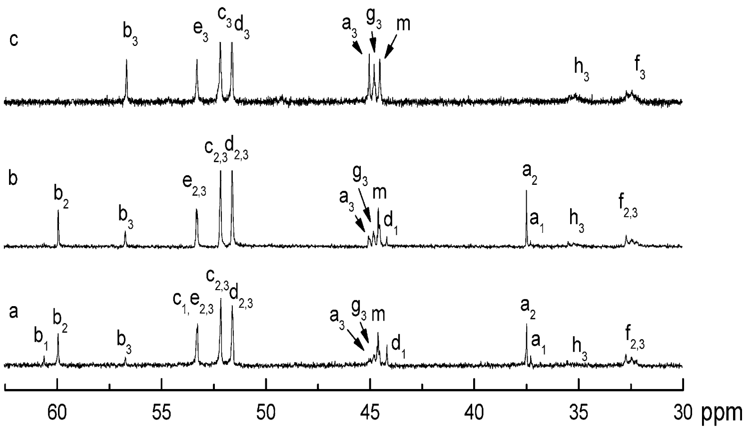


Fig. 4. A comparison of the enlarged ^{13}C NMR spectra (INVGATE) recorded in situ for the polymerization of AEPZ with an equimolar MDA at 50 °C for (a) 4 min; (b) 8 min and (c) 300 min.

and tertiary amines in the backbones were obtained in the Michael addition polymerizations of AMPD, MEDA and AEPZ, with an equimolar MDA, respectively, which agrees with the results obtained from the Michael addition polymerizations of these trifunctional amines with an equimolar diacrylate [25,26]. It is reasonable to speculate that the mechanisms of the Michael addition polymerizations of these trifunctional amines with diacrylamides are also similar to those of these amines with diacrylates [26]. In order to verify this speculation, as an example, the mechanism of the Michael addition polymerization of AEPZ and an equimolar MDA was investigated using NMR to monitor the polymerization process.

3.3. Mechanisms of the polymerization of MDA+AEPZ

The polymerization of MDA+AEPZ was performed at 50 °C. Fig. 4 shows the ^{13}C NMR spectra of carbons adjacent to amines at different stages of the polymerization. Fig. 4(a) shows that the relative integral intensity of the peaks of AEPZ such as the peak of carbon a_1 at 37.3 ppm was low after the polymerization started only for 4 min, indicating that most of the AEPZ had joined in the reaction. Similar to these changes occurred in ^{13}C NMR spectra for the Michael addition polymerization AEPZ and an equimolar diacrylate BDA [26], the conjugation of secondary amines in piperazine rings to vinyl groups in MDA relocated the peaks of carbon a_1, b_1, c_1, and d_1 in AEPZ from ca. 37.3, 60.6, 53.2, and 44.1 ppm to a_2, b_2, c_2, and d_2 at ca. 37.5, 59.9, 52.1, and 51.6 ppm, and rendered new peaks attributed to carbon e_2 and f_2 at ca. 53.2 and 32.6 ppm, respectively; Fig. 4(b) and (c) depict that the following reactions of the primary amines in AEPZ changed the peaks of carbon a_2 and b_2 from 37.5 and 59.9 to 45.0 and 56.7 ppm further, and produced carbon g_3 and h_3 with the peaks locating at 44.8 and 35.5 ppm, respectively, but showed little effect on the positions of c_2, d_2, e_2 and f_2.

On the basis of the ^{13}C NMR (INVGATE) spectra as shown in Fig. 4, the conversions of different types of amines at different polymerization stages were obtained via Eq. (2), and the results are listed in Table 1 together with the conversions of MDA, which are used as an indicator of the polymerization process.

$$
\begin{aligned}
&2° \text{ amines (original) } (\%) \\
&\quad = (I_{b2} + I_{b3})/(I_{b1} + I_{b2} + I_{b3}) \times 100\% \\
&\quad\ 1° \text{ amines } (\%) \\
&\quad = I_{b3}/(I_{b1} + I_{b2} + I_{b3}) \times 100\%
\end{aligned}
\tag{2}
$$

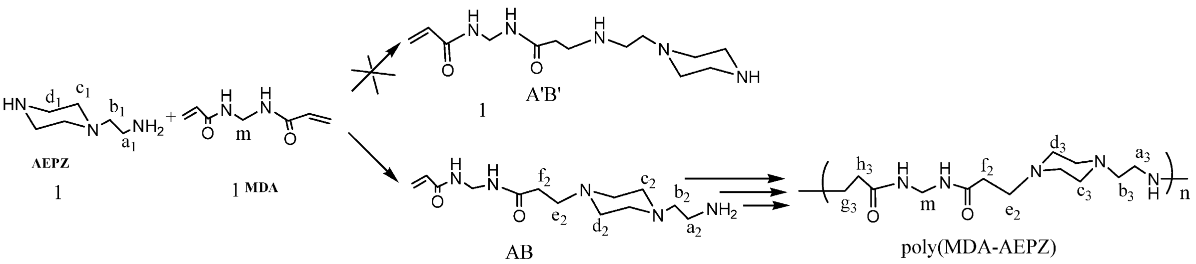
where I_{b1}, I_{b2} and I_{b3} stand for the integral intensity of peak b_1, b_2 and b_3 in Fig. 4. Table 1 shows that when the conversion of MDA was about 50% after the polymerization had been performed for 4 min, ca. 88% of 2° amines (original) and only ca. 16% of 1° amines in AEPZ joined in the reaction. When ca. 98% of the 2° amines (original) were consumed, ca. 32% of the 1° amines participated in the reaction, and the 2° amines (formed) were kept intact. When the conversion of MDA was close to 100%, almost 100% of the 2° amines (original) and 1° amines with a negligible amount of the 2° amines (formed) involved in the reaction. Hence it was clear that the reactivity of the three types of amine in AEPZ was rather different and the reactivity

Table 1
The conversions of different functional groups at different stages in the polymerization of AEPZ with an equimolar MDA performed at 50 °C

Reaction time (min)	Conversion (100%)			
	MDA	2° Amines[a]	1° Amines[b]	2° Amines formed
4	50	87.5	16.3	0
8	63	97.6	32.1	0
300	100	100	~100	~0

[a] 2° amines conversion(%) = $(I_{b2}+I_{b3})/(I_{b1}+I_{b2}+I_{b3})] \times 100\%$;

[b] 1° amines conversion(%) = $I_{b3}/(I_{b1}+I_{b2}+I_{b3}) \times 100\%$, where I_{b1}, I_{b2} and I_{b3} stand for the integral intensity of peak b_1, b_2 and b_3 in Fig. 4.



Scheme 5. The mechanism of the Michael addition polymerization of AEPZ with MDA.

sequence was 2° amine (original) > 1° amine ≫ 2° amine (formed). Formation of the linear poly(amido amine)s resulted from that the 2° amines (formed) were kept out of the reaction due to its too low reactivity. Therefore, the mechanism of the polymerization could be described as in Scheme 5. Only AB type intermediates were presented in the polymerization, and no A′B′ type intermediates existed due to that no corresponding peaks appeared in Fig. 4. These results demonstrated that the mechanisms of the Michael addition polymerization of trifunctional amines with diacrylamide were really similar to those of these trifunctional amines with an equimolar diacrylate [26]. Among the three types of amines, i.e. 2° amines (original), 1° amines, and 2° amines (formed), capable of performing Michael addition reaction with MDA, the lowest reactivity of the 2° amine (formed) was due to high steric hindrance of polymer chains. However, steric hindrance of cyclic aliphatic rings in AEPZ, AMPD and of methyl groups in MEDA on the 2° amines (original) was much lower, and the inductive effect of aliphatic substituents on the nitrogen atoms increased the electron density leading to a higher reactivity of the 2° amines (original) as compared with the 1° amines.

3.4. Properties of polymers

All the linear polym(amido amine)s obtained are soluble in water, but insoluble in acetone, tetrahydrofuran, and chloroform. Table 2 lists the polymerization conditions and the properties of the polymers. Reaction temperature had a significant effect on the polymerization rates but showed an insignificant effect on the properties of polymers. GPC results reflected that polydispersity indexes (PDI) of molecular weights of the polymers are high, probably due to the staged reactions happened in the polymerizations. DSC results indicated that the polymers obtained are noncrystalline, Tgs of poly(MDA–AEPZ) and poly(MDA–AMPD) are higher than that of poly(MDA–MEDA) probably caused by a higher rigidity of the former backbones containing aliphatic cyclic rings. TGA results demonstrated the reasonable thermal stability of these polymers.

4. Conclusions

The Michael addition polymerizations of trifunctional amines with diacrylamide are similar to the polymerizations of these amines with diacrylate in the structures of polymers and the mechanisms of polymerizations. Novel linear poly(amido amine)s containing secondary and tertiary amines in the backbones are obtained from the Michael addition polymerizations of AEPZ, AMPD and MEDA with an equimolar diacrylamide MDA. Formation of the linear poly(amido amine)s is due to the different reactivity of the three types of amines in these trifunctional amines, i.e. 2° amines (original) > 1° amines ≫ 2° amines (formed), and the 2° amines (formed) being kept out of the reactions due to the lowest reactivity induced by high steric hindrance of polymer backbones. These linear poly(amindo amine)s are noncrytalline, have high PDIs, and reasonable thermal stability. The investigation on the applications of these novel linear poly(amido amine)s are in progress.

Table 2
The conditions of the polymerizations of trifunctional amines with an equimolar MDA and the properties of polymers obtained

Amine	Temperature (°C)	Time (h)	Yield(%)	M_n[a]	M_w/M_n	Tg (°C)	T_d (°C)[b]
AEPZ	50	10	93	8293	3.39	69.6	265.3
AMPD	50	10	90	6415	1.99	71.4	258.3
MEDA	50	10	88	3261	1.64	46.6	237.8
AEPZ	20	48	92	7458	3.35	71.8	267.6
AMPD	20	48	90	5212	2.14	73.7	259.9
MEDA	20	48	87	3656	1.64	41.3	240.9

[a] Obtained by GPC using 0.5 M acetic acid/0.5 M sodium acetate as eluent and poly(ethylene oxide) standards.

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

Acknowledgements

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