Effects of Chemistries of Trifunctional Amines on Mechanisms of Michael Addition Polymerizations with Diacrylates

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ABSTRACT: The mechanisms of the Michael addition polymerizations of different trifunctional amines with an equimolar 1,4-butanediol diacrylate (BDA) were investigated by using ^{1}H and ^{13}C NMR to in situ monitor the polymerization processes. The trifunctional amine monomers adopted were 1-(2-aminoethyl)piperazine (AEPZ) and 4-(aminomethyl)piperidine (AMPD) and linear aliphatic amines with different steric hindrance on the 2° amines (original), i.e., *N*-methylethylenediamine (MEDA), *N*-ethylethylenediamine (EEDA), and *N*-hexylethylenediamine (HEDA). For AEPZ, AMPD, and MEDA with low steric hindrance on the 2° amines (original), the reactivity sequence of the three types of amines was 2° amines (original) > 1° amines ≫ 2° amines (formed) and linear poly(amino ester)s were formed via AB-type intermediates due to the 2° amines (formed) being kept out of the reaction. However, AB-type intermediates were only formed from the 2° amines (original) for AEPZ and AMPD, but from both the 2° amines (original) and 1° amines due to their smaller reactivity difference for MEDA. Nevertheless for EEDA and HEDA, the increased steric hindrance on the 2° amines (original) changed the reactivity sequence of the three types of amines to 1° amines > 2° amines (original) > 2° amines (formed) and branched polymers with degrees of branching of ca. 33% and 37%, respectively, were obtained due to all the three types of amines participating in the reaction. The molecular weights, glass transition temperatures, and thermal stability of the linear or branched poly(amino ester)s obtained were characterized by GPC, DSC, and TGA, respectively.

Introduction

Gelation happens in polymerizations of $A_2 + B_3$ monomers of equal reactivity when monomer conversions surpass gel points, which can be predicted theoretically on the basis of chemistries and compositions of feed monomers.[1] However, for polymerizations of $A_2 + B_3$ monomers of unequal reactivity, more parameters, i.e., the ratios of kinetic reaction constants of the functional groups of different reactivity, are needed for predicting the gel points, but it is difficult to get these parameters accurately.[1,2] Furthermore, the mechanisms of the polymerizations of $A_2 + B_3$ monomers of unequal reactivity get complicated due to many possible reaction routes.[3] When the reactivity of functional groups was sufficiently different, the polymerizations were suggested to be multistage processes.[4]

Hyperbranched polymers have attracted much attention due to their distinct structures and properties from their linear analogues and wide applications.[5] Recently some of the polymerizations of $A_2 + B_3$ monomers of unequal reactivity have been demonstrated to be practical approaches to preparing hyperbranched polymers.[6−9] For example, hyperbranched polyamides were prepared from commercial available diamines (A_2) and trimesic acid (B_3),[6] hyperbranched polyimides could be synthesized from diamines (A_2) and trifunctional anhydrides-(B_3)[7] or dianhydrides (A_2) and trifunctional amines (B_3)[8] by adopting practical monomer concentrations and performing polymerizations in one pot, and hyperbranched polyurethanes were obtained from diisocyanate (A_2) and polyol (B_3).[9] In comparison, AB_m monomer approaches started from specific AB_m monomers normally prepared by several steps,[10] and stringent polymerization conditions, such as very low monomer concentrations, strictly controlled feed molar ratios, slow monomer addition rates, and conversions below gelation points, needed to be obeyed for the polymerizations of $A_2 + B_3$ monomers of equal reactivity to avoid gelation, which would hinder their practical applications.[11−13] Nevertheless, a clear understanding of the complicated mechanisms of the polymerizations of $A_2 + B_3$ monomers of unequal reactivity is a prerequisite to properly apply this approach to preparing hyperbranched polymers.

Recently, poly(amino ester)s only containing tertiary amines prepared from the Michael addition polymerizations of diamines and diacrylates have been demonstrated to be promising biomaterials for delivery of DNA and pH-sensitive drug delivery;[14,15] however, novel kinds of poly(amino ester)s of different amine constitutions such as containing primary/secondary/tertiary amines and different architectures are still desirable due to their different functions in these applications.[16] For this purpose, we have investigated the Michael addition polymerizations of trifunctional amines and diacrylates, and the preliminary results have shown that the Michael addition polymerization of trifunctional amine, 1-(2-aminoethyl)piperazine (AEPZ), with an equimolar 1,4-butanediol diacrylate (BDA) produced a novel linear poly(amino ester) containing secondary and tertiary amines.[17] Therefore, we were motivated to get a clear understanding of the mechanisms of the Michael addition polymerizations of trifunctional amines and

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diacrylates and thereon design and synthesize novel poly(amino ester)s. Here the mechanisms of the Michael polymerizations of some typical trifunctional amines and diacrylate are investigated by using NMR to in situ monitor the polymerization processes, and the effects of the chemistries of trifunctional amines on the mechanisms of polymerizations are discussed.

Experimental Section

Characterization. ^{1}H NMR and ^{13}C NMR studies were performed on a Bruker DRX-400 spectrometer. Gel permeation chromatography (GPC) was implemented on a Waters 2690 apparatus with a Waters 410 refractive index detector, using two columns in series (Waters Ultrahydrogel 250 and 200), 0.5 M acetic acid/0.5 M sodium acetate as eluent, and poly(ethylene oxide) standards for water-soluble samples, and employing Waters Styragel HR 4E and 5E, 0.1 M piperidine/THF as eluent and polystyrene standards for water-insoluble samples. Thermogravimetric analysis (TGA) was conducted by scanning from 50 to 700 °C under nitrogen at a heating rate of 20 °C/min using a PerkinElmer TGA7, and T_d was taken as the temperature at which a 5% weight loss happened. Differential scanning calorimetry (DSC) was carried out on a TA modulated DSC 2920 under nitrogen. T_g was obtained in the second scan at a heating rate of 10 °C/min from −150 to 180 °C after samples were heated from 25 to 180 °C followed by being quenched to −150 °C using liquid nitrogen.

Materials. 1,4-Butanediol diacrylate (BDA, 90%), 1-(2-aminoethyl)piperazine (AEPZ, 99%), *N*-ethylethylenediamine (EEDA, 98%), *N*-hexylethylenediamine (HEDA, 97%), and *N*-methylpiperazine (MPZ, 99%) were purchased from Aldrich, 4-(aminomethyl)piperidine (AMPD, 99%) and *N*-methylethylenediamine (MEDA, 95%) were from Lancaster, chloroform, acetone, diethyl ether, and hexane were from Tedia. All the reagents were used as received.

In Situ Monitoring Polymerization Processes. Typically, an equimolar BDA was added into the solution of AMPD in deuterium chloroform in a NMR tube. The monomer concentration was around 25% (w/v), and the polymerization was performed at 40 °C. The ^{13}C NMR spectrum was recorded by using a power-gated decoupling program (PD). 200 times scan taking around 10 min was enough to get a good ^{13}C NMR spectrum. Meanwhile, the conversions of BDA were measured by ^{1}H NMR based on eq 1.

$$\text{BDA \% (conversion)} = (1 - 2I_{5.6-6.4}/3I_{4.0}) \times 100\% \quad (1)$$

where $I_{5.6-6.4}$ and $I_{4.0}$ were the integral intensities of peaks at ca. 5.6−6.4 and 4.0 ppm attributed to the protons attached to the carbons in the vinyl groups and the α-carbons in the 1,4-butanediol units, respectively.

Syntheses of Polymers. A typical process was that 2.02 g (9.2 mmol) of BDA was added into a solution of 1.06 g (9.2 mmol) of AMPD in 10 mL of chloroform. The polymerization was performed at 50 °C and monitored by ^{1}H NMR. When the peaks attributed to the vinyl groups at around 5.6−6.4 ppm almost disappeared, 0.1 g of AMPD (or MPZ) was added to terminate the residual vinyl groups to avoid side reactions during purification. 24 h later, the solution was precipitated into 300 mL of diethyl ether or hexane under vigorous stirring. The polymer was collected and purified by reprecipitation from a chloroform solution into diethyl ether followed by being dried under vacuum at 50 °C for 3 days.

Results and Discussion

1. Mechanisms of Polymerizations. Typical trifunctional amines AEPZ, AMPD, MEDA, EEDA, and HEDA were adopted for the Michael addition polymerization with an equimolar BDA. AEPZ and AMPD contain one secondary cyclic aliphatic amine and one primary amine; meanwhile, MEDA, EEDA, and HEDA are linear aliphatic amines containing one secondary amine and one primary amine, but steric hindrance on the secondary amines increases consecutively. The polymerizations of these trifunctional amine monomers and BDA would take days to complete in chloroform at ca. 40 °C, and a good ^{13}C NMR spectrum could be obtained in around 10 min with a suitable monomer concentration, so NMR was applied to in situ monitoring the polymerization processes. On the basis of the changes in the characteristic peaks during the polymerizations, especially those of carbons adjacent to the amines, the mechanisms of polymerizations were investigated. The peaks of these carbons adjacent to amines in ^{13}C NMR spectra were ascribed on the basis of the ^{13}C NMR spectra of the pure trifunctional amines and the principles to predict the positions of carbons in ^{13}C NMR spectra.[18]

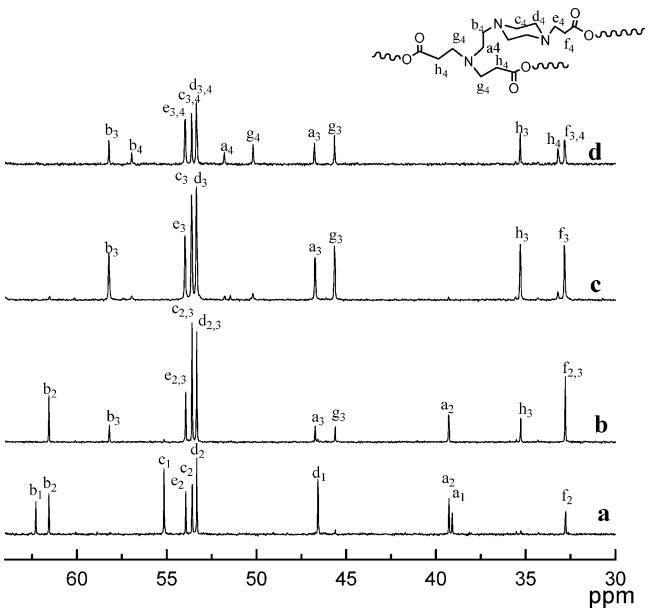


Figure 1. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + AEPZ with a 1:1 feed molar ratio of AEPZ to BDA and a monomer concentration of 25% (w/v) at 40 °C for (a) 1.16 h, (b) 12.50 h, (c) 313.3 h, and (d) 433.5 h (for d, the feed molar ratio of AEPZ to BDA was 1:2).

Polymerization of BDA + AEPZ and BDA + AMPD. The polymerizations of BDA + AEPZ and BDA + AMPD have similar mechanisms, which was reasonable due to the similar primary and secondary amine chemistries in AEPZ and AMPD. Figures 1 and 2 show the ^{13}C NMR spectra of carbons adjacent to amines at different stages of the polymerizations of BDA + AEPZ and BDA + AMPD, respectively, and the ascription of peaks in ^{13}C NMR is indicated in Schemes 1 and 2. At the early stage of polymerizations, only the 2° cyclic aliphatic amines (original) in AEPZ and AMPD are conjugated to the vinyl groups of BDA. Figure 1a shows that this reaction relocates the peaks of carbon a_1, b_1, c_1, and d_1 in AEPZ from ca. 39.1, 62.3, 55.2, and 46.6 ppm to a_2, b_2, c_2, and d_2 at ca. 39.3, 61.6, 53.6, and 53.3 ppm and produces new peaks attributed to carbon e_2 and f_2 at ca. 53.9 and 32.8 ppm; Figure 2a reflects that the peak positions of carbon a_1, b_1, c_1, and d_1 in AMPD are shifted from ca. 48.9, 40.2, 31.5, and 46.9 ppm to those of carbon a_2, b_2, c_2, and d_2 at ca. 48.4, 39.5, 30.2, and 53.7 ppm, and new peaks attributed to carbon e_2 and f_2 at 54.2 and 32.7 ppm appear. Figure 1b reveals that the following reaction of the 1° amines in AEPZ changes the peaks of carbon a_2 and b_2 from ca. 39.3 and

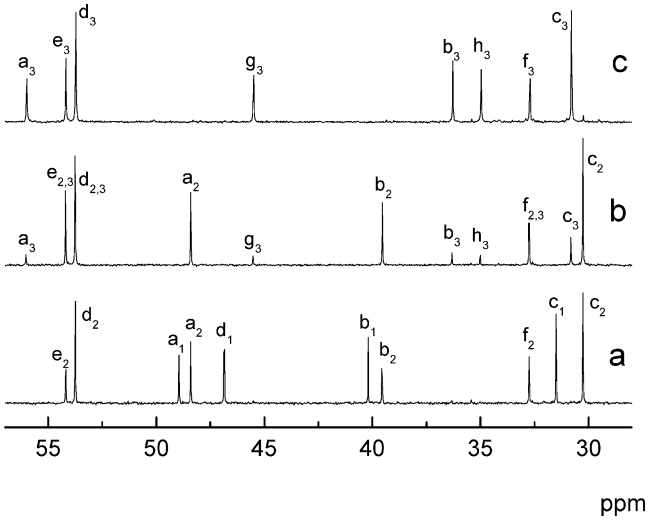


Figure 2. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + AMPD with a 1:1 feed molar ratio of AMPD to BDA and a monomer concentration of 25% (w/v) at 40 °C for (a) 0.25 h, (b) 5.40 h, and (c) 174.3 h.

61.6 ppm to those of a_3 and b_3 at ca. 46.9 and 58.2 ppm further and renders carbons g_3 and h_3 with peaks located at ca. 45.7 and 35.3 ppm but has no effect on the positions of the peaks of carbon c_2, d_2, e_2, and f_2, respectively. Similarly, Figure 2b depicts that the reaction of 1° amines in AMPD alters the peak positions of carbon a_2, b_2, and c_2 from ca. 48.4, 39.5, and 30.2 ppm to a_3, b_3, and c_3 at ca. 56.0, 36.3, and 30.8 ppm further and forms carbon g_3 and h_3 with peaks located at ca. 45.5 and 35.0 ppm but keeps the positions of the peaks of carbon d_2, e_2, and f_2, respectively. To identify the peaks related to the participation of the 2° amines (formed) in the polymerization, a polymerization adopting a double molar BDA for the polymerization of BDA + AEPZ was monitored, and the evidential results are shown in Figure 1d, which clearly indicates that the changes from the 2° amines (formed) to tertiary amines shifts those peaks of carbon a_3, b_3, g_3, and h_3 to ca. 51.6, 56.8, 50.0, and 32.7 ppm, respectively, with those of carbon c_3, d_3, e_3, and f_3 unchanged.

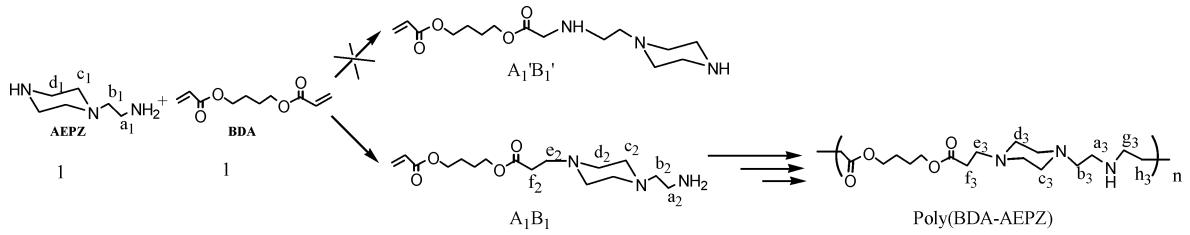
The conversions of the three types of amines, i.e., 2° amines (original), 1° amines, and 2° amines (formed), in AEPZ and AMPD during the polymerizations could be calculated on the basis of Figures 1 and 2. The results are tabulated in Table 1 together with the conversions of BDA, which can be used as an indicator of the polymerization process. As listed in Table 1, for the polymerization of BDA + AEPZ, almost only 80% of the 2° amines (original) attend the reaction when the conversion of BDA reaches ca. 40%; for the polymerization of BDA + AMPD, almost only 60% of the 2° amines (original) attend the reaction when the conversion of BDA is ca. 30%, so intermediate A_1B_1 and A_2B_2 as illuminated in Schemes 1 and 2 should be formed in the two polymerizations, respectively. Further, when the conversions of BDA are increased to ca. 72% for BDA + AEPZ and ca. 63% for BDA + AMPD, all the 2° amines (original) are used out and all the 2° amines (formed) are kept intact in both polymerizations, and ca. 44% and 26% of the 1° amines join in the reactions for the polymerization of BDA + AEPZ and BDA + AMPD, respectively. When the conversion of BDA is close to 100% for the two polymerizations, all the 1° amines participate in the reactions, but a negligible amount of the 2° amines (formed) is involved in the reactions. Furthermore, the reactions of the 1° amines only produce linear poly(amino ester)s without forming a detectable amount of intermediate $A_1'B_1'$ or $A_2'B_2'$ as

Table 1. Conversions of Different Functional Groups in the Polymerization Processes of the Trifunctional Amine Monomers with an Equimolar BDA[a]

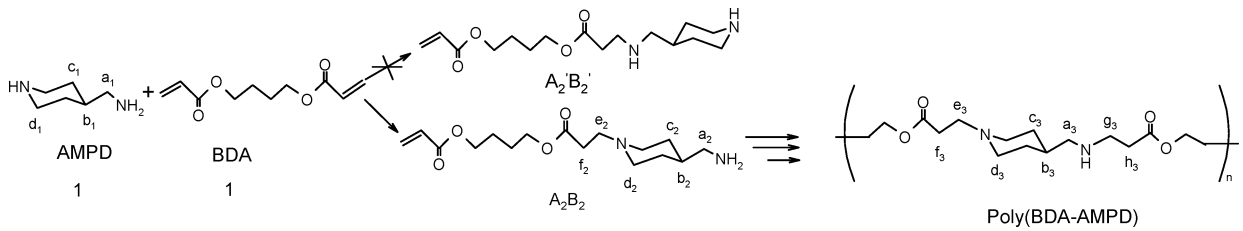
		conversion (%)			
amine	reaction time (h)	BDA[b]	2° amine (original)	1° amine[d]	2° amine (formed)
AEPZ	1.16	40	80[c]	0	0
	12.50	72	100	44	0
	313.3	100	100	100	0
AMPD	0.25	30	60[c]	0	0
	5.40	63	100	26	0
	174.3	100	100	100	0
MEDA	0.60	22			0
	29.25	85	100	70	0
	173.5	100	100	100	0

[a] The polymerizations were performed with a monomer concentration of ca. 25% (w/v) at 40 °C in deuterium chloroform. [b] BDA % (conversion) = $(1 - 2I_{5.6-6.4}/3I_{4.0}) \times 100\%$; $I_{5.6-6.4}$ and $I_{4.0}$ were the integral intensities of the peaks at ca. 5.6−6.4 and 4.0 ppm attributed to the protons attached to the carbons in the vinyl groups and the α-carbons in the 1,4-butanediol units in ^1H NMR, respectively. [c] 2° amine (original)% = BDA% × 2. [d] 1° amine % = BDA% × 2−2° amine (original)%.

Scheme 1. Mechanism of the Michael Addition Polymerization of AEPZ with an Equimolar BDA



Scheme 2. Mechanism of the Michael Addition Polymerization of AMPD with an Equimolar BDA



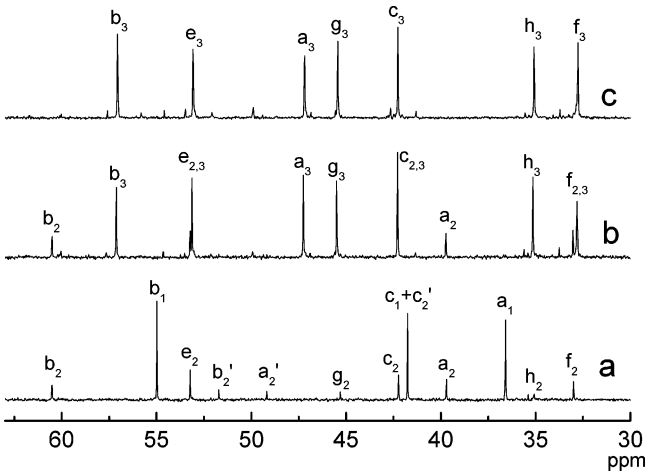


Figure 3. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + MEDA with a 1:1 feed molar ratio of MEDA to BDA and a monomer concentration of 25% (w/v) at 40 °C for (a) 0.60 h, (b) 29.25 h, and (c) 173.5 h.

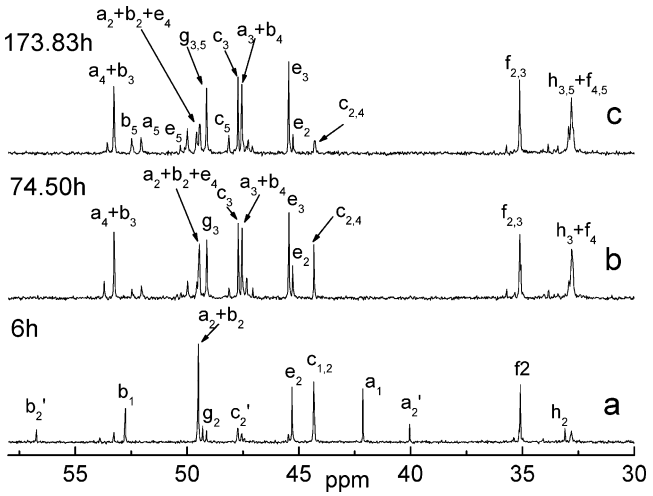


Figure 4. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + EEDA with a 1:1 feed molar ratio of EEDA to BDA and a monomer concentration of 25% (w/v) at 40 °C for (a) 6.00 h, (b) 74.50 h, and (c) 173.8 h.

shown in Schemes 1 and 2 due to no corresponding peaks appearing in Figures 1 and 2. Apparently, the reactivity of the three types of amines in AEPZ and AMPD was significantly different, and the reactivity sequence was 2° amines (original) > 1° amines ≫ 2° amines (formed). These result verified our previous speculation that the formed 2° amines were kept out of the reaction.[17] The mechanisms of the Michael addition polymerizations of BDA + AEPZ and BDA + AMPD can be described by Schemes 1 and 2, respectively.

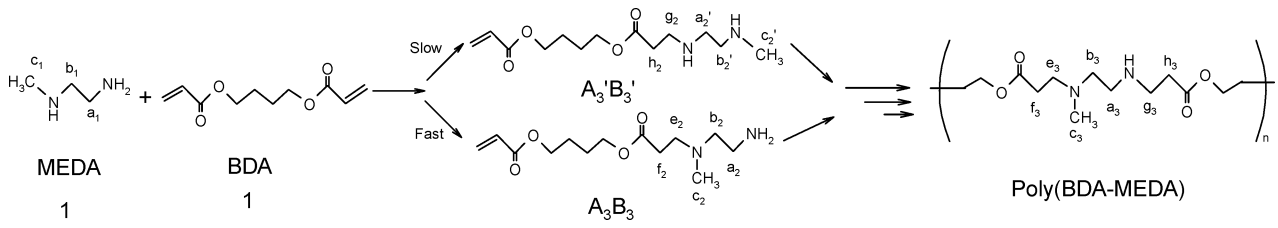
Polymerization of BDA + MEDA. The mechanism of the polymerization of BDA + MEDA was different from that of BDA + AEPZ or BDA + AMPD at the early stage of polymerization. Figure 3 depicts the changes in the peak positions of carbons adjacent to amines in MEDA during the polymerization, and the peaks ascription is depicted in Scheme 3. Figure 3a reflects that both the 2° (original) and 1° amines join in the reaction at the early stage of polymerization. The conjugation of the 2° amines (original) to the vinyl groups shifts the peaks of carbon a_1, b_1, and c_1 in MEDA from ca. 36.6, 55.0, and 41.8 ppm to a_2, b_2, and c_2 at ca. 39.7, 60.5, and 42.2 ppm and produces new peaks attributed to carbon e_2 and f_2 at ca. 53.2 and 33.0 ppm, respectively; the conjugation of the 1° amines moves the peaks of carbon a_1 and b_1 from ca. 36.6 and 55.0 to a_2' and b_2' at ca. 49.2 and 51.7 ppm and renders new peaks attributed to carbon g_2 and h_2 at ca. 45.3 and 35.1 ppm, respectively, but has no effect on the position of the peak of carbon c_1. Therefore, two kinds of intermediates, A_3B_3 and $A_3'B_3'$, appear at the early stage of polymerization as described in Scheme 3. Figure 3b,c shows that the further reaction of the 1° amines in intermediate A_3B_3 and the 2° amines (original) in $A_3'B_3'$ leads to formation of a linear poly(amino ester) as reflected by the disappearance of the characteristic peaks of A_3B_3 and $A_3'B_3'$, the appearance of the peaks attributed to carbon a_3, b_3, c_3, e_3, f_3, g_3, and h_3 of linear poly(amino ester) at ca. 47.1, 57.1, 42.2, 53.1, 32.8, 45.1, and 35.1 ppm, respectively, and a negligible amount of the 2° amines (formed) involved in the polymerization as shown by the relatively very small corresponding peaks.

The conversions of the 2° (original) and 1° amines were not pursued for the early stage of polymerization but were calculated on the basis of Figure 3 for later stages and are tabulated in Table 1. When the conversion of BDA is ca. 85%, all the 2° amines (original) disappear, 70% of the 1° amines attend the polymerization, and no detectable 2° amines (formed) are consumed. When the conversion of BDA is ca. 100%, the conversion of the 1° amines is ca. 100% with the 2° amines (formed) being intact. On the basis of these results, it could be concluded that the amine reactivity sequence still was 2° amines (original) > 1° amines ≫ 2° amines (formed), but the reactivity difference between the 2° amines (original) and 1° amines was not so big as in AEPZ and AMPD. The mechanism of the polymerization of BDA + MEDA can be described as in Scheme 3.

Polymerization of BDA + EEDA or BDA + HEDA. The mechanisms of the polymerization of BDA + EEDA or BDA + HEDA got even more complicated as compared with that of BDA + MEDA, and branched polymers were produced in the polymerizations.

Figures 4a and 5a indicate that both the 2° (original) and 1° amines in EEDA and HEDA participate in the reaction at an early stage of polymerizations. In Figure 4a for EEDA, the conjugation of 1° amines to vinyl groups forming intermediate A_4B_4 moves the peak

Scheme 3. Mechanism of the Michael Addition Polymerization of MEDA with an Equimolar BDA



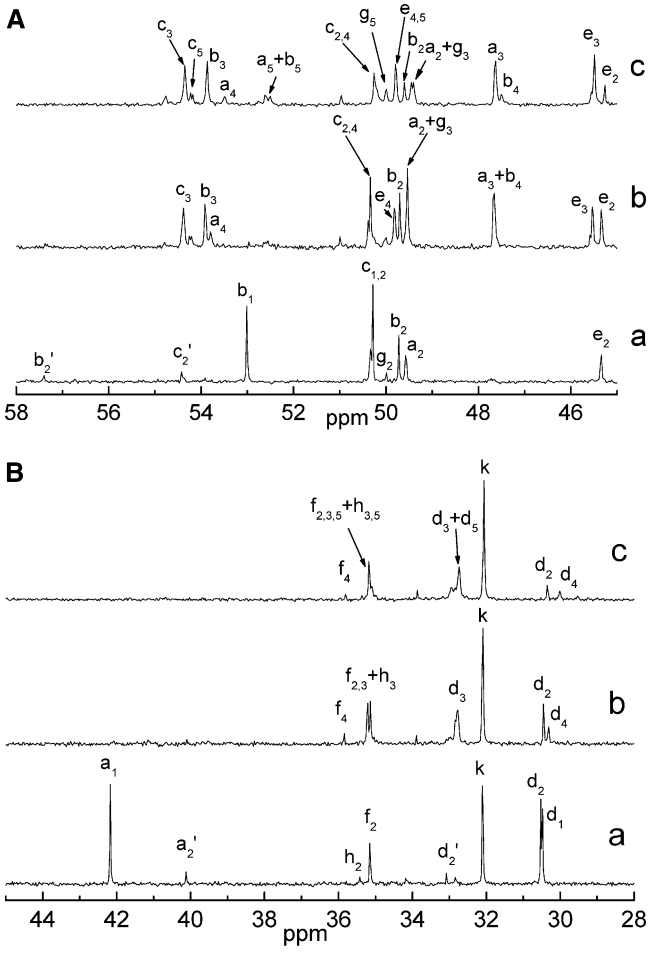


Figure 5. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + HEDA with a 1:1 feed molar ratio of HEDA to BDA and a monomer concentration of 25% (w/v) at 40 °C for (a) 5.75 h, (b) 74.33 h, and (c) 174.2 h.

positions of carbon a_1 and b_1 at ca. 42.1 and 52.8 ppm to a_2 and b_2 both at 49.5 ppm and produces new peaks attributed to carbon e_2 and f_2 at 45.3 and 35.1 ppm, respectively, but has no effect on the peak position of carbon c_1. Meanwhile, the reaction of 2° amines (original) leading to intermediate $A_4'B_4'$ shifts the peak positions of carbon a_1, b_1, and c_1 from ca. 42.1, 52.8, and 44.3 ppm to a_2', b_2', and c_2' at ca. 40.0, 56.7, and 47.8 ppm and renders new peaks attributed to carbon g_2 and h_2 at 49.3 and 33.1 ppm, respectively. Similarly in Figure 5a for HEDA, the reaction of 1° amines leading to intermediate A_5B_5 shifts the peak positions of carbon a_1 and b_1 from ca. 42.2 and 53.0 ppm to a_2 and b_2 at 49.6 and 49.7 ppm and provides new peaks attributed to carbon e_2 and f_2 at 45.3 and 35.2 ppm, respectively, but almost has no effect on the peak positions of carbon c_1 and d_1. Meanwhile, the reaction of the 2° amines (original) forming intermediate $A_5'B_5'$ moves the peak positions of carbon a_1, b_1, c_1, and d_1 from ca. 42.2, 53.0, 50.3, and 30.5 ppm to a_2', b_2', c_2', and d_2' at ca. 40.1, 57.4, 54.4, and 33.1 ppm and produces new peaks attributed to carbon g_2 and h_2 at 50.0 and 35.4 ppm, respectively. For both EEDA and HEDA, the higher integral intensities of the characteristic peaks of the intermediate A_4B_4 or A_5B_5 than those of $A_4'B_4'$ or $A_5'B_5$'suggest that the 1° amines are more reactive than the 2° amines. (We found that the quantitative results obtained from ^{13}C NMR acquired by a power-gated decoupling program (PD) were close to these obtained from quantitative ^{13}C NMR acquired by an inverse-gated broadband decoupled technique (INVGATE).)

When the polymerizations proceeded, Figure 4b or 5b reflects all the intermediate $A_4'B_4'$ or $A_5'B_5'$ vanishes, leading to linear units L_4 or L_5 through the reaction of the 1° amines, which further confirms that the 1° amines are more reactive than the 2° amines (original). These reactions are illustrated by the disappearance of the characteristic peaks of $A_4'B_4'$ such as the a_2' peak at ca. 40.0 ppm and the appearance of these peaks of L_4 such as c_3 at ca. 47.7 ppm in Figure 4b and by the disappearance of peaks of $A_5'B_5'$ such as the a_2' peak at ca. 40.1 ppm in Figure 5B-b and the appearance of peaks of L_5 such as a_3 at ca. 47.6 ppm in Figure 5A-b.

The linear unit L_4 or L_5 could also be formed from the intermediate A_4B_4 or A_5B_5 via the reaction of the 2° amines (original). In addition, Figure 4b or 5b displays that the 2° amines (formed) in the intermediate A_4B_4 or A_5B_5 can also join in the reaction forming linear units L_4' or L_5'. In Figure 4b for EEDA, the characteristic peaks of L_4' are overlapped with other peaks; however, in Figures 5A-b for HEDA, the characteristic peaks of L_5' are identifiable such as a_4 at 53.8 ppm whereas the contents of this type of unit are low. The continued reactions of both the original and formed 2° amines in L_4 and L_4' for EEDA, or L_5 and L_5' for HEDA, form branched poly(amino ester)s as indicated by the appearance of characteristic peaks such as a_5 at ca. 52.0 ppm in Figure 4c for EEDA and a_5 at ca. 52.5 ppm in Figure 5A-c for HEDA. On the basis of these results, the reactivity sequence of amines should be 1° amines > 2° amines (original) > 2° amines (formed), and the mechanisms of the polymerizations of BDA + EEDA or BDA + HEDA can be described as in Scheme 4 and 5, respectively.

The degree of branching (DB) of the polymers obtained was calculated on the basis of ^{13}C NMR (INVGATE) using the definition put forward by Hawker et al.[10e] Dendritic, linear, and terminal units are defined as in Schemes 4 and 5, and DB could be obtained on the basis of eq 2:

$$\mathrm{DB} = (D + T)/(D + T + L) \qquad (2)$$

where D and T stand for the amount of the dentritic and terminal units and L is the summed amount of the two types of linear units. For the branched polymers obtained from BDA + EEDA, DB was calculated by eq 3:

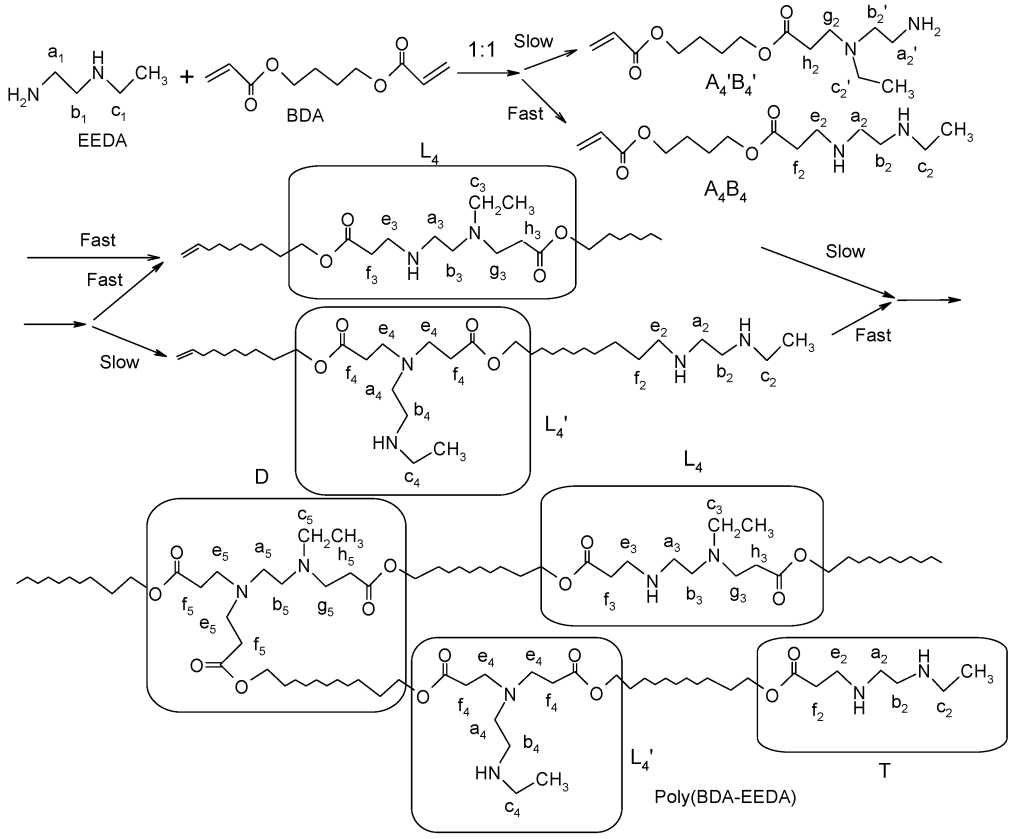
$$\mathrm{DB\ (BDA-EEDA)} = (I_{c5} + I_{e2})/(I_{c5} + I_{e2} + I_{a4} + I_{b3}) \qquad (3)$$

where I_{c5}, I_{e2}, I_{b3}, and I_{a4} are the integral intensities of the peak c_5, e_2, b_3, and a_4 as indicated in Figure 4c, respectively. For the branched polymers obtained from BDA + HEDA, DB was calculated by eq 4:

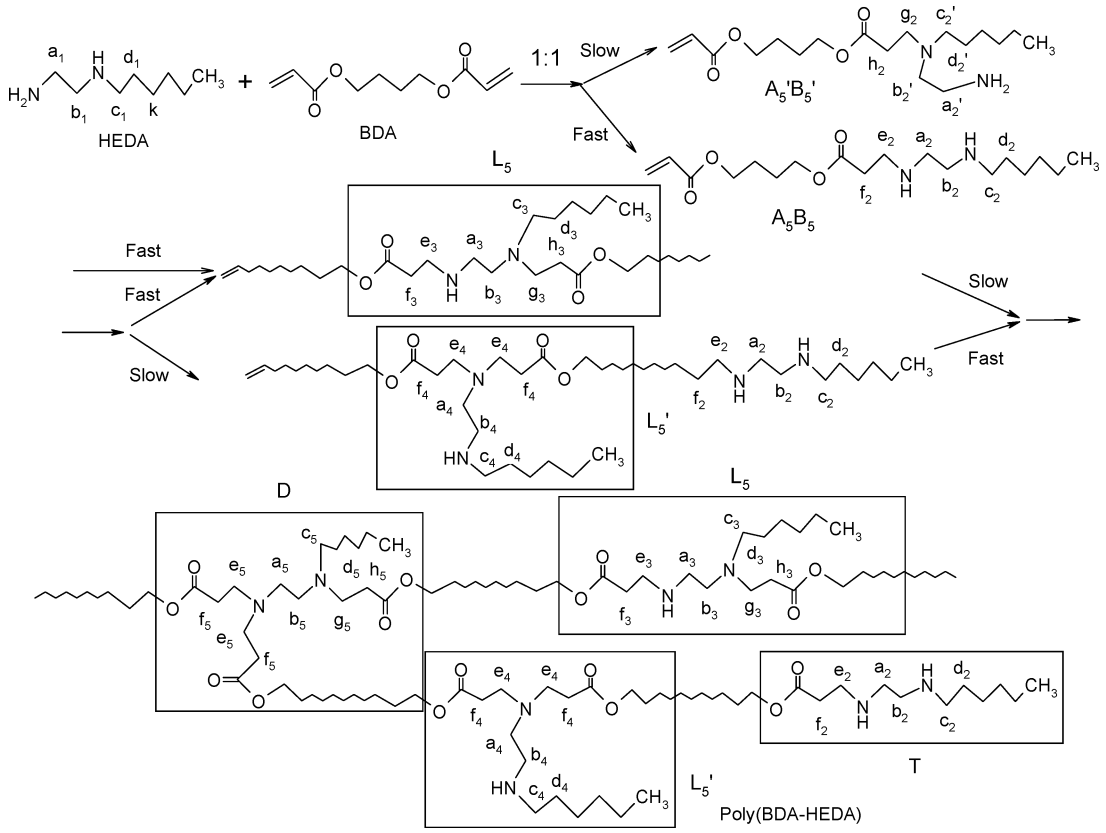
$$\mathrm{DB\ (BDA-HEDA)} = (I_{g5} + I_{e2})/(I_{g5} + I_{e2} + I_{a4} + I_{b3}) \qquad (4)$$

where I_{g5}, I_{e2}, I_{b3}, and I_{a4} are the integral intensities of the peak g_5, e_2, b_3, and a_4 as indicated in Figure 5c, respectively. As listed in Table 2, the DB values of the branched polymers obtained from BDA + EEDA and BDA + HEDA are ca. 33% and 37%, respectively.

Scheme 4. Mechanism of the Michael Addition Polymerization of EEDA with an Equimolar BDA



Scheme 5. Mechanism of the Michael Addition Polymerization of HEDA with an Equimolar BDA



2. Effects of the Chemistries of Trifunctional Amines. There are three types of amines, i.e., 2° amines (original), 1° amines, and 2° amines (formed), capable of performing Michael addition reaction with BDA. The reactivity of 1° amines in all the trifunctional amines can be considered to be similar; meanwhile, steric hindrance plays an important role in determining the reactivity of the secondary amines including the 2°

Table 2. Conditions of the Polymerizations of Trifunctional Amines with an Equimolar BDA and the Properties of the Poly(amino ester)s Obtained[a]

polymer	reaction time (h)	yield (%)[b]	M_w[c]	PDI[c]	T_d (°C)	T_g (°C)	DB (%)
poly(BDA−AMPD)	294	86	19 662[d]	3.48	263.5	−8.8	
poly(BDA−AEPZ)	274	84	23 462[d]	3.11	296.1	−21.7	
poly(BDA−MEDA)	248	80	5 450[d]	2.93	228.7	−43.0	
poly(BDA−EEDA)	366	82	10 400[e]	3.11	210.7	−33.9	33
poly(BDA−HEDA)	510	75	13 165[e]	3.05	218.2	−53.4	37

[a] The polymerizations were performed at 50 °C with a monomer concentrations of ca. 30% (w/v) in chloroform. [b] The yields of the polymerizations. [c] Determined by GPC. [d] Using 0.5 M acetic acid/0.5 M sodium acetate as eluent and poly(ethylene oxide) standards. [e] Using 0.1 M piperidine/THF as eluent and polystyrene standards.

amines (original) and the 2° amines (formed) and therefore the reactivity sequence of the three types of amines in the polymerizations. The high steric hindrance of polymer chains was responsible for the lowest reactivity of the 2° amines (formed) among all the amines. Whereas when the steric hindrance of cyclic aliphatic rings in AEPZ, AMPD, and methyl groups in MEDA on the 2° amines (original) was low, 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 in the Michael addition reactions with BDA. So for AEPZ, AMPD, and MEDA, the reactivity sequence of amines was 2° amines (original) > 1° amines ≫ 2° amines (formed), and the reactivity difference between the 1° amines and the 2° amines (formed) was so significant that all the 2° amines (formed) were kept out of the reactions, leading to formation of the linear poly(amino ester)s when the feed molar ratios of BDA to the trifunctional amines were 1:1. But the reactivity difference between the 2° amines (original) and 1° amines was reduced in some degree in MEDA as compared with those for AEPZ and AMPD probably due to the different steric hindrance of the cyclic aliphatic rings and the linear aliphatic chains on the 2° amines (original). However, the increased steric hindrance on the 2° amines (original) in EEDA and HEDA reduced their reactivity so remarkably that their reactivity was lower than that of the 1° amines and even comparable by that of the 2° amines (formed). Therefore, the reactivity sequence of amines was 1° amines > 2° amines (original) > 2° amines (formed), and even the 2° amines (formed) could join in the polymerizations forming branched poly(amino ester)s with low DBs.

Our results were different from those reported for the Michael addition polymerizations of trifunctional amines with divinyl sulfone or diacrylate in two ways, i.e., the different reactivity sequences of the amines and the different structures of the polymers obtained.[19,20] It was reported that the reactivity sequence of amines was 2° amines (original) > 1° amines = 2° amines (formed), and hyperbranched polymers with DBs higher than 50% and primary amines at periphery were formed via AB_2-type intermediates for the Michael addition polymerizations of trifunctional amines with divinyl sulfone or diacrylate. But in our work, for the polymerization of BDA + AEPZ, BDA + AMPD, and BDA + MEDA, the reactivity sequence was 2° amines (original) > 1° amines ≫ 2° amines (formed), and linear poly(amino ester)s containing secondary and tertiary amines were produced; for the polymerization of BDA + EEDA and BDA + HEDA, the reactivity sequence was 1° amines > 2° amines (original) > 2° amines (formed) and branched poly(amino ester)s having DBs of ca. 33% and 37% and containing secondary and tertiary amines, but no terminal primary amines were obtained. The causes for the differences would be investigated further.

3. Property of Polymers. The conditions of polymerizations with 1:1 feed molar ratios of trifunctional amine monomers to BDA are summarized in Table 2. All the obtained polymers could dissolve in chloroform, methylene chloride, acetone, DMSO, DMF, and THF; however, the linear polymers, poly(BDA−AEPZ), poly(BDA−AMPD), and poly(BDA−MEDA), were soluble in water, but the branched polymers, poly(BDA−EEDA) and poly(BDA−HEDA), were insoluble in water probably due to the longer hydrophobic aliphatic side chains. The molecular weights of the polymers obtained were evaluated by GPC. As shown in Table 2, the polymers have high molecular weight polydispersity indexes, which probably resulted from the multistage processes of these polymerizations as suggested above. Similar results were found for some of the poly(amino ester)s prepared from the polymerization of diacrylates and difunctional amines.[14] As reflected by Table 2, T_ds of the polymers are higher than 200 °C, which indicates their reasonable thermal stability. Meanwhile, DSC studies shows that all the poly(amino ester)s are amorphous due to no melting and crystallization peaks in DSC curves and have glass transition temperatures (T_g) lower than ambient temperature, which should result from the flexible backbones.

Conclusions

The chemistries of trifunctional amines had remarkable effects on the mechanisms of the Michael addition polymerizations with diacrylate. The steric hindrance on the secondary amines in trifunctional amines such as AEPZ, AMPD, and MEDA was low so the reactivity sequences of the amines were 2° amines (original) > 1° amines ≫ 2° amines (formed). The high steric hindrance of polymer backbones reduced the reactivity of 2° amines (formed) so significantly that they were kept out of the reaction leading to formation of the linear poly(amino ester)s via AB type intermediates when the feed molar ratios of trifunctional amines to diacrylate were 1:1. The increased steric hindrance on the secondary amines in EEDA and HEDA reduced the reactivity of 2° amines (original) to such a degree that the reactivity sequences of amines changed to 1° amines > 2° amines (original) > 2° amines (formed) and the 2° amines (formed) joined in the polymerizations, leading to formation of the branched poly(amino ester)s when the feed molar ratios of trifunctional amines to diacrylate were 1:1. Both the linear and branched poly(amino ester)s obtained have good solubility, reasonable thermal stability, and glass transition temperatures lower than room temperature, but high molecular weight polydispersity indexes.

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