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In situ FT-IR spectroscopic investigation on the microstructure of hyperbranched aliphatic polyesters

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Abstract

The synthetic process of hyperbranched aliphatic polyesters based on 2,2-bis(hydroxymethyl)propionic acid (AB_2-type monomer) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (B_3-type core) was investigated with in situ Fourier transform infrared (FT-IR) spectroscopic analysis. The experimental parameter was the stoichiometric ratio between monomer and core moiety corresponding to theoretical first, second and third generation. In the theoretical first generation, monomers were directly combined with a core molecule. In the theoretical second and third generation, oligomers derived from the reaction between monomers were gradually combined with a core moiety as the reaction time increased. The microstructure of the main product was surmised from the peak integration of in situ FT-IR spectra, the intensity of each repeating unit on ^{13}C NMR spectra and the number average molecular weight. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: In situ FT-IR spectroscopic analysis; Hyperbranched aliphatic polyesters; Microstructure

1. Introduction

Nonlinear architecture, such as hyperbranched or dendritic macromolecules, has attracted considerable and increasing interest during recent years. Dendritic macromolecules or dendrimers have perfect branching, with at least one branching point per monomer unit (AB_x, $x \geq 2$), whereas hyperbranched polymers are randomly branched and contain varying amounts of linear segments.

Dendrimers are built of monomers coupled in several layers around a central core molecule where each layer is called a generation. Due to their specific architecture, dendrimers exhibit properties different from those of linear polymers of the same molar mass, such as lack of significant entanglement in the solid state [1], high solubility in various solvents and low melt viscosity [2,3]. Dendrimers can be synthesized through convergent or divergent growth approach [4,5]. These syntheses are tedious as they often require several protection and deprotection steps as well as extensive purification between successive generations. The synthesis of dendrimers is not only expensive but also restrictive for the use of those in large scale applications.

Hyperbranched polymers show properties resembling those of dendrimers [6,7]. The one-step polymerization process used to produce hyperbranched polymers is advantageous when compared with the multi-step synthesis of dendrimers as it is capable of the rapid production of large quantities of highly functionalized globular polymer. Therefore hyperbranched polymers are better suited for applications. There are various application fields such as toughening agents [8], coatings [9–13], additives [14], blends [15], nonlinear optics [16], composites and copolymers [17–18].

Molar masses for polymers are often determined with gel permeation chromatography (GPC). The separation phenomenon of GPC is based on molecular size, i.e. hydrodynamic volume. The hydrodynamic volume of a dendritic macromolecule is smaller than that of its linear analog of the same molar mass. Therefore, the values measured with GPC, calibrated with, e.g. linear polystyrene standards, will probably be lower than real values. Further, depending on how the hyperbranched molecule interacts with the solvent, it may occupy different volumes [19]. The newly developed matrix-assisted laser desorption-ionization time-of-flight (MALDI/TOF) mass spectroscopy has been used for dendritic macromolecules with good results [20–21].

The degree of branching (DB) for hyperbranched polymers based on AB_2 monomers is defined according to Hawker et al. [22] as follows:

$$DB = \frac{\sum \text{dendritic units} + \sum \text{terminal units}}{\sum \text{dendritic units} + \sum \text{terminal units} + \sum \text{linear units}}$$

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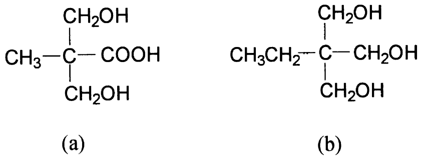

Fig. 1. Chemical structures of monomer and core molecule: (a) bis-MPA; (b) TMP.

For an ideal dendrimer, the DB is equal to unity. A hyperbranched polymer takes DB values between 0 and 1.

The synthesis of hyperbranched aliphatic polyesters, based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) as an AB_2 monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) as a core moiety, was described earlier by Malmström et al. [23]. The DB for these hyperbranched polyesters was reported to be close to 80%, as determined by ^{13}C NMR in acetone-d_6. However, since the ^{13}C NMR study was performed in acetone and small residues of acid were present, most end-groups were transformed into acetonide endgroups. This made the calculation of DB incorrect. When the DB was re-estimated from dimethyl sulfoxide-$d_{6,}$ the right value was calculated to be close to 0.5 [24].

Mansfield concluded that it was important to keep the molecule as perfect as possible in low generations to suppress polydispersity [25]. Therefore, the investigation of microstructure of hyperbranched polymers corresponding to low generations is of importance.

In this study we monitored the synthetic process of hyperbranched aliphatic polyesters, corresponding to theoretical first, second and third generation, with in situ FT-IR spectroscopic analysis and investigated the microstructure of the main product with the peak integration of in situ FT-IR spectra, the intensity of each repeating unit on ^{13}C NMR spectra and the number average molecular weight.

2. Experimental

2.1. Materials

2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) was used as an AB_2 type monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) was used as a B_3 type core moiety. Fig. 1 shows their chemical structures. *p*-Toluenesulfonic acid (*p*-TSA) was used as an acid catalyst. All chemicals were purchased from Aldrich and were used as received.

2.2. Sample preparation

The samples for the measurement of the fraction of each repeating unit and molecular weight were synthesized on the direction described by Malmström et al. [23]. The synthesis was not a pseudo-one-step reaction, but a one-pot polymerization process. The samples for in situ FT-IR spectroscopic experiment were prepared under following directions.

2.2.1. Theoretical first generation

Bis-MPA (225 mg, 1.68 mmol), TMP (75 mg, 0.56 mmol) and *p*-TSA (1.1 mg, 0.5 wt% based on bis-MPA) were dissolved in a beaker containing 20 ml of tetrahydrofuran (THF). The several drops of the solution was coated on KBr pellet by spoid and the pellet was dried in vacuum oven at 40°C for 30 min. Then the pellet was covered with another pure KBr pellet and was set up on in situ FT-IR spectroscopic apparatus. The sample was denoted as sample 1.

2.2.2. Theoretical second generation

Bis-MPA (278 mg, 2.07 mmol), TMP (31 mg, 0.23 mmol) and *p*-TSA (1.4 mg, 0.5 wt% based on bis-MPA) were dissolved in a beaker containing 20 ml of THF. The sample was prepared by the same method as described in theoretical first generation and denoted as sample 2.

2.2.3. Theoretical third generation

Bis-MPA (338 mg, 2.52 mmol), TMP (16 mg, 0.12 mmol) and *p*-TSA (1.7 mg, 0.5 wt% based on bis-MPA) were dissolved in a beaker containing 20 ml of THF. The sample was prepared by the same method as described in theoretical first generation and denoted as sample 3.

2.3. Instrumental analysis

Infrared spectra were recorded on a Bomem MB100 Fourier Transform Infrared (FT-IR) Spectrometer. Differential scanning calorimetry (DSC) analysis was performed on a TA instrument using a heating/cooling rate of 10°C/min. The reaction temperature was determined as tip point of the peak of melting in the curve. Relatively low esterification temperatures were chosen to suppress unwanted side reactions such as etherification and trans-esterification. The reaction temperatures for sample 1, 2 and 3 were 142°C, 147°C and 153°C. The reaction time was 2 h. Even though it was shorter than real reactor scale, the conversion was close to 100% because small amounts of reactants were used on in situ FT-IR spectroscopic experiment.

Nuclear magnetic resonance (NMR) spectra were recorded on a Lambda (JEOL) 300 MHz using dimethyl sulfoxide-d_6 (DMSO) as a solvent and using the solvent signal as reference. The ^{13}C NMR spectra were obtained using the inverse gated decoupling mode (NNE: non NOE experiment, $T_1 = 6$ s, $D_1 = 50$ s) where the NOE effect was suppressed. The degree of branching was evaluated with the method reported by Malmström et al. [23].

Matrix-assisted laser desorption-ionization time-of-flight (MALDI/TOF) mass spectra were recorded on a HP G2025

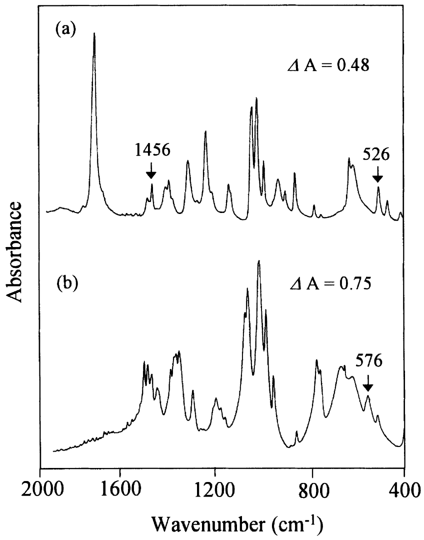

Fig. 2. FT-IR spectra of monomer and core molecule: (a) bis-MPA; (b) TMP.

LD/TOF. The matrix used for all samples was 2,5-dihydroxy-benzoic acid (DHB) and the solvent was THF.

3. Results and discussion

The FT-IR spectra of bis-MPA (monomer) and TMP (core) are shown in Fig. 2. On the spectrum of bis-MPA, the peak observed at 526 cm^{-1} is due to the bending vibration of primary alcohol C–C–O. The peak at 1456 cm^{-1} is due to the CH_3 asymmetric deformation vibration. On the spectrum of TMP, the peak at 576 cm^{-1} is assigned to the bending vibration of primary alcohol skeleton. The assignment of FT-IR bands is shown in Table 1.

3.1. Theoretical first generation (Sample 1)

The change of in situ FT-IR spectra during synthesis of sample 1 is shown in Fig. 3. The decrease of absorption intensity of the peak at 526 $^{-1}$ cm^{-1} was mainly due to the esterification between bis-MPAs because the reaction was superior to the etherification between the primary alcohol of bis-MPA and the primary alcohol of TMP. The absorption intensity of the peak at 576 cm^{-1} was decreased as the esterification between bis-MPA and TMP proceeded. The internal standard band, of which the intensity was not affected even though the reaction proceeded, appeared at 1456 cm^{-1} due to CH_3 asymmetric deformation vibration.

The peaks were separated by Lorentzian curve fitting method. The absorption intensities of the peaks at 526 and 576 cm^{-1} were calibrated with that of the internal standard band and plotted as a function of reaction time. The result is shown in Fig. 4. The alcohol groups of TMP were more reactive than those of bis-MPA even if the number of alcohol groups of bis-MPA (6) was more than that of TMP (3). One of the reasons is melting point difference between bis-MPA and TMP. The melting point of TMP (57°C) is lower than that of bis-MPA (181–185°C). The reaction temperature of sample 1 was 142. In the early stage of reaction, primary alcohol groups of all TMPs were reactive, but those of all bis-MPAs were not reactive. Bis-MPAs were molten into TMP and the molten bis-MPAs were reacted with TMP. Another reason is inductive effect. The carbonyl group of bis-MPA is electron-withdrawing group. Therefore, the primary alcohol groups of bis-MPA are less

Table 1
Vibrational bands of bis-MPA and TMP and their assignments

Bis-MPA		TMP	
ν/cm^{-1}	Assignment	ν/cm^{-1}	Assignment
1687(vs)[a]	Carboxyl acid C=O str	1463(s)	CH_3 asym def
1475(w)	CH_2 scissors def	1384(m)	CH_3 sym def
1456(m)	CH_3 asym def	1235(m)	C–C–O asym str
1401(w)	CH_2 wag	1164(m + sh)	In phase C–C–C str mixed with in plane CH_3 rock
1387(m)	CH_3 sym def	1058(s)	
1308(s)	Carboxyl acid C–O str	1035(s)	Primary alcohol C–O str
1235(m)	C–C–O asym str	1012(s)	
1142(m + sh)	In phase C–C–C str mixed with in plane CH_3 rock	864(w)	CH_3 rock mixed with C–C str
1046(vs)	Primary alcohol C–O str	777(m)	CH_2 rock
1025(vs)		642(m,b)	Primary alcohol C–OH def (out of plane)
997(s)	Carboxyl acid OH def (out of plane)	576(m)	Primary alcohol skeleton bend
869(m)	CH_3 rock mixed with C–C str	537(w)	C–C in plane bend
790(w)	CH_2 rock		
636(m,b)	Primary alcohol C–OH def (out of plane)		
526(m)	Primary alcohol C–C–O bend		

[a] Intensity: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

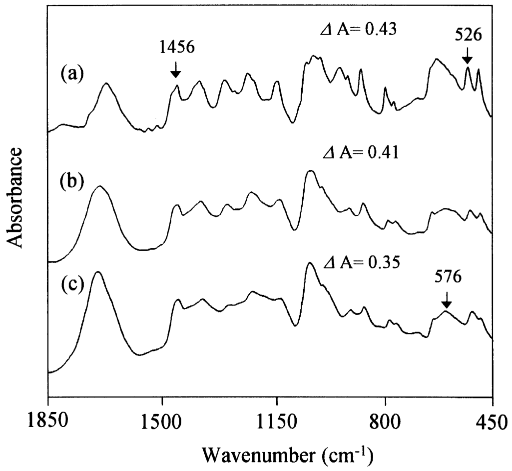

Fig. 3. In situ FT-IR spectral change during synthesis of sample 1: (a) 0 min; (b) 15 min; (c) 30 min.

reactive than those of TMP. The absorption intensity of the peak at 576 cm^{-1} was decreased to a finite value (about 31%) within 30 min. Since one TMP molecule has three primary alcohol groups, two primary alcohol groups in a TMP molecule are believed to be combined with bis-MPAs.

The fraction of each repeating unit was obtained by inverse gated decoupling ^{13}C NMR technique where the NOE effect was suppressed. Each repeating unit was assigned on ^{13}C NMR spectra with the same method as described by Malmström et al. [23]. They assigned each repeating unit using the chemical shift difference [terminal unit (ppm): 50.65, linear unit (ppm): 48.85, dendritic unit (ppm): 46.80] of the quaternary carbon in model compounds and obtained the DB by integrating its intensity. The ^{13}C NMR spectrum of sample 1 is illustrated in Fig. 5. The integrated intensities of terminal, linear and dendritic unit were 1.30, 1.00 and 0.00, respectively. The number average molecular weight of sample 1 measured with MALDI-TOF technique was 620 g/mol. The molecular weight of a TMP is 134 g/mol. The total weight of bis-MPAs coupled around a TMP was approximately obtained by subtracting the molecular weight of a TMP from that of sample 1, i.e. 486 g/mol. The molecular weights of terminal, linear and dendritic unit are 117, 116 and 115 g/mol, respectively. Therefore, the number of all repeating units coupled around a core moiety was about 4. Consequently, the numbers of terminal, linear and dendritic units were evaluated to be about 2, 2 and 0, respectively. Table 2 shows the theoretical and experimentally measured values such as the number average molecular weight, the DB, ^{13}C NMR intensity and the number of each repeating unit. Although the input molar ratio of monomer and core was 3: 1, 4 monomers were coupled around a core molecule. The result obtained from MALDI-TOF technique showed the existence of molecules having high molar masses (e.g. 968, 1084 g/mol). Therefore, it is believed that small molecules could be combined with each other.

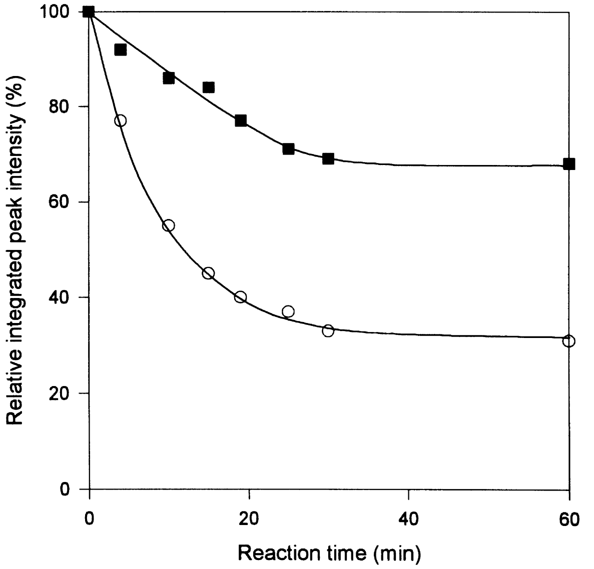

Fig. 4. Peak integration of in situ FT-IR spectra of sample 1: (■) 526 cm^{-1}; (○) 576 cm^{-1}.

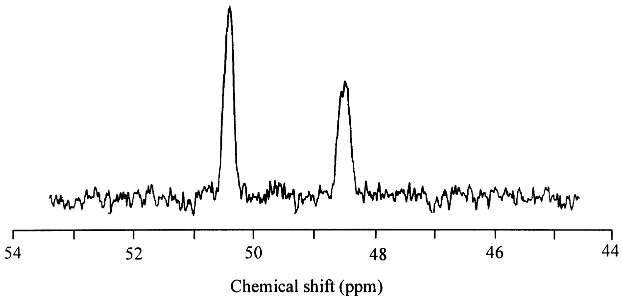

Fig. 5. ^{13}C NMR spectrum of sample 1.

Judging from these results, it is possible to determine the main structure of theoretical first generation. Fig. 6 shows the main structure of sample 1. This correlates well to the structure predicted by in situ FT-IR spectroscopic analysis.

3.2. Theoretical second generation (Sample 2)

Fig. 7 shows the change of absorption intensity of the peaks at 526 and 576 cm^{-1} during the synthesis of theoretical second generation. The absorption intensity of the peak at 576 cm^{-1} was decreased rapidly in the early stage of synthesis and decreased slowly to a finite value (about 29%) in the later stage of synthesis. Therefore, two primary alcohol groups in a TMP molecule are believed to be combined with bis-MPAs. Unlike theoretical first generation, the absorption intensity of the peak at 526 cm^{-1} was decreased rapidly within 25 min, afterwards remained constant. That means the reaction between bis-MPAs proceeded actively. This phenomenon can be explained as follows. The elevation of reaction temperature (147°C) enables more bis-MPAs to be molten actively. Since the amount of bis-MPAs in the second generation was relatively

Table 2
Theoretical and experimentally measured values for the hyperbranched aliphatic polyesters

Sample no.	Molar ratio (TMP:bis-MPA)	Theor. gen.[a]	M_n(g/mol)	DB[b]	^{13}C NMR intensity			No. of each unit		
					T[c]	L	D	T	L	D
1	1:3	1	620	0.57	1.30	1.00	0.00	2	2	0
2	1:9	2	1231	0.45	4.59	6.83	1.00	3	5	1
3	1:21	3	1688	0.44	2.80	4.83	1.00	4	7	2

[a] Theoretical generation.

[b] The degree of branching.

[c] T, terminal unit; L, linear unit; D, dendritic unit.

more than that in first generation, the molten bis-MPAs could react easily on each other as well as on TMP.

Considering the above results, it is believed that in the early stage of synthesis, oligomers such as dimers or trimers were formed from bis-MPAs and these oligomers were combined with core moiety as the reaction time increased.

There is another evidence that supports the supposition. The wavenumber of the band due to C=O stretching of ester groups shifted gradually from 1716 to 1722 cm^{-1} as the reaction time increased (Fig. 8). The hydrogen bond is most stable when elements are located to form six-membered ring. In these oligomers and a TMP reacted with bis-MPAs, the oxygen in C=O of ester group can form the stable hydrogen bond with the hydrogen of primary alcohol of bis-MPA. Then, the force constant of C=O bond is weakened and the band appears at low wavenumber. The hydrogen bond is broken as the oligomers are combined to core moiety. Therefore the force constant of the C=O bond augments and the band due to C=O stretching shifts to a higher wavenumber.

The integrated intensities of repeating units on ^{13}C NMR spectra are listed in Table 2. The number average molecular weight of sample 2 was 1231 g/mol. The total weight of all repeating units coupled around a TMP was about 1097 g/mol. Therefore, the number of all repeating units coupled around a core moiety was about 9. From the number of all repeating units and the fraction of each repeating unit, the numbers of terminal, linear and dendritic units incorporated into a TMP were evaluated to be approximately 3, 5 and 1, respectively.

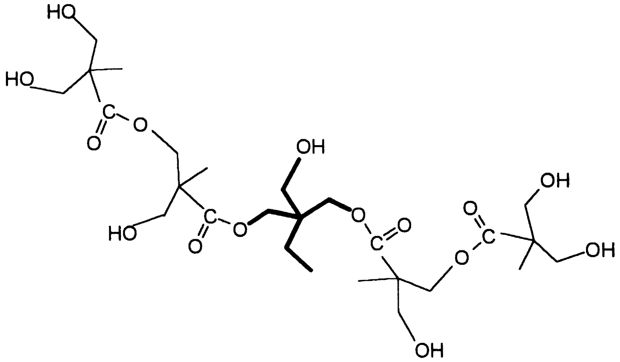

Fig. 6. The microstructure of sample 1.

Considering above results and steric hindrance, we can conjecture the synthetic route and the plausible structure of main product. The schematic diagram of synthetic process of theoretical second generation is shown in Fig. 9. The architecture can be changed as the different incorporation of the repeating units occurs.

3.3. Theoretical third generation (Sample 3)

Fig. 10 shows the integration of the peaks at 526 and 576 cm^{-1} during the synthesis of theoretical third generation. The synthetic route of sample 3 followed the similar way as that of theoretical second generation. The absorption intensity of the peak at 526 cm^{-1} was decreased rapidly between 20 and 60 minutes. This means the esterification between bis-MPAs proceeded actively and oligomers such as dimers or trimers were formed as the result. Like sample 2, the wavenumber of the band due to C=O stretching of ester group shifted gradually from 1717 cm^{-1} to 1724 cm^{-1} as the reaction time elapsed. It means that oligomers were

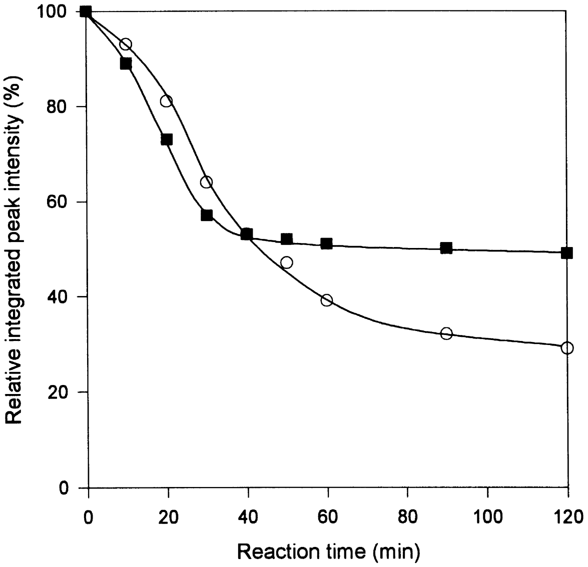

Fig. 7. Peak integration of in situ FT-IR spectra of sample 2: (■) 526 cm^{-1}; (○) 576 cm^{-1}.

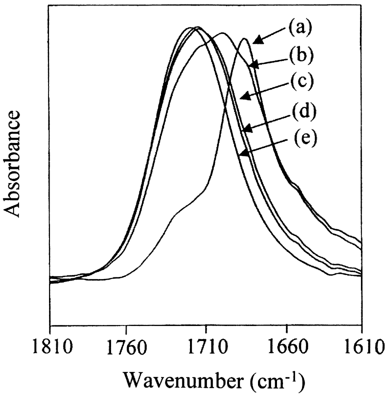

Fig. 8. Shift of the band due to carbonyl stretching during synthesis of sample 2: (a) 10 min; (b) 20 min; (c) 30 min; (d) 60 min; (e) 90 min.

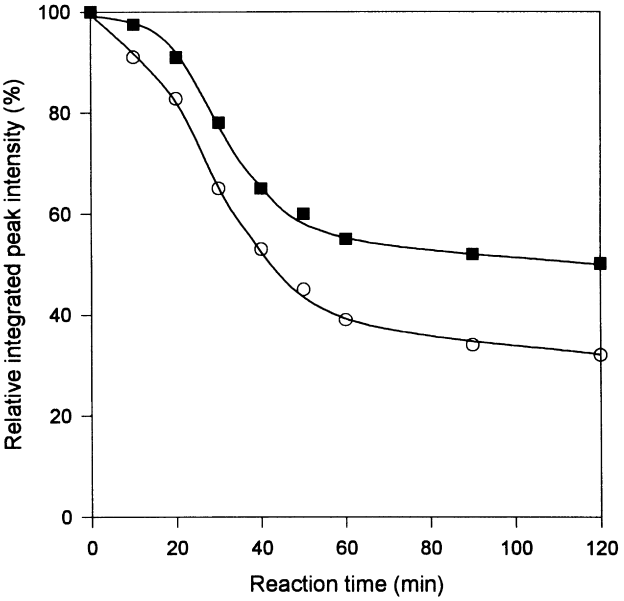

Fig. 10. Peak integration of in situ FT-IR spectra of sample 3: (■) 526 cm^{-1}; (○) 576 cm^{-1}.

combined with core moiety in the later stage of synthesis. Since the integrated intensity of the peak at 576 cm^{-1} was decreased to about 32% similar to sample 1 and 2, two primary alcohol groups in a TMP molecule are believed to be reacted with bis-MPAs.

In the early stage of reaction, the absorption intensity of the peak at 576 cm^{-1} was decreased faster than that of the band at 526 cm^{-1}. This phenomenon was opposite to that of the synthesis of sample 2. This can be explained as follows. For in situ experiment of sample 3, the esterification reaction between bis-MPAs proceeded for 1 h. Whereas, for the in situ experiment of sample 2, the esterification reaction between bis-MPAs proceeded for 40 min. The perfect melting of bis-MPAs in sample 3 took more time than that in sample 2. The amount of bis-MPAs in sample 3, whose melting point (181°C–185°C) is higher than the reaction temperature, was relatively more than that in sample 2. The elevation of reaction temperature in theoretical third generation was less effective than that in theoretical second generation. Therefore, it is concluded that the reaction temperature played a important role in the consumption rate of functional groups of reactants and the synthetic process.

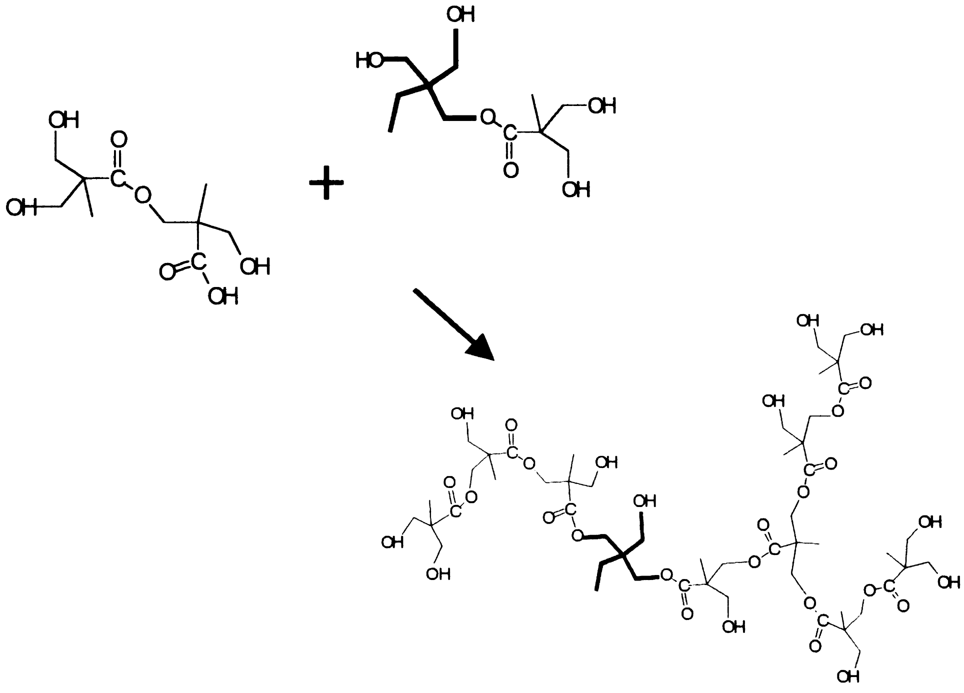

Fig. 9. The schematic diagram of synthetic process of sample 2.

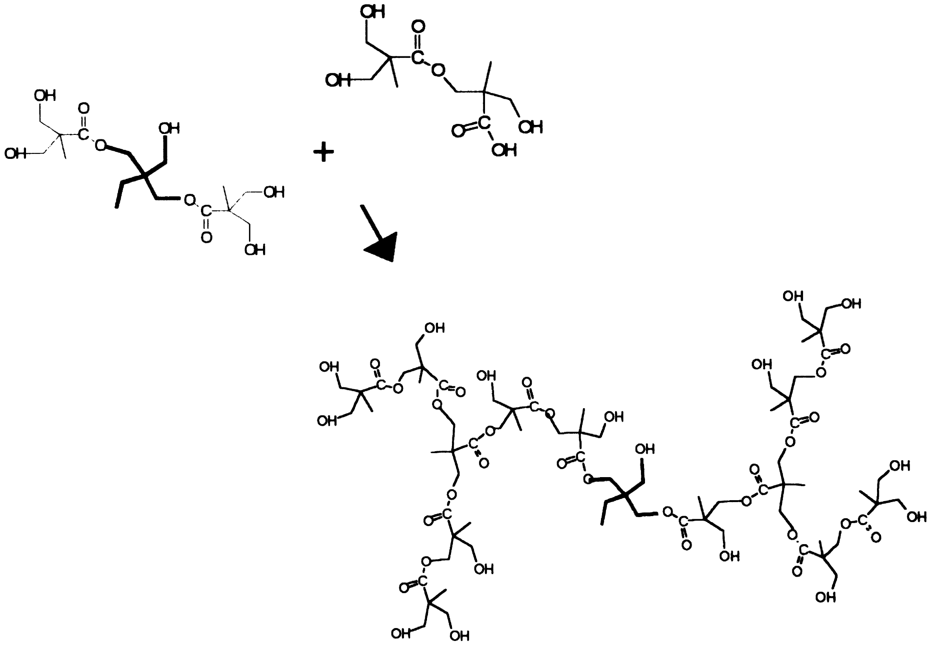

Fig. 11. The schematic diagram of synthetic process of sample 3.

The integrated intensities of repeating units on ^{13}C NMR spectra are listed in Table 2. The number average molecular weight of theoretical third generation was 1688 g/mol. Except a core moiety, the total weight of all repeating units was approximately 1554 g/mol. From the molar mass and ^{13}C NMR intensity of each repeating unit, the numbers of terminal, linear and dendritic units incorporated into a TMP were evaluated to be about 4, 7 and 2, respectively.

Considering these results and steric hindrance, the synthetic route and the feasible structure of main product are believed to be like Fig. 11. The architecture can be changed as the different incorporation of the repeating units occurs.

4. Conclusions

The synthetic process and microstructure of hyperbranched aliphatic polyesters was investigated by in situ FT-IR spectroscopic analysis with the help of peak intensity of ^{13}C NMR and molecular weight. In theoretical first generation, four bis-MPAs were mainly combined with a TMP core molecule, even though the molar ratio of bis-MPA and TMP was 3:1. The result obtained from the MALDI-TOF technique showed the existence of molecules having high molar masses, which meant the small molecules could be combined with each other. The microstructure of the main product had two terminal units and two linear units. In theoretical second and third generation, oligomers were formed through the esterification of bis-MPAs in the early stage and combined with a core moiety in the later stage. The main structure of theoretical second generation had three terminal units, five linear units and one dendritic unit. The main structure of theoretical third generation had four terminal units, seven linear units and two dendritic units. In the early stage, the reaction rate of TMPs of theoretical third generation was higher than that of theoretical second generation. The reaction temperature played a important role in the consumption rate of functional groups of reactants and the synthetic process.

Acknowledgements

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