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Structure Buildup in Hyperbranched Polymers from 2,2-Bis(hydroxymethyl)propionic Acid

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ABSTRACT: The structure buildup in hyperbranched polyesters from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) was studied experimentally. Bis-MPA and its dendritic trimer were both polymerized in bulk using acid catalyst. The fractions of terminal, dendritic, and linear repeating units were monitored by ^{13}C NMR during the course of reaction. Effect of slow monomer addition on the degree of branching in the final product was also studied. Hyperbranched polymers from bis-MPA with and without a core molecule were kept at the polymerization temperature in order to examine the effect of heat treatment on composition in the polymer. The fractions of the different repeating units were changing to a large extent with conversion. Slow monomer addition to a trifunctional core molecule gave a product with a degree of branching of 47%. Heat treatment of hyperbranched materials gave small changes in the fractions of the different repeating units in both materials and, eventually, gelling in the material without a core.

Introduction

Hyperbranched polymers have gained large interest in recent years. Like dendrimers they are built from AB_x functional monomers giving $x - 1$ potential branch points per repeating unit. Because of their highly branched structure, hyperbranched polymers have many attractive features in common with dendrimers,[1−4] such as improved solubility compared to that of linear polymers of the same molecular weight and a large number of end groups. Compared to dendrimers, they are easier and cheaper to produce and therefore more suitable for large-scale production.

In hyperbranched polymers there are three different kinds of repeating units—dendritic, linear, and terminal—while dendrimers contain dendritic and terminal units. In 1991, Fréchet et al. introduced the term average degree of branching to describe hyperbranched polymers.[5] The degree of branching (DB) is a measure of the fraction of the repeating units that form branch points or terminal groups and was defined as the sum of the terminal and dendritic units divided by the total sum of all repeating units.

$$\mathrm{DB} = \frac{D + T}{D + L + T}$$

For a perfect dendrimer the degree of branching is one, and for hyperbranched polymers it is less than unity. Another approach to describe the branching in hyperbranched polymers has been proposed by Frey et al.[6,7] In this concept, the number of growth directions of the polymer chain is compared to the maximum number of growth directions. The calculations are applicable to both AB_2 systems and AB_m systems with $m > 2$.

$$\mathrm{DB} = \frac{2D}{2D + L}$$

The structure buildup in hyperbranched polymers has earlier been studied by computer simulation.[7−9] In these studies the reaction between the A and B functionalities of the mixture have been assumed to be completely random. Effects of increasing viscosity of the reaction mixture, changes in reactivity when one of the B groups has reacted, and possible hindrance in the growing polymer, making some of the functional groups less available for reaction, have therefore been neglected. To increase the degree of branching in a hyperbranched polymer, different methods have been suggested on the basis of results from computer simulation: Increase the reactivity of B groups in the linear repeating units compared to the B groups in the terminal repeating units, polymerization of dendrons that are prefabricated from the monomer, and core dilution/slow monomer addition to the reaction mixture.[7,10] The concept of using preformed dendrons as monomers in polymerization has previously been explored by Hawker et al.[10] Linear and dendritic units were deliberately inserted in the monomer used in synthesis of hyperbranched polymers, and the effect on the degree of branching was studied. Fréchet et al. compared hyperbranched siloxanes from AB_2, AB_4, and AB_6 monomers.[11]

In our group, dendrimers and hyperbranched polymers derived from 2,2-bis(hydroxymethyl)propionic acid have been studied since 1990.[12−15] In the present study, we examine the formation of hyperbranched polymers experimentally. Are the proportions of different repeating units in the hyperbranched structure the same throughout the reaction, or is the composition of the polymer changing with conversion? Will the composition of the product be different if the monomer is added more slowly to the mixture? Is the final composition of the product constant, or will it change if the material is kept under reaction conditions for longer time periods? To optimize the material with respect to degree of branching, it is necessary to know more about the structure buildup during polymerization.

Results and Discussion

The hyperbranched structure contains three different kinds of repeating units: dendritic, linear, and terminal. Each one of them can also exist as a focal point, attached to an acid group. In the ^{13}C NMR spectrum, the

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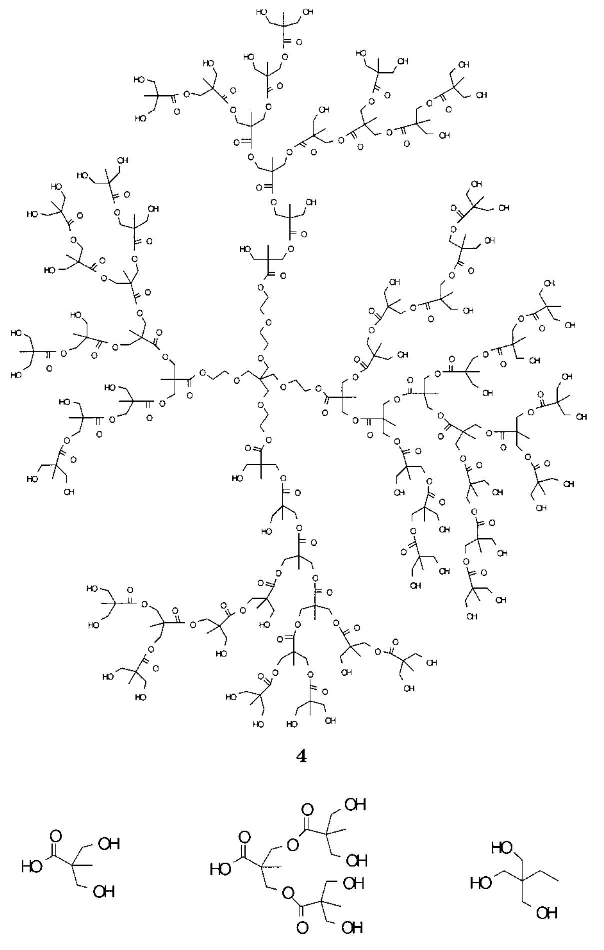

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Figure 1.

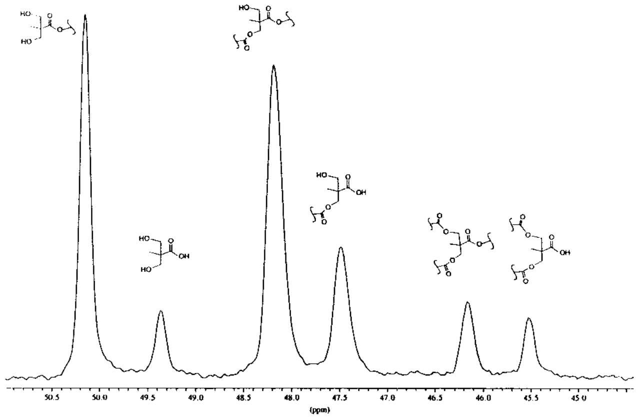

Figure 2. Magnification of the quaternary carbon region of the ^{13}C NMR spectrum of hyperbranched polymer at an early stage of reaction. The peaks of terminal, dendritic, and linear repeat units are all present as well as the corresponding acid functional repeat units.

quarternary carbons of the different repeating units are easily distinguished from each other (Figure 2). Their peaks appear at different chemical shifts depending on the degree of substitution of the repeating unit. Therefore, the relative amounts of the different repeating units can be determined from the quantitative spectrum by comparing the integrals of the different peaks.

In this study we have analyzed samples taken from the reaction mixture during polymerization to determine the composition of the polymer. We have also compared our empirical results to those obtained from equations presented by Frey et al.[7] To investigate whether the composition of the hyperbranched material is at equilibrium, hyperbranched polymers have been kept for at 140 °C a long time. Samples were taken out during the heat treatment for analysis by ^{13}C NMR to examine whether the relative amount of the different repeating units changes with time. In a final experiment we used a core molecule and added the monomer slowly in small portions to the mixture.

Conversion as a Function of Time. The conversion of acid groups is defined as the number of acid groups present in the mixture at a certain time over the number of acid groups present before any reaction has occurred

$$p = \frac{A_0 - A}{A_0}$$

where A_0 is the number of acid groups at $t = t_0$ and A is the number of acid groups at $t = t$. The conversion of acid groups can be monitored by acid number titration of samples taken out at different times during polymerization or by calculations from the corresponding ^{13}C NMR spectra.

At higher conversion, the number of acid groups left in the mixture is very low, and therefore small volumes of base are needed to neutralize the sample in acid number titration. The sample is therefore easily over titrated, the real volume of base needed to neutralize the sample is smaller than the observed volume, and the conversion is slightly underestimated. The experimental error in acid number and conversion is larger the higher the conversion is.

Information about the conversion of acid groups can also be obtained from the ^{13}C NMR spectrum (Figure 2). In this case, A_0 equals the sum of the integrals of all quarternary carbons while A equals the sum of the integrals of quarternary carbons attached to an acid group. When conversion is calculated from the ^{13}C NMR spectrum, the peak correlating to the quarternary carbon close to the acid group is very small and difficult to integrate at higher conversion. This might introduce an error in the measurement, and the ^{13}C NMR spectra therefore have to be of very good quality. To compare the two methods, both acid number titrations and calculations from ^{13}C NMR spectra were performed for the bis-MPA system.

The results were plotted against time (Figure 3). Both methods give approximately the same result. At 140 °C, no esterification occurred in the trimer system. This is in correspondence with earlier results.[15] Therefore, the trimer was polymerized at 160 °C. The trimer system, though polymerized at a higher temperature, was much slower than the bis-MPA system and had only reached a conversion of less than 50% at the time where the bis-MPA polymerization reached completion. The acid group in the trimer, **2**, was less accessible for reaction than the acid group in bis-MPA, **1** (Figure 1). The trimer reaction mixture also contained fewer reactive groups per weight. The dilution of reactive groups and the poorer accessibility of the acid group are probably the main reasons for the slower reaction of the trimer system. Because of the small scale of the trimer polymerizations, only very small samples could be taken out each time from the reaction mixture, and acid number titration was not possible. Therefore, the conversion has

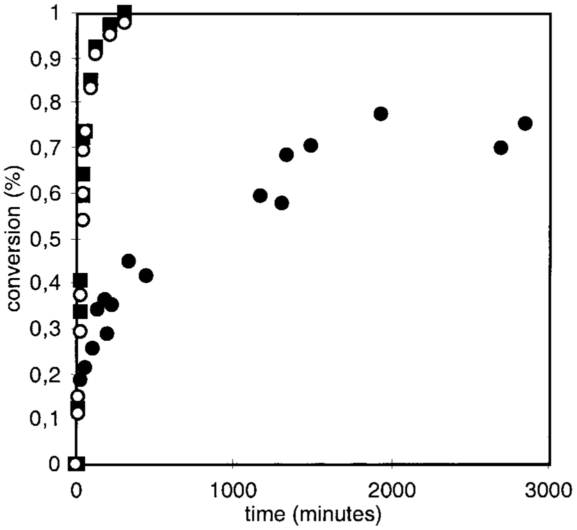

Figure 3. Conversion of acid groups plotted as a function of reaction time. The upper curve (■) represents the conversion in AB_2 polymerization calculated from ^{13}C NMR spectra while the middle curve (○) represents the conversion in AB_2 polymerization calculated from acid number titration. The lower curve (●) represents the conversion in AB_4 polymerization calculated from ^{13}C NMR spectra.

been calculated from the ^{13}C NMR spectra only. In trimer polymerization, the peaks from the linear and dendritic repeating units formed were very small and broad during the first hours of reaction. The broad base of the peaks made integration very sensitive to noise. This is probably the main reason for the scattering of the plotted results of the trimer polymerization (Figure 3). Because of the much smaller scale of the trimer experiments (80 times more monomer by weight was used in the bis-MPA case), stirring of the reaction mixture became more difficult. A stirring bar had to be used instead of an overhead stirrer, leading to less efficient stirring. The results presented in Figure 3 clearly show the difference in reaction rate between the polycondensation of bis-MPA (**1**) and its dendritic trimer **2** (Figure 1). Because of the scattering of data, the results from trimer polymerization should be regarded as a trend only. Molecular weights of the hyperbranched polymers have been calculated from ^{13}C NMR spectra and from conversion as proposed by Frey et al.[6] As expected, the molecular weight increases faster with conversion when the trimer is polymerized than if bis-MPA is polymerized. Furthermore, the molecular weights calculated from conversion agree well with those calculated from ^{13}C NMR spectra in bis-MPA polymerizations (Figure 4).

Polymerization of Bis-MPA. Polymerization was performed at 140 °C, where the monomer is crystalline (melting point 189−191 °C). When the reaction started, the monomer was slowly dissolved in the polymer melt. First a thick dispersion of the solid monomer in the polymer melt was formed. When all bis-MPA was dissolved, a clear liquid was formed. As the reaction proceeded, the viscosity of the reaction mixture increased.

^{13}C NMR analyses of samples from the reaction mixture clearly showed the change in composition with conversion (Figure 5). Before any reaction has taken place, one peak corresponding to the quarternary carbon in bis-MPA was visible at δ 49.45. As the reaction proceeds, terminal, linear, and dendritic repeating units were formed. The signals of their quarternary carbons appeared at δ 50.20, δ 48.20, and δ 46.20, respectively. When the quarternary carbon is attached to an acid group, it resonates at a slightly lower chemical shift due to the more electron-withdrawing character of the acid group compared to that of the ester group. We have chosen to call these acid functional repeating units “dendritic acid repeating units” and “linear acid repeating units” referring to the kind of repeating unit that will form once their acid groups are reacted. Because of the solid monomer which continuously dissolved in the polymer formed, free monomer was present in the reaction mixture for a long time. It was found that free monomer was present in the mixture even at a conversion higher than 80% (Figure 6). The dissolved monomer acted as a plasticizer in the polymer melt and decreased its viscosity. To study the structure buildup in the hyperbranched structure during polymerization, the relative distribution of terminal, linear, and dendritic repeating units was examined. The composition obtained from ^{13}C NMR spectra and the composition calculated from the equations derived by Frey et al.[7]

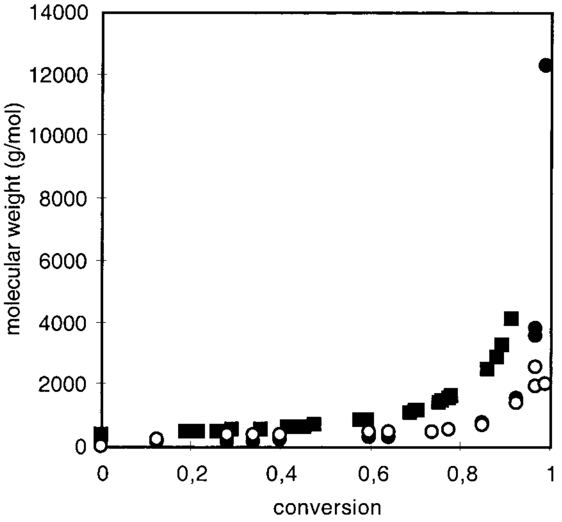

Figure 4. Molecular weights during structure buildup as a function of conversion of acid groups. The molecular weights of AB_4 (■) and AB_2 (●) polymers are calculated from ^{13}C NMR spectra and, in the AB_2 case, predicted by the model presented by Frey et al.[6] (○).

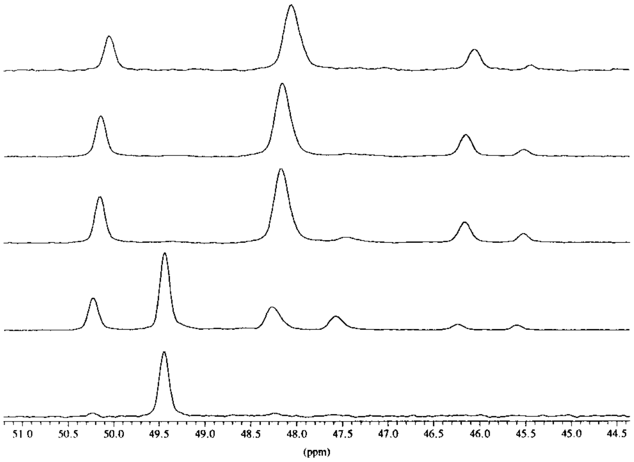

Figure 5. ^{13}C NMR spectra of samples from the reaction mixture at different conversions in polymerization of bis-MPA. Magnification of the quarternary carbon region of the spectrum.

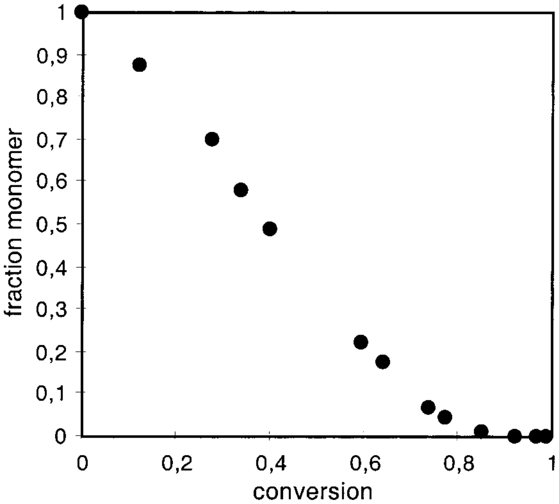

Figure 6. Fraction of monomer in the reaction mixture as a function of conversion of acid groups.

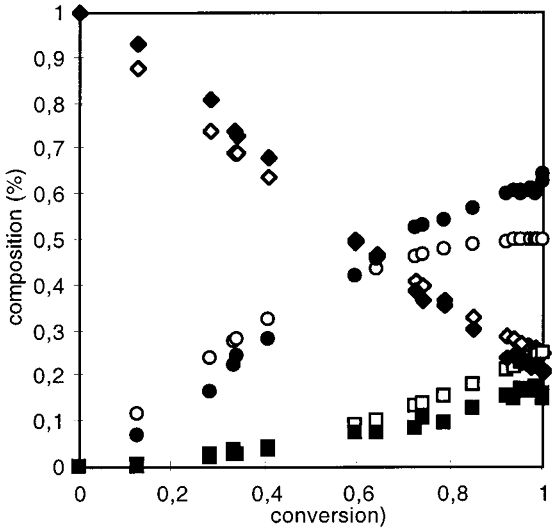

Figure 7. Composition of the hyperbranched structure as a function of conversion. Fractions of terminal (◆), linear (●), and dendritic (■) repeat units are calculated from ^{13}C NMR spectra in AB_2 polymerization. Experimental data (filled) are compared to data from equations presented by Frey et al.[7] (unfilled).

were plotted as functions of conversion (Figure 7). The experimental data fit well to the ones calculated from the model, especially at low to moderate conversions. At 70% conversion, the fraction of linear units became larger than predicted while the fraction of dendritic units was smaller than predicted from the model. The effect increased with increasing conversion. At 70−80% conversion, the concentration of free monomer was very low (Figure 6), and its plasticizing effect could be expected to be negligible. The viscosity of the mixture increased, and subsequently, the diffusion of the molecules was slowed. At 80% conversion, the species present in the mixture had an average molecular weight of about 800. The number of hydroxyl groups in terminal repeating units was approximately the same as the number of hydroxyl groups in linear repeating units. When the two kinds of hydroxyl groups are compared (Figure 2), it seems likely that the hydroxyl groups of terminal repeating units are more accessible for reaction than those of linear repeating units. While the terminal repeating unit is attached to a hyperbranched substituent at its acid group only, the linear repeating unit is attached to hyperbranched substituents at both its acid group and one hydroxyl group. The reaction of an acid group with a terminal hydroxyl group to form a linear repeating unit is therefore slightly favored compared to the statistical case. At conversions of 96−98%, the experimental data deviated from the simulated values more and more. The fraction of linear units increased rapidly while the fraction of dendritic units decreased. At this conversion, the viscosity of the reaction mixture is very high. The average molecular weight, calculated from ^{13}C NMR spectra, of the species was 6000−7000 g/mol. The formation of linear repeating units was strongly favored under these conditions compared to the formation of dendritic units. The maximum degree of branching, occurring at 96−98% conversion, as defined by Fréchet et al.[5] and Frey et al.[6] respectively was 40% and 37%. The DB of the final product was 35% according to the definition introduced by Fréchet et al.[5] and 32% according to the definition suggested by Frey et al.[6]

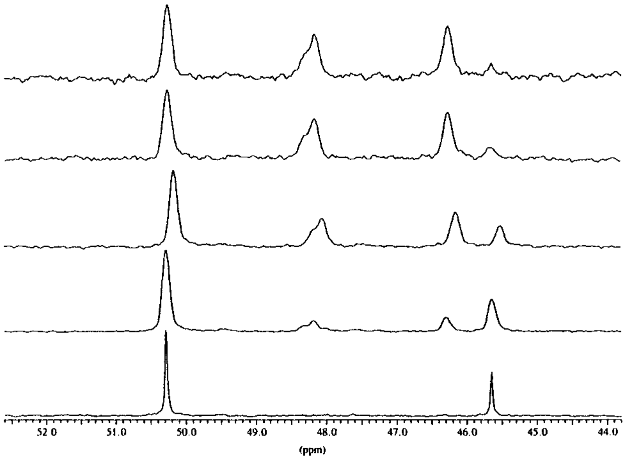

Figure 8. ^{13}C NMR spectra of samples from the reaction mixture at different conversions in polymerization of dendritic bis-MPA trimer. Magnification of the quarternary carbon region of the spectrum.

Polymerization of the Dendritic Bis-MPA Trimer. The polymerization of the trimer was performed at 160 °C where the monomer immediately formed a homogenouos, clear melt of low viscosity (melting point 112 °C). The sulfuric acid catalyst was added in water solution in order to make the concentration of catalyst as accurate as possible. As in the case of AB_2 polymerization, samples were taken out during the reaction for analysis by ^{13}C NMR (Figure 8). The composition in each sample was determined by ^{13}C NMR and plotted as a function of composition (Figure 9). Previous experiments have shown that the dendritic bis-MPA trimer did not start to polymerize at 140 °C even after 12 h.[15] Still after $1^1/_2$ h, only very small traces of linear repeating units and dendritic units incorporated in the structure could be detected by ^{13}C NMR. Because of the small size of the peaks, both conversion and composition were difficult to determine accurately (Figures 3 and 9). Once started, the reaction was very slow compared to the polymerization of bis-MPA. After nearly 95 h reaction, a conversion of only 95% was reached. As the viscosity of the trimer reaction mixture was observed to be lower than that of the bis-MPA reaction mixture during the first hours of reaction, the increase of viscosity was not a cause of the slow reaction during early stages of reaction. As the same amount of catalyst per weight was

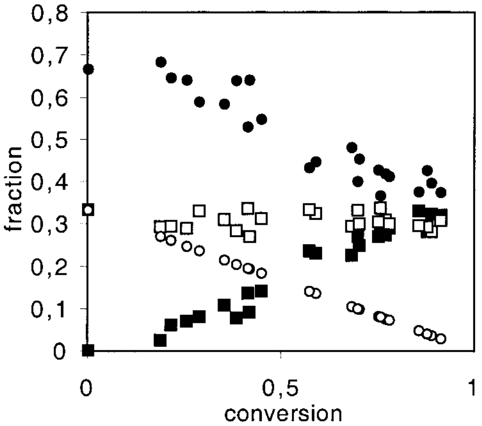

Figure 9. Composition as a function of conversion in polymerization of bis-MPA trimer. Fractions of terminal (●), linear (■), dendritic (□), and dendritic acid (○) repeat units are calculated from the ^{13}C NMR spectra of samples from the reaction mixture at different conversions.

added to the trimer system (0.2%), the molar fraction of catalyst added was 4 times larger in the trimer system than in the bis-MPA system. It has earlier been suggested[13] that the sulfuric acid catalyst might evaporate from the reaction mixture under reduced pressure and that the reaction therefore might slow down due to lack of catalyst. To check whether this was the case in the polyesterification of bis-MPA trimer at 160 °C, the 1 mg H_2SO_4 was divided into four equal portions and added continuously during reaction in a separate experiment. Small amounts of bis-MPA were formed and sublimed on the walls of the vessel in this experiment. From ^{13}C NMR spectra it was observed that some linear units attached to acid groups had been formed. As all linear segments formed during polymerization would appear inside the structure and therefore could not be attached to acid groups, this proved that side reactions did occur when H_2SO_4 was continuously added. The fraction of dendritic units in the mixture decreased during the course of reaction from 33% in the monomer to 30% in the product. The fraction of linear units in the product was 35%. The degree of branching was then 76% according to the definition by Fréchet et al.[5] and 70% according to the definition by Frey et al.[6]

Heat Treatment of Hyperbranched Polymer with and without a Core Molecule. In order to examine whether the hyperbranched polyester was in its equilibrium composition or whether the fractions of dendritic, linear, and terminal units would change if the material was left at its polymerization temperature for a long time, two hyperbranched materials were kept at 140 °C for several days. At this temperature, the polymer is a clear melt of high viscosity. One of the samples, **4** (Figure 1), contained a core molecule while the other sample was synthesized in our lab and did not contain a core molecule. Both samples contained a small fraction of acid functional material corresponding to an acid number of about 10. Samples for ^{13}C NMR analysis were taken out from the melt during the heat treatment and dissolved in DMSO-d_6. In both cases, all acid groups present in the sample before the heat treatment were consumed according to ^{13}C NMR spectra.

On heat treatment, the samples behaved differently depending on whether a core molecule was present or not. The sample without the core molecule tended to gel a few hours after being heated. The polymer melt then became rubberlike and insoluble. Theoretically the whole sample consisted of one single, insoluble molecule when all acid groups were consumed. The sample containing a core molecule, on the other hand, did not show any tendency to gel even after 4 days at 140 °C. The fraction of different repeating units in both samples changed very little during the heat treatment.

Slow Addition of Bis-MPA to a Core Molecule. The first portion of bis-MPA was mixed with an excess of the core molecule, trimethylolpropane (TMP), **3** (Figure 1). The vessel was immersed in a preheated oil bath and left for 2 min before the second monomer addition. The mixture was then left to react for 2 min between each addition, which was enough for the added amount of bis-MPA to dissolve completely in the polymer melt before the next addition. As more monomer was continuously added to the melt, viscosity was kept low during the whole reaction. ^{13}C NMR analysis indicated that slow monomer addition increased the degree of branching. In our experiment, a degree of branching[6] of 47% was obtained in the product, compared to 42% using standard methods. This result agrees well with the results predicted by computer simulation.[9,10] Compared to the focal-point acid groups, the acid groups of bis-MPA were a lot more assessable for reaction. Because of their small size, the bis-MPA molecules can readily react with hydroxyl groups of linear repeating units to form dendritic units. A focal point acid group and a hydroxyl group from a linear repeating unit, on the other hand, are hindered to approach each other from the bulkiness of the hyperbranched structure and therefore unlikely to react with each other. Instead, the focal point acid groups tend to react with one of the less hindered hydroxyl groups of terminal repeating units to form linear units.

Conclusions

In acid-catalyzed polymerization of bis-MPA (**1**) in bulk at 140 °C without a core molecule the proportion of dendritic units in the polymer increased to a maximum value of 17% at 95−97% conversion of acid groups. At higher conversion, the proportion of dendritic units decreased again, and the proportion of linear units increased, probably due to hindered accessibility of the reacting groups. The degree of branching in the final product according to the definition by Fréchet et al.[5] was 35% and 32% according to the definition by Frey et al.[6] Up to 70% conversion, the experimental results followed computer simulated models[8−10] of the bis-MPA polymerization well. Thereafter, the fraction of linear repeating units increased above the predicted value, and the fraction of dendritic units decreased. At very high conversions, 96−98%, the fraction of linear repeating units increased steeply. The main reason for the deviation from the calculated results was probably differences in accessibility for reaction between terminal and linear hydroxyl groups favoring the formation of linear repeating units.

The polymerization of the dendritic bis-MPA trimer (**2**) at 160 °C was considerably slower than that of bis-MPA. During polymerization the fraction of linear repeating units increased while the fraction of dendritic repeating units decreased. The main reasons for the slow reaction of the trimer system were probably the dilution of functional groups and the lower accessibility of the acid groups compared to that of the bis-MPA system. As the viscosity was lower during early stages of the trimer polymerization than in the bis-MPA polymerization, it is probably of little importance for the difference in reaction rate between the two systems.

If the hyperbranched polymer was kept at its polymerization temperature for a long time, the composition changed slightly. If no core molecule was present, the material gelled after a few hours heat treatment. If a core molecule was used, no gelling was observed even after 4 days at the polymerization temperature. By slow addition of monomer in small portions to a reaction mixture containing a core molecule, the degree of branching in the product was increased to 47% according to the definition by Fréchet et al.[5] and 44% according to the definition by Frey et al.[6]

Experimental Section

General Directions. ^{13}C NMR spectra of all bis-MPA polyesters and the low conversion samples from trimer polymerizations were recorded on a Bruker 400 MHz spectrometer. ^{13}C NMR spectra of most trimer polyesters as well as samples from the heat treatment experiments were recorded on a Varian 600 MHz spectrometer. Size exclusion chromatography (SEC) was performed on a Waters GPC system using a solvent delivery system (model 510), automatic injector (WISP 712), and a differential refractometer (Waters 410) as detector. All measurements were made at 25 °C with a 10 μm mixed B column from Polymer Labs. THF was used as solvent at a flow rate of 1.0 mL/min. Linear polystyrenes were used for calibration.

Materials. 2,2-Bis(methylol)propionic acid (bis-MPA) and hydroxy-functional hyperbranched polyester (Boltorn H40, commercial hyperbranched polyester from bis-MPA with ethoxylated Pentaerythritol (average 5 EO/molecule) as core molecule, fourth generation) were kindly supplied by Perstorp Polyols AB and used as received. KOH, 0.1 M solution in ethanol, was purchased from Merck and standardized against potassium hydrogen phthalate. Sulfuric acid, 98%, was purchased from J. T. Baker and used as received. Hexamethyldisilazane, 98%, was purchased from Acros and used as received.

Analysis of Acid End Groups by Acid Number Titration. Samples of approximately 0.2 g each, taken out from the reaction mixture at different times during reaction, were dissolved in 50 mL of a 50:50 mixture of acetone:ethanol. The samples were titrated with 0.10 M KOH using thymol blue as indicator. The volume of KOH solution corresponding to the titration of the pure solvent was subtracted and the acid number calculated.

^{13}C NMR Analysis of Degree of Branching. For analyzing the degree of branching in hyperbranched polyesters, ^{13}C NMR is used. To obtain quantitative spectra, D1 was set to 12 s for the quaternary carbons to relax completely. All measurements were performed using DMSO-d_6 as solvent.

Polycondensation of Bis-MPA (1). Bis-MPA (40 g, 0.3 mol) and H_2SO_4 (0.08 g, 0.82 mmol) were added to a four-necked reaction vessel. The vessel was immersed in a preheated oil bath at 140 °C, and the mixture was stirred using a mechanical stirrer at approximately 70 rpm. A stream of argon was applied in order to continuously remove the water formed. The argon flow was set to approximately 1 bubble per second. During the course of reaction, samples were taken out from the mixture for analysis by ^{13}C NMR and acid number titration.

Polycondensation of Dendritic Bis-MPA Trimer (2). Monomer **2** (0.50 g, mol) and H_2SO_4 (1 mg, 0.05 mL from a 0.02 g/mL solution of H_2SO_4 in water, 0.010 mmol) were added to a round-bottomed flask. A stirring bar was added, and the vessel was immersed in a preheated oil bath at 160 °C. A stream of argon, 1 bubble per second, was applied in order to remove water from the mixture. During the reaction, samples were taken out from the vessel for analysis by ^{13}C NMR.

Heat Treatment of Hyperbranched Polymer without a Core. Hyperbranched polymer (4.1 g) without a core molecule of an acid number about 10 was crushed to a fine powder and kept at 140 °C in a round-bottomed flask. Samples were taken out from the melt at different times during the heat treatment and dissolved in DMSO-d_6 for ^{13}C NMR analysis. After 3 h the material became rubberlike and insoluble. The heat treatment was then stopped.

Heat Treatment of Hyperbranched Polymer Containing a Core. Hyperbranched polymer of the fourth generation containing a core molecule (4.0 g) was crushed and kept at 140 °C. The acid number of the polymer was determined using standard methods and found to be approximately 10. Samples were taken out at different times during the heat treatment and dissolved in DMSO-d_6 for ^{13}C NMR analysis. After 4 days the vessel was removed from the heat.

Polycondensation of Bis-MPA Using a Trifunctional Core Molecule and Slow Addition of Monomer. Trimethylolpropane (TMP), **3** (1 g, 7.46 mmol), bis-MPA (0.3 g, 0.22 mmol), and H_2SO_4 (2.6 mg, 0.027 mmol) were added to a four-necked reactor. The vessel was immersed in a preheated oil bath at 140 °C. Bis-MPA (45.0 g, 335.7 mmol) corresponding to a fourth-generation dendrimer was added in portions of 0.1 g each for 7 h. After the addition of the monomer corresponding to a full generation, H_2SO_4 catalyst for the next generation was added. Two samples were taken out for NMR analysis, one 45 min after the last addition of monomer and another 2 h later.

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