Kinetics of Formation of Hyperbranched Polyesters Based on 2,2-Bis(methylol)propionic Acid

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ABSTRACT: The aim of this study was to gain information on the influence of the core moiety on the kinetics of the synthesis of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid (bis-MPA). Bis-MPA was esterified in the melt using sulfuric acid as a catalyst, yielding a highly polydisperse polyester. Bis-MPA was also esterified with different polyols as core moieties. The parameters varied were polyol structure, reaction temperature, and amount of added catalyst. A stoichiometry of 1:1 for carboxylic- and hydroxyl groups on the polyol was used. The reaction rates were found to be strongly dependent of the miscibility of bis-MPA and the polyol. Higher concentrations of catalyst lead to higher rates of reaction. Tris(methylol)propane (TMP) and bis-MPA exhibited the highest rate of reaction, which is due to the low melting point of TMP and good solubility of bis-MPA in the TMP melt.

Introduction

Dendrimers and hyperbranched polymers have attracted increasing interest during recent years as interest in molecular architecture has increased. The field of dendrimers was pioneered by Tomalia *et al.*[1] and Newkome *et al.*,[2] and extensive reviews have been published.[3a–c] Flory first introduced the concept of hyperbranched polymers[4] but treated the subject strictly in a theoretical sense. It was Kim and Webster[5] and Fréchet *et al.*[6] who published the first papers concerning the one-pot synthesis of hyperbranched polymers.

Dendrimers consist of AB_x monomers attached in layers to a central core. Hyperbranched polymers resemble dendrimers with the difference that the degree of branching[6] for a dendrimer is equal to one while it is always lower than one for a hyperbranched polymer. Both dendrimers and hyperbranched polymers are highly branched structures with similar properties.[7] One of their most applicable properties is that they exhibit lower melt viscosity than the corresponding linear counterparts of the same molar mass. Fréchet *et al.*[8] recently published a paper where the properties of dendrimers and hyperbranched and linear polymers based on the same repeating unit were compared.

Dendrimers are often tedious and expensive to synthesize while hyperbranched polymers are easier and cheaper to produce on a large scale. Subsequently, hyperbranched polymers are more interesting for material-consuming applications such as coatings and adhesives.

Almost all hyperbranched polymers reported in the literature are synthesized from stepwise reaction of AB_2 monomers in the absence of a central core. Kim and Webster[5] used Suzuki conditions on (3,5-dibromophenyl)boronic acid. Fréchet *et al.*[6] used 3,5-bis(trimethylsiloxy)benzoyl chloride and Turner *et al.*[9] the latter monomer and 3,5-diacetoxybenzoic acid. Kricheldorf *et al.* used silylated 5-acetoxyisophthalic acid[10] and more recently trimethylsilyl 3,5-diacetoxybenzoate.[11] The idea of making a hyperbranched polyester by copolymerizing an AB_2 monomer with an A_y functional core has been presented by our group[12] and more recently also by Feast and Stainton.[13]

Polyesterifications, both catalyzed and uncatalyzed, have been extensively studied over the years and an extensive review has been published by Fradet and Maréchal.[14] Flory proposed one of the first mechanisms[15] for polyesterification reactions. He stated that the reactivity of a functional group is independent of molecular size and that the reaction rate is independent of the viscosity of the reaction mixture.[16] Since then, several mechanisms and kinetic models have been proposed by different authors, especially for uncatalyzed reactions.[14]

Polyesterification reactions are very complex since the reaction mixture undergoes a dramatic change in polarity (dielectric constant) and viscosity when the reaction proceeds to higher conversion. Due to this, the same experimental data can be interpreted in different ways depending on what assumptions are made. For acid-catalyzed reactions, most authors report a second overall order (first with respect to both carboxylic acid and hydroxyl groups) and first order in catalyst. This was found by Fradet and Maréchal,[17] for instance, when they studied the acid-catalyzed reaction of 1-octadecanol and octadecanoic acid. Tang and Yao[18] studied the acid-catalyzed equimolar reaction between a dibasic acid and glycol and found the same rate equations.

The rate equations become more complicated when the ratio of carboxylic acid to hydroxyl groups is nonstoichimetric. Lin *et al.*[19–21] examined esterification reactions with a large excess of diol. They found the reaction to be second order with respect to carboxylic acid and zero order with respect to alcohol.

In a previous paper,[12a] we reported on the pseudo-one-step synthesis of hyperbranched aliphatic polyesters based on 2,2-bis(methylol)propionic acid (bis-MPA) and tris(methylol)propane (TMP) as a central core. These hyperbranched polyesters were found to have a high degree of branching,[6] ~0.8. This is higher than most of the systems reported in the literature (0.5–0.6), and we suggested that this was due to the kinetics of the system. The present work concerns the acid-catalyzed polyesterification reactions between bis-MPA and various polyols. It is the first attempt to investigate the influence of the core moiety on the formation of the hyperbranched skeleton. Pure bis-MPA was polyesterified in the absence of a core moiety as well as copolymerized with different polyols. All monomers are shown

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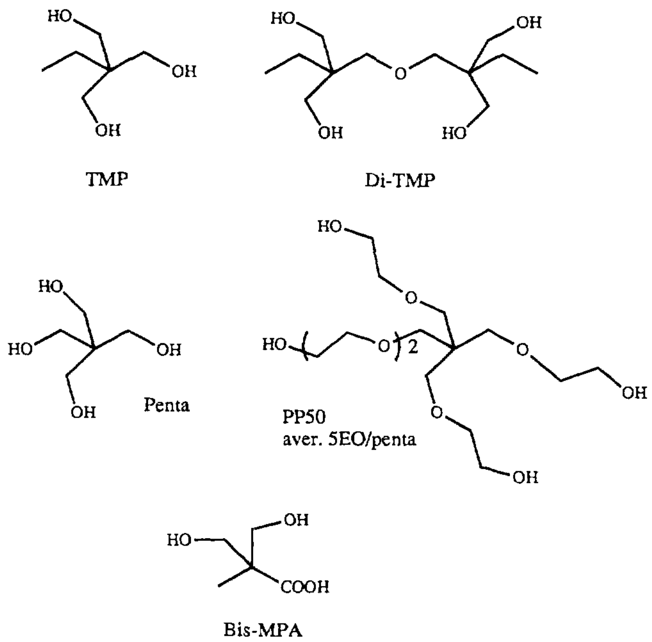

Figure 1. Bis-MPA and the polyols used in the experiments.

in Figure 1. As the influence of the core in a hyperbranched polymer is strongest at low molar masses, only "one-generation" stoichiometry of 1:1 for carboxylic groups and hydroxyl groups on the core was studied.

Experimental Section

Materials. 2,2-Bis(methylol)propionic acid (99%, bis-MPA), tris(methylol)propane (TMP), di(trimethylolpropane) (Di-TMP), pentaerytritol (Penta), and ethoxylated pentaerytritol (PP50, average 5EO/Penta), Figure 1, were all kindly supplied by Perstorp Polyols AB, Sweden, and used as received. Sulfuric acid (98%) was purchased from Aldrich and used as received; 0.1 M potassium hydroxide in ethanol was purchased from Merck and standardized against potassium hydrogen phthalate in accordance with standard procedures.

Reaction Apparatus. A four-necked glass reaction vessel (~200 mL) and a mechanical stirrer were used. The vessel was equipped with a stirring rod, an argon inlet, a drying tube, and a stopper. An argon flow was used to remove the water formed during the early stages of the reaction. At higher conversion reduced pressure (~50 mmHg) was applied to the vessel. The oil bath temperature was fixed at $t_{\mathrm{react}} \pm 2$ °C; temperature control was achieved with a contact thermometer and a thermostat.

General Reaction Procedure. In order to imitate an industrial batch process as much as possible, single-run[12] kinetic experiments were chosen. The reactants were weighed to 0.1% except for the sulfuric acid, which was weighed to 1% due to the small quantitites used. The vessel was placed in a preheated oil bath. A stoichiometry of 1:1 for carboxylic groups to hydroxyl groups on the core was used in all experiments where a core moiety was used. Data for all experiments are listed in Tables 1 and 2. The reaction mixture was stirred under a stream of argon for at least 1 h at atmospheric pressure followed by a further reaction time under reduced pressure. Aliquots were withdrawn at intervals throughout the reaction. The conversions reached were typically 90–95%.

Characterization Techniques. Determination of Acid Number by Titration. Samples of 0.1–0.2 g of polyol were taken from the reaction vessel at specific reaction times. The samples were dissolved in 50 mL of acetone/ethanol (1:1 by volume) and titrated with 0.100 M potassium hydroxide in ethanol using thymol blue as an indicator. Blank tests were performed on the pure solvent mixture. The standard deviation in acid number and conversion, p, is typically on the order of 1%. Higher standard deviations is encountered at high conversion due to the smaller volume of KOH solution consumed during the titration.

Table 1. Experiments Where Bis-MPA Was Esterified in the Absence of a Polyol Core

exp no.	reaction temp (°C)	catalyst[a] (wt %)	rate const[a] (slope[COOH]$_0$])
1	140	0.1	0.041
2	140	0.5	0.294
3	150	0.1	0.051
4	160	0.1	0.086
5	170	0.1	0.091

[a] All rate constants are calculated from the slopes of $1/(1-p)$ *versus* reaction time and obtained by curve fit (correlation coefficient $r_c \geq 0.98$) in the conversion range 50–90%.

Table 2. Experiments Where Bis-MPA Was Mixed with Different Polyol Cores

exp no.	polyol	reaction temp (°C)	catalyst[a] (wt %)	rate const
6	TMP[a]	140	0.1	0.013
7	TMP[a]	140	0.3	0.035
8	TMP[a]	140	0.5	0.055
9	TMP[a]	150	0.1	0.016
10	Di-TMP[b]	140	0.1	0.047
11	Di-TMP[b]	140	0.5	1.2
12	Di-TMP[b]	150	0.1	0.075
13	Penta[b]	140	0.1	0.025
14	Penta[b]	140	0.5	0.055
15	Penta[b]	150	0.1	0.023
16	PP50[a]	140	0.1	0.011
17	PP50[a]	140	0.2	0.014
18	PP50[a]	140	0.5	0.044
19	PP50[a]	150	0.1	0.024

[a] All rate constants are calculated from the slopes of $1/(1-p)$ *versus* reaction time and obtained by linear regression (correlation coefficient $r_c \geq 0.99$) in the conversion range 50–90%. [b] All rate constants are calculated from the slopes of $\ln[(r-p)/(1-p)]$ *versus* reaction time and obtained by linear regression ($r_c \geq 0.99$) in the conversion range 50–90%.

Size Exclusion Chromatography (SEC). SEC measurements were performed on some of the polyesters at room temperature using five μ-Styragel columns (500, 10^3, 10^4, 10^5, and 100 Å). A Waters 510 pump was used with a DRI detector (Waters 410). THF was used as eluent; the flow rate was 1 mL min^{-1}. Data recording and calculations were made on a Copam PC-501 Turbo Unit. As no appropriate hyperbranched polymer standards are available for calibration, the results obtained were relative to linear polystyrene standards and are therefore not absolute values. However, SEC measurements can give an idea of the polydispersity of the polymer and the molar masses can be used for comparisons between different samples. A further difficulty with SEC measurements on these strongly polar polymers is that they interact with the column packing to an extent that is difficult to determine. It has even been claimed that the column packing can be ruined by this interaction.[22]

Theory

Branching Theory and Gelation. The polycondensation of $A-B_{f-1}$ monomers, where f is the total functionality of the molecule, has been theoretically treated by Flory[4] and Stockmayer.[23] To simplify the calculations, they assumed that the only reaction allowed is the one between an A group and a B group, no intramolecular condensation reactions occur, and the reactivity of a functional group is independent of molecular size. This is especially valid for these particular hyperbranched polymers as steric hindrance discourages cyclization.

If x monomers are coupled together, the resulting molecule will contain only a single A group and $(fx - 2x + 1)$ B groups. This paper deals with bis-MPA as an AB_2 monomer and therefore the following discussion will concern an $A{-}B_{f-1}$ monomer with $f = 3$. The probability that an arbitrarily chosen B group has reacted is p_b and equals the reacted fraction of B groups. The reacted fraction of A groups, p_a, is $p_b(f - 1)$ due to the structure of the monomer. An expression for the branching coefficient, α, is obtained if p_a is replaced with the conversion, p:

$$\alpha = p/(f - 1) \qquad (1)$$

As the conversion, p, increases toward 1, α goes towards α_c. α_c can be interpreted as the point where infinite structures start to form. As f equals 3 for bis-MPA, α_c is 0.5.

It is possible to derive the number-average degree of polymerization, X_n, as

$$X_n = \frac{1}{1 - p} = \frac{1}{[1 - \alpha(f - 1)]} \qquad (2)$$

and also the weight-average degree of polymerization, X_w, as

$$X_w = \frac{[1 - \alpha^2(f - 1)]}{[1 - \alpha(f - 1)]^2} \qquad (3)$$

The dispersity of the system, X_w/X_n is possible to calculate from eqs 2 and 3:

$$\frac{X_w}{X_n} = \frac{[1 - \alpha^2(f - 1)]}{[1 - \alpha(f - 1)]} \qquad (4)$$

From eq 4 it can be seen that as the conversion is driven toward completion, i.e., $p = 100\%$, the dispersity of the system increases dramatically. Theoretically, polycondensation of AB_2 monomers should form an infinite, totally insoluble network at extremely high conversions, though practically this is seldom observed. The infinite parts can affect the polymer properties in a negative way. At high molar masses, gel particles will be present and make the polymer partly insoluble. Flory predicted the point of gelation[24] and experimentally established that the theoretical value for conversion at gelation was too low. This was due to cyclization of linear polyesters and might not apply to these hyperbranched systems where less cyclization is anticipated.

Kinetics of the Esterification Reaction. In the pioneering theoretical[4] and practical[15,16] work of Flory on esterification reactions it was proposed that the acid-catalyzed reaction follows a second-order rate equation,

$$-\frac{d[COOH]}{dt} = k[COOH][OH][H^+] = K[COOH][OH] \qquad (5)$$

where K is the true rate constant and dependent only on the reaction temperature. The most common mechanism found in textbooks[25] for esterification reactions is outlined in Figure 2. Equation 5 can be regarded as the appropriate rate equation for the proposed mechanism. As the aim of these studies was to gain information on how the polyol core affects the formation of the hyperbranched skeleton, a 1:1 stoichiometry between the number of moles of monomer, hence carboxylic acid, and the number of molar equivalents of hydroxy groups on the core was used ($[COOH]_0 = [OH]_{0,core}$). The remaining amount of carboxylic acid after a reaction time t, $[COOH]_t$, was determined by acid-number titrations and the consumed amount of carboxylic acid, $[COOH]_r$, calculated as

$$[COOH]_r = [COOH]_0 - [COOH]_t \qquad (6)$$

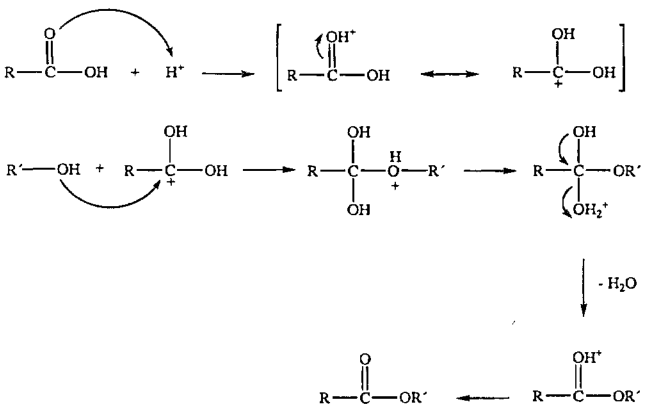

Figure 2. Common acid-catalyzed esterification process.

Subsequently, it is possible to express the total amount of hydroxyl groups, $[OH]_t$, as a function of the amount of carboxylic acid groups at all reaction times t, $[COOH]_t$,

$$[OH]_t = 2[COOH]_0 + [OH]_{core,0} - [COOH]_r \qquad (7)$$

where $2[COOH]_0$ is the hydroxyl concentration at $t = 0$ originating from bis-MPA and $[OH]_{core,0}$ is the contribution from the core at $t = 0$. Combining eqs 6 and 7 results in

$$[OH]_t = [COOH]_0 + [COOH]_t + [OH]_{core,0} \qquad (8)$$

Substitution of eq 8 into eq 5 yields

$$-\frac{d[COOH]}{dt} = [COOH]_t([COOH]_0 + [COOH]_t + [OH]_{core,0})[H^+]k \qquad (9)$$

Integration of eq 9 and introduction of $r = ([OH]_0 + [OH]_{core})/[COOH]_0$ gives the following equation where $a = (r - 1)[COOH]_0$. Subsequently, a is dependent on the stoichiometry of hydroxyl and carboxylic acid groups and will be different for polyols with different numbers of hydroxyl groups.

$$\ln\frac{r - p}{1 - p} = ak't - \ln\frac{1}{r} \qquad (10)$$

k' is used to distinguish this rate constant from the rate constant in eq 9. If this rate equation is valid, a plot of $\ln[(r - p)/(1 - p)]$ *versus* reaction time would give a straight line with a slope corresponding to ak' and an intercept equal to $-\ln(1/r)$.

Lin and *et al.*[19-21] found that Flory's equations were not appropriate for nonstoichiometric systems and subsequently proposed another rate expression:

$$-\frac{d[COOH]}{dt} = k''[COOH]^2 \qquad (11)$$

This rate equation was proposed on the basis that the reaction is catalyzed by protons emanating from the externally added acid. Integration, using the same notations as above yields

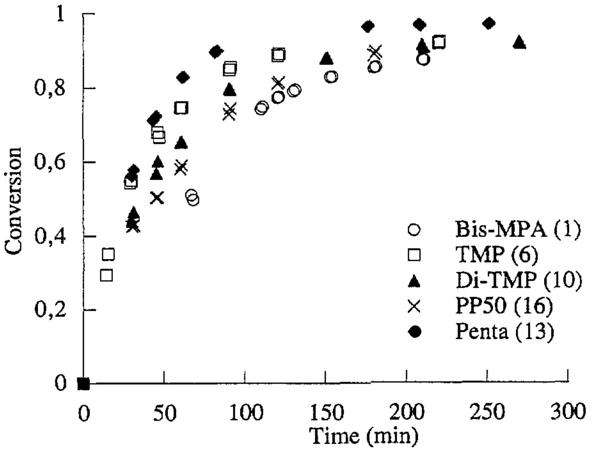

Figure 3. Conversion of carboxylic acid groups as a function of reaction time for a selection of experiments (t = 140 °C, [H$^+$] = 0.1 wt % sulfuric acid). The experiment numbers are given in parentheses.

$$\frac{1}{1-p} - 1 = [\mathrm{COOH}]_0 k''t \qquad (12)$$

where $1/(1 - p)$ *versus* reaction time should give a straight line if this *is* the equation corresponding to the reaction mechanism.

Results and Discussion

Experimental Aspects. Polyesterifications are equilibrium reactions. To obtain high molar mass, i.e., high conversion, it is necessary to remove the water that is formed during the reaction. This was done with argon as carrier gas at low conversions and by reduced pressure at higher conversions. Conversion of carboxylic acid groups as a function of reaction time for a selection of reactions (140 °C, 0.1 wt % sulfuric acid) is shown in Figure 3. At high conversion (>90%), an equilibrium level is reached. Most likely, it is a steady state where the diffusion of water becomes so retarded that the forward reaction proceeds at the same rate as the reverse reaction. The water removal is hindered by the increasing viscosity as the reaction proceeds to higher conversions.

Several experiments were performed where argon flow and time under reduced pressure were varied, in order to verify that water removal was not the rate-determining step until this equilibrium level was reached. As single-run experiments, with successive withdrawals of sample, were chosen it was of no use to correct the obtained results for the decrease in volume due to loss of water, as otherwise recommended by Fradet and Maréchal[26] for nonstoichiometric reactions. This study is mainly a comparison between different reaction systems, and as the stoichiometry was kept the same for all experiments, the error connected to the decrease in volume will be approximately the same for all cases.

The reaction temperature was maintained in the range 140−170 °C, in order to suppress unwanted side reactions, such as etherifications, transesterifications, and the formation of cyclic ethers by dehydration of bis-MPA. As the reactants were not preheated it took ~15 min before temperature control was regained in the oil bath. This will be further discussed below.

A general outline for an esterification reaction is given in Figure 3. If a higher load of catalyst (sulfuric acid) is used the reaction rate is increased, (Tables 1 and 2). However, larger amounts of remaining acid will increase the susceptibility of the final polymer to hydrolysis.

As the studied systems were all acid-catalyzed there was no need to take the dissociation of carboxylic acid and hydroxyl groups[27] into account. The amount of protonated species was taken to be equal to the amount of added catalyst.. Sulfuric acid was used as catalyst as its use is widespread for industrial polyesterifications. The catalytic effect of the sulfuric acid may not be constant throughout the reaction, possibly due to formation of sulfonic esters. The decline in reaction rate may also have been due to loss of sulfuric acid as the vessel was evacuated during the later stages of the reaction. The reaction rate could also have been slowed by entrapment of unreacted carboxylic acid groups by hydrogen bonding, either inter- or intramolecularly alternatively. The carboxylic acid groups could become shielded from the surrounding media by the rest of the molecule. This would make the acid less susceptible to further reactions and could be one of the contributing factors explaining why the conversion never reaches 100%.

One major difficulty when esterification reactions are studied in the melt is the polarity change of the reaction medium during the reaction. The polarity will change dramatically going from a melt consisting of carboxylic acid groups and hydroxyl groups to esters (dielectric constant, ε[28], acetic acid 6.15 (t = 20 °C), ethanol 24.30 (t = 25 °C), and ethyl acetate 6.02 (t = 20 °C)). Due to this, it is often difficult to study a whole reaction range where the conversion of acid groups comes close to 100%. However, this effect should be somewhat counteracted in this system as a large number of unreacted hydroxyl groups remain even if the acid groups are consumed to 100%. Another difficulty is that the activities of the reactants are not necessarily proportional to their concentration. The experimental window was narrowed to 50−90% conversion to reduce the effect of the problems discussed above.

Polyesterification of Pure Bis-MPA. Hyperbranched polymers reported in literature[5−7a] are almost exclusively synthesized *via* condensation reactions of AB$_2$ monomers in an one-step manner in the absence of a core moiety. The main interest of this study was focused on the influence of the core moiety, but for comparison, esterifications without a polyol core were also performed. Bis-MPA was condensed at different oil bath temperatures and different amounts of acid catalyst. A selection of experimental results are shown in Figure 4, where conversion of carboxylic acid groups is shown as a function of reaction time.

From considerations of space, the experimental data obtained for all experiments are not listed. Experimental data of a typical polyesterification (no. 4) of bis-MPA are listed in Table 3. The experiment was performed at 160 °C with 0.1% by weight of sulfuric acid added as catalyst.

All polyesterification reactions were performed at lower temperatures (140−170 °C) than the melting point of bis-MPA (180−190 °C) (Table 4). At very low conversions the reaction mixture was a two-phase system. Bis-MPA melted quite slowly, and the reaction could be diffusion-controlled from the very beginning. The effect was higher at lower oil bath temperatures. At very high conversion other difficulties were encountered, mainly due to retained water and a lowered catalytic activity due to loss or deactivation, through complex formation, of the catalyst. The overall reaction

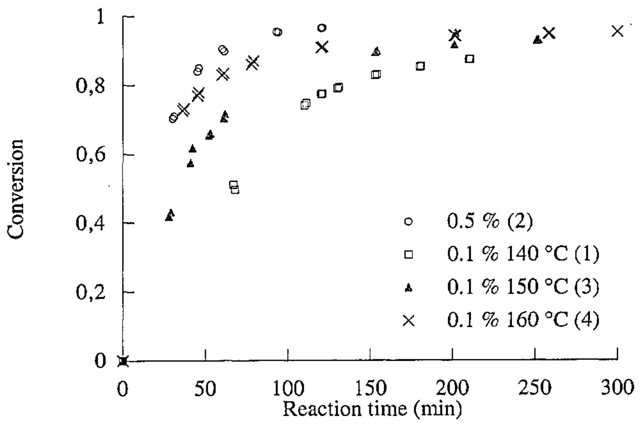

Figure 4. Conversion of carboxylic acid groups, p, as a function of reaction time for bis-MPA at different reaction temperatures and different amounts of sulfuric acid. The experiment numbers are given in parentheses.

Table 3. Experimental Data of a Typical Polyesterification of Bis-MPA (60 °C and 0.1 wt % Sulfuric Acid (Exp 4))[a]

reaction time (min)	acid no.	conversion p	$1/(- p)$	$\ln r - p/1 - p$
0	417	0	1.00	0.69
36	114	0.73	3.66	1.54
37	112	0.73	3.73	1.55
45	96.14	0.77	4.35	1.68
46	92.34	0.78	4.52	1.71
60	70.98	0.83	5.88	1.93
61	68.75	0.84	6.08	1.96
78	58.23	0.86	7.17	2.10
79	54.30	0.87	7.69	2.16
120	38.13	0.91	10.9	2.48
121	37.32	0.91	11.2	2.50
201	23.86	0.94	17.5	2.92
202	24.12	0.94	17.3	2.92
258	21.5	0.95	19.4	3.02
259	20.8	0.95	20.0	3.05
300	19.6	0.95	21.3	3.11
301	19.3	0.95	21.6	3.12

[a] The standard deviation in acid number and conversion, p, is typically in the order of 1% in the conversion range 50–90%.

Table 4. Melting Temperatures for the Monomers Used in the Experiments

core molecule	functionality	mp (°C)
TMP	3	60–62
Di-TMP	4	108–111
Penta	4	255–259
PP50	4	<25
Bis-MPA		180–190

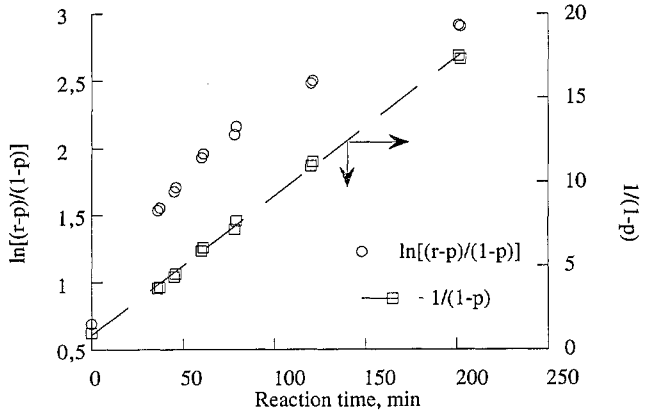

Figure 5. Comparison of kinetic models (eqs 10 and 12) for bis-MPA esterified at 160 °C with 0.1 wt % sulfuric acid (experiment 4). Best fit was obtained with eq 12.

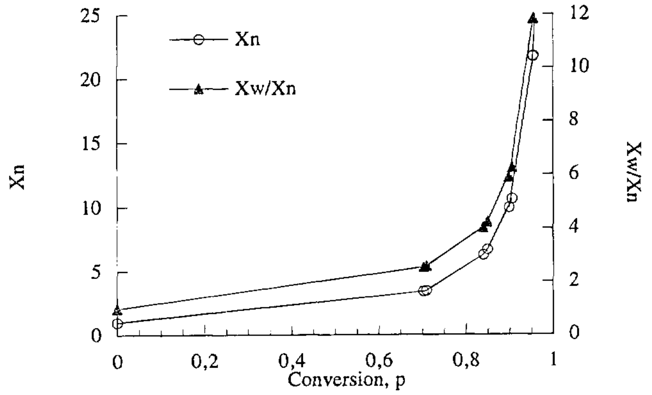

Figure 6. X_n and X_w/X_n as a function of conversion, p, for bis-MPA esterified at 150 °C with 0.1 wt % sulfuric acid (experiment 3).

rate increases with increasing oil bath temperature up to 160 °C (Figure 5, Table 1). The increase was less pronounced for 170 °C, which may be due to loss of sulfuric acid. As expected, the highest reaction rate was observed for the experiment with highest amount of sulfuric acid (0.5% by weight) added as catalyst.

Experimental data were fitted to eqs 10 and 12 (Figure 5). The best fit for experimental data of pure bis-MPA was obtained using eq 12, indicating that the rate equation is second order with respect to carboxylic acid groups. The results are presented in Table 1. The rate constants were calculated from the slopes of the lines of $1/(1 - p)$ *versus* reaction time.

In order to apply the theories proposed by Flory[4] and Stockmayer[23] to the present bis-MPA system, X_n (eq 2) and X_n/X_w (eq 4) were calculated from experimental data obtained from experiment 2. As seen in Figure 6, a highly disperse polymer is obtained. This is also verified by SEC analysis (sample no. 3: $M_w = 1121$, $M_n = 197$, and $M_w/M_n = H = 5.7$). Pure bis-MPA formed an insoluble lump after conversions of approximately 90–92%. Even at conversions lower than the gel point, insoluble particles were present in the reaction mixture.

Polyesterification of Bis-MPA with a Polyol Core. By copolymerizing bis-MPA with a polyol core, the risk of gelation was almost eliminated and the dispersity greatly reduced (SEC analysis sample no. 19: $M_w = 1576$, $M_n = 709$, and $M_w/M_n = H = 2.2$) This also yields a hyperbranched structure built around a central core. In order to mimic a perfect dendrimer as closely as possible, it is essential to chose a core moiety that favors consumption of the functional groups situated on the core. To further study this, bis-MPA was polyesterified with various polyols which are shown in Figure 1. A selection of the results are shown in Figure 4, presented as conversion of carboxylic acid groups as a function of reaction time.

One easy way to treat the results would be to take the initial rate (the initial slope in curves of conversion as a function of reaction time). However, the initial composition is not the true composition, due to melting and mixing differences between the systems. All polyol cores and bis-MPA have different melting temperatures (Table 4). As a consequence of this, two main reaction paths are possible. Bis-MPA can either be soluble in the polyol melt or the polyol core can be soluble in the already formed polyester of bis-MPA. In the former case, the statistics for a carboxylic acid groups to react with a hydroxyl group on the core will increase as the

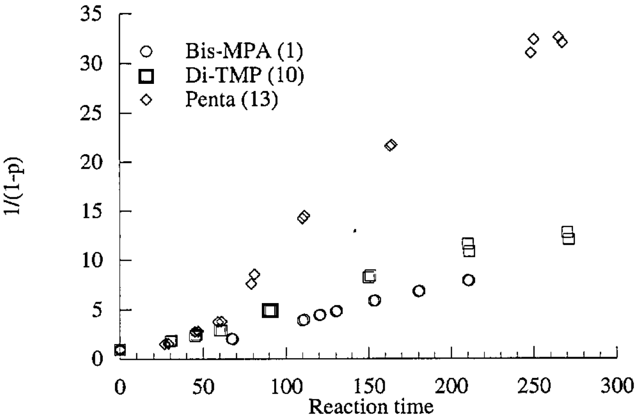

Figure 7. Comparison of different polyols obeying eq 12. The highest rate of reaction is obtained for Penta mixed with bis-MPA. The experiment numbers are given in parentheses.

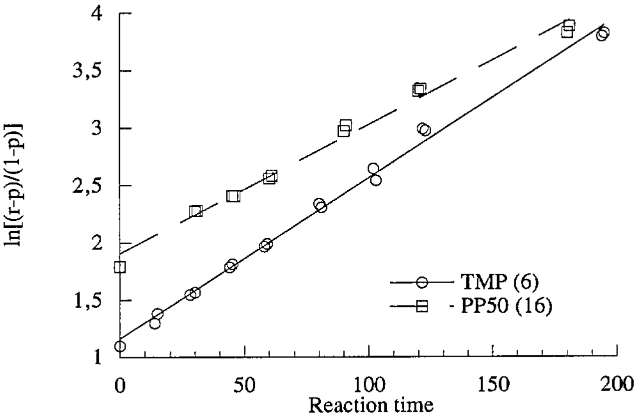

Figure 8. Comparison of different polyols obeying eq 10. The experiment numbers are given in brackets.

availability of hydroxyl groups on the core will be higher than hydroxyl groups on bis-MPA. In the latter case, the statistics will decrease as the availability of hydroxyl groups on the core will be lower than on bis-MPA. Which route that dominates is dependent on the melting and mixing features of each system. It is not apparent whether the catalyst, sulfuric acid, is mixed during the early stage of reaction. However, we assume that the acid is equally distributed all over the reaction mixture.

To simplify the comparison between different experiments, the experimental window was decreased to 50–90% conversion, in the same way as for the condensation of pure bis-MPA. Experimental data were fitted to eqs 10 and 12. Best linearity for Di-TMP and Penta was obtained with eq 12 (Figure 7), as was the case for pure bis-MPA, indicating that the rate equation is second order with respect to carboxylic acid. Somewhat surprisingly, best linearity for PP50 and TMP was obtained with eq 10 (Figure 8). This is indicative of a shift in mechanism when bis-MPA is mixed with TMP or PP50 compared to Penta or Di-TMP.

PP50 is a viscous liquid at room temperature and TMP melts at 60–62 °C. The esterifications were performed at reaction temperatures (140–160 °C) well above the melting point of both PP50 and TMP. Bis-MPA, on the other hand, melts at 180–190 °C and the reaction mixture will be phase-separated as bis-MPA will solubilize in the polyol melt only as the reaction proceeds. The solubilization can be regarded as a very slow continous addition of bis-MPA to the polyol melt. The reaction rate will be higher than if it had been just bis-MPA in the vessel as the accessability of carboxylic groups is increased. The reaction mixture stayed phase-separated longer when PP50 was used instead of TMP. This was probably due to the less polar structure of PP50. It was seen that the time for 90% conversion of all carboxylic acid groups was shorter for TMP than for PP50.

Di-TMP melts at ~110 °C, which is quite close to the reaction temperature. This reaction was found to proceed with the same main features as for pure bis-MPA, even though a linear fit was almost as good using eq 10 as it was using eq 12. This can be interpreted as being the borderline where the core molecule no longer affects the reaction mechanism. Penta melts well above 200 °C. In this reaction, the mixture first contains melted bis-MPA and dissolved Penta. This will give the opposite case where the polyester melt dissolves the core. In this case, the consumption of hydroxyl groups on the core will be reduced due to the reasons mentioned above. Somewhat surprisingly, the rate of reaction seems to increase remarkedly when Penta is used as a polyol core. The same observation has been made in the synthesis of alkyds.[29]

To summarize the results obtained from these experiments, two parameters seem to be important, the melting temperature of the polyol and the miscibility of the polyol and bis-MPA.

It is not straightforward to draw any immediate conclusions from these results when it comes to the formation of hyperbranched polyesters. On one hand, a fast reaction is desirable from an industrial point of view. On the other hand, it is more important that all hydroxyl groups on the core molecule are consumed. This is probably best achieved by a reaction mixture consisting of a polyol and partly soluble bis-MPA. More bis-MPA will solubilize in the melt as the reaction proceeds. This would be favored by choosing the system that remains phase-separated as long as possible while still obtaining an acceptable overall reaction rate.

The findings from these experiments may explain the remarkably high degree of branching obtained for our hyperbranched polyesters reported earlier.[11] The phase-separation phenomenon described herein will be the same between successive additions of more bis-MPA as a pseudo-one-step reaction procedure is utilized when hyperbranched polyesters of higher molar mass are synthesized. The solubilization of bis-MPA in the polyester melt will be quite slow, favoring the reaction with hydroxyl groups on the hyperbranched skeleton instead of with hydroxyl groups originating from bis-MPA. This will produce a high degree of branching (db ≈ 0.8) which should be compared to hyperbranched polymers synthesized *via* one-step procedures (db ≈ 0.5–0.6).[6,9]

Conclusions

The acid-catalyzed polyesterification of bis-MPA yields insoluble polymers if the reaction is driven to a conversion of the carboxylic acid groups higher than ~92%. If the reaction was stopped before gelation, the resulting polymers were highly disperse. By copolymerizing bis-MPA with a polyol core the risk of gelation was greatly reduced and the dispersity lowered.

The choice of polyol core is of great importance when hyperbranched polyesters are produced. In order to obtain a high degree of conversion of hydroxyl groups on the core, it is essential to select a polyol that favors this. This can achieved by changing the melting temperature of the core, adjusting the reaction mixture to be phase-separated for an optimized time. By doing this, the statistics for the reaction between the carboxylic acid and a hydroxyl group on the hyperbranched skeleton can be strongly improved. This discussion is also valid for the formation of hyperbranched polymers of high molar mass.

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