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Etherification as Side Reaction in the Hyperbranched Polycondensation of 2,2-Bis(hydroxymethyl)propionic Acid

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ABSTRACT: The existence of ether byproducts could be clearly proven for the hyperbranched polymerization of 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) using NMR spectroscopy. Polymerization experiments were performed under standard conditions with different catalysts. The ether structures were identified by characteristic ^{13}C NMR signals of the quarternary carbons and of the ether methylene carbons. Different substitution pattern of these ether units could be distinguished. Using high-resolution magic-angle spinning (HR-MAS) NMR spectroscopy also cross-linked, swollen samples could be analyzed. The amount of ether side products was calculated from ^{1}H NMR spectra after alkaline hydrolysis of the polymer samples. Etherification can occur as an intramolecular reaction resulting in cycles. Intermolecular etherification results in molecules with two or more focal groups which can act as cross-linker in the polymerization. Thus, cross-linked samples were obtained at high degrees of conversion.

Introduction

In the past decade hyperbranched (hb) polymers have gained a broad interest which is reflected in a great variety of hb structures studied for different applications and in a profound theoretic understanding of the hb polymerization.[1−4] In most cases the hb polymers were synthesized from AB$_x$ monomers ($x \geq 2$). The theoretical growth of highly branched polymers obtained by polycondensation of such AB$_x$ monomers was first discussed by Flory.[5] The resulting macromolecules are characterized by one A group (focal group) and numerous B groups. Depending on the number of remaining B groups per reacted monomer unit terminal (**T**, two B groups), linear (**L**, one B group), and dendritic (**D**, no B group) repeating units were distinguished for hb polymers based on AB$_2$ monomer. The degree of branching DB can be calculated from DB = $(\mathbf{T} + \mathbf{D})/(\mathbf{T} + \mathbf{L} + \mathbf{D})$ according to Fréchet et al.[6] These considerations are based on the assumption[5] that all of the functional groups of a given type (A or B) are of equal reactivity at any stage of the polymerization. In this case, the ratio of the three units is 1:2:1 at high conversion for AB$_2$ monomers (DB = 0.5). This assumption seems to be valid in most cases. However, several papers report on different reactivities of A and/or B groups depending on the substitution pattern of the reacting units which results in a DB $\neq$ 0.5.[6−9] The case of nonequal reaction rates in a hyperbranched polymerization is also treated theoretically.[9−14] A second assumption[5] was the reaction only between A and B groups as an intermolecular reaction. The intramolecular reaction between the focal group A and a B group resulting in cyclization is neglected in most theoretical treatments. This seems to be legitimate when the monomer is less flexible.[15] However, cyclization was observed for highly flexible monomers[16−21] or when special geometries are possible.[22] Mass spectrometric methods were commonly used to prove cyclization. Although both nonequal reaction rates and the formation of rings influence the overall structure of the hb polymer, reactions between A and B do not result in cross-linking at a conversion < 100%.

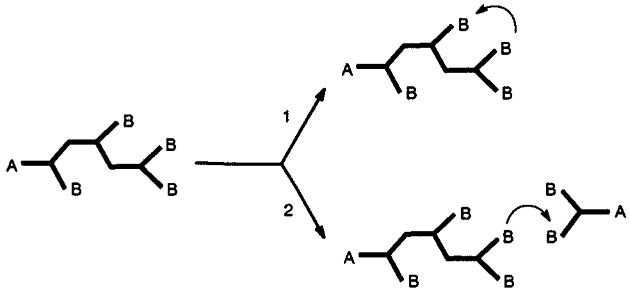

Figure 1. Possible reaction pathways for the reaction of two B functionalities of a hyperbranched polymer from an AB$_2$ monomer: pathway 1, *intra*molecular reaction (cyclization); pathway 2, *inter*molecular reaction (formation of a molecule with more than one A unit).

The reaction between two B groups as side reaction is usually only mentioned very briefly. The occurrence of this side reaction depends on the monomer and the reaction conditions used and often it can be excluded. However, if the monomer and the reaction conditions allow such a reaction, it can occur at any stage of the reaction but especially at a high degree of conversion of A groups, when it can compete with the desired reaction between A and B groups. Such reactions can occur between B groups of one molecule resulting in ring formation or between B groups of different molecules. This *inter*molecular reaction results in molecules with two or more A groups which can act as cross-linking agent in the polycondensation (Figure 1).

The aim of this paper is to prove side reaction between B groups experimentally. For industrial synthesis and application of hb polymers the knowledge of this potential side reaction is very important to circumvent cross-linking of the product. We have chosen the acid-catalyzed polycondensation of 2,2-bis(hydroxymethyl)propionic acid (bis-MPA = AB$_2$ monomer), a well studied reaction used for a commercial hb product (Boltorn, Perstorp). Properties of such polymers were reviewed by Ihre et al.[23] In this polymer gelation was

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Table 1. Reaction Conditions, Molar Masses (by SEC), and Polydispersity (PD) for Different Experiments in Synthesis of Poly(bis-MPA)

expt	amount of monomer (mol)	catalyst	concn (mol %)	reaction temp (°C)	reaction time (h)[a]	M_n (g/mol)	M_w (g/mol)	PD
1	0.23	pTSA	0.26	140	1.5/6	4600	8600	1.87
2	1.8	pTSA	0.13	185	2/8	11 200	18 600	1.66
3	0.46	pTSA	0.26	185	2/6	8300	11 700	1.41
4	1.8	pTSA	0.26	185	2/7.5	4300	8800	2.05
5	0.3	H_2SO_4	0.2[b]	140	0.5/1	6700	10 000	1.49
6	0.46	H_2SO_4	0.2[b]	140	1/6	gelled product		
7	0.46	H_2SO_4	0.2[b]	185	1/6	gelled product		
8	0.46	$Ti(^iPrO)_4$	0.26	185	1.5/6	5100	17 500	3.43
9	1.0	$Ti(^iPrO)_4$	0.26	185	1.5/8	5600	14 400	2.57

[a] Nitrogen flow/vacuum. [b] Sulfuric acid (96%) in mass%.

observed in hb polycondensation.[8,24] It is known that under the acidic conditions used for the polycondensation of bis-MPA in principle etherification of aliphatic alcohols (reaction between two B groups) can occur.[25] The kinetics and structure build up in the polycondensation of pure bis-MPA was extensively studied by Hult et al.[8,24,26] They found that the proportion of dendritic units is smaller than the expected value of 25% also at 95−97% of conversion. Hindered accessibility of the reacting groups was given as a possible reason. The polymer material gelled after a few hours heat treatment. For this reason a relatively low esterification temperature (140 °C) was recommended. Gelation was not observed when the A groups were reacted with a core molecule.

The occurrence of cyclized species was also reported.[20,21] This was concluded from peaks in ESI[20] and MALDI−TOF[21] mass spectra characterized by a mass lowered by 18 g/mol (elimination of water) with respect to the set of peaks originating from the regular polymer structure. The intramolecular reaction of an A (COOH) and a B (OH) functionality under the formation of poly-B-functional macrocycles was given as reason. Unquestionable, this is one reaction which is of importance in cyclization. However, also etherification results in loss of water and can cause the observed mass difference.

The formation of macrocyclic polyesters is difficult to prove by spectroscopic methods (NMR, IR) because only the smallest possible cycles should result in chemical shifts or wavenumbers which can be distinguished unequivocally from the polymer backbone. However, such sterical crowded rings are unlikely. In contrast, ether bonds result in new structures compared to the regular polyester which should be detectable by spectroscopic methods. For this reason, a series of polyesters from bis-MPA was prepared under different conditions and investigated by NMR spectroscopy. High-resolution magic-angle spinning (HR-MAS) NMR spectroscopy was applied to also investigate the structure of polymer gels obtained in this investigation.

Experimental Section

Materials and General Reaction Procedure. 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA, > 98%) was received from Lancaster. *p*-Toluenesulfonic acid (pTSA, > 98%) and tetraisopropyl titanate ($Ti(^iPrO)_4$, > 98%) were purchased from Merck. Sulfuric acid (95−98%) was received from Acros. All solvents were used without any further purification. The monomer and the solid catalysts were weighed in a three necked flask equipped with stirrer and gas-inlet and -outlet tubes and heated to the reaction temperature. In the case where a fluid catalyst was used, the catalyst was added at the reaction temperature. The temperature was maintained for a first time period with a constant nitrogen flow; finally a vacuum (about 3×10^{-2} mbar) was applied for a second time period. Molar amount of monomer, reaction temperature, catalyst concentration, and reaction time under nitrogen flow and vacuum, respectively, are given in Table 1 for the different experiments. The cold product was dissolved in tetrahydrofuran (THF). The polymer is precipitated into cold diethyl ether and dried at 40 °C in a vacuum.

NMR Spectroscopy. The NMR analysis was carried out on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^1H and at 125.75 MHz for ^{13}C NMR spectra. DMSO-d_6 was used as solvent, lock, and internal standard ($\delta(^1H) = 2.50$ ppm, $\delta(^{13}C) = 39.60$ ppm). The spectra were measured at 303 K using 5 mm o.d. sample tubes. ^{13}C HR-MAS NMR spectra were recorded using a $^1H/^{13}C$ HR-MAS probe and 4 mm o.d. rotors. About 6 mg polymer was swollen in 55 μL of DMSO-d_6. A spinning frequency of 5 kHz was applied. Quantitative ^{13}C NMR spectra were obtained using inverse gated decoupling, 90° pulses, and a pulse delay of 30 s. The quantification of different structural units was accomplished by signal integration based on the following assignments for quarternary carbon signals: 50.44 (**2t**), 49.64 (**1t**), 49.5 (**2l**$_{\mathbf{E}}$), 48.6 (**1l**$_{\mathbf{E}}$), 48.45 (**2l**), 47.76 (**1l**), 47.43 (**2d**$_{\mathbf{E}}$), 46.78 (**1d**$_{\mathbf{E}}$), 46.48 (**2d**), and 45.84 (**1d**). The error in determining the mole fractions of the different units from a NMR spectrum is ≤ 2 mol % depending on the signal-to-noise ratio for the individual signal. The 1D NMR measurements were completed by $^1H-^{13}C$ one- and multiple-bond shift-correlated (HMQC, HMBC) spectra using the standard pulse sequences provided by Bruker.

Alkaline hydrolysis was carried out with $NaOD/D_2O$ (about 1 N) directly in the sample tube (20 mg polymer in 1 mL solvent). ^1H and ^{13}C NMR spectra were referenced on internal sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 ($\delta(^1H) = 0$ ppm, $\delta(^{13}C) = 0$ ppm). NMR data for **I** (two diastereomers, molar ratio about 1:1): $\delta(^1H)$ 1.60 (s, 12H, assigned from HMBC spectrum), 3.48 (d, 4H), 3.58 (d, 2H), 3.59 (d, 2H), 3.59 ppm (s, 8H, assigned from HMBC spectrum); $\delta(^{13}C)$ 20.63 (C_1), 52.33 and 52.37 (C_2), 68.31 (C_4), 77.59 and 77.62 (C_5), 185.87 and 185.88 ppm (C_3). The content of **I** in the hydrolyzed polymer was determined as described in the text. The error is estimated to be smaller than 0.5 mol %.

Size Exclusion Chromatography (SEC). The SEC measurements were performed with modular chromatographic equipment containing a refractive index detector. A combination of Zorbax PSM 60 and 300 columns (Rockland Technologies) was used. The measurements were carried out at room temperature with dimethylacetamide containing 2 vol % water and 3 g/L of LiCl as mobile phase. The molecular weights were calculated by the use of poly(2-vinylpyridine) standards (Polymer Standards Services).

Results and Discussion

Pure bis-MPA has been polymerized in bulk using different esterification catalysts. Acid catalysts like sulfuric acid[8,24] and *p*-toluenesulfonic acid (pTSA)[20,21,26] are commonly used in a bis-MPA polycondensation. In addition, tetraisopropyl titanate, $Ti(^iPrO)_4$, a well-

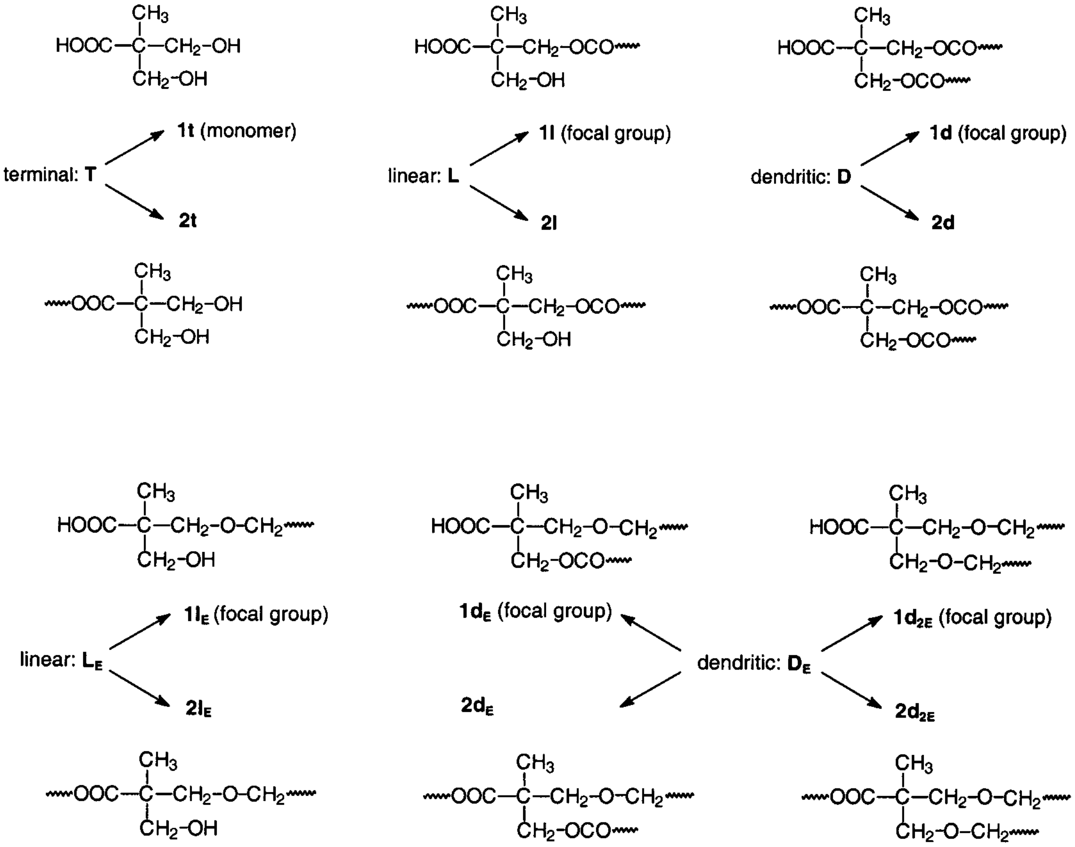


Figure 2. Structural units for the polycondensation of bis-MPA. Monomer (**1t**) and units formed by esterification reaction of a COOH group and an OH group: **1l**, **1d**, **2t**, **2l**, and **2d**. Units formed by etherification reaction of two OH groups: **1l**$_E$, **2l**$_E$ **1d**$_E$, **2d**$_E$, **1d**$_{2E}$, and **2d**$_{2E}$.

known catalyst for polycondensation was used. Experimental conditions for the different polymerizations are summarized in Table 1.

Identification of Ether Groups. Six differently incorporated repeating units are possible for a regular hyperbranched polyester based on bis-MPA, Figure 2. The postulated formation of ether groups may result in six additional structures. Single etherification of **1t** and **2t** instead of esterification results in the linear units **1l**$_E$ and **2l**$_E$. Further etherification or esterification results in four ether-containing dendritic units (**D**$_E$). All these structures and their notation are given in Figure 2.

In the ^{13}C NMR spectrum, the six regular units (**1t**, **1l**, **1d**, **2t**, **2l**, and **2d**) can easily be distinguished from each other by their quaternary carbon signals.[8] Figure 3 depicts this signal region for different experiments. From the assignments, two chemical shift effects for the quaternary carbons can be determined: esterification of COOH results in $\Delta\delta = -0.75$ ppm and esterification of CH_2OH results in $\Delta\delta = -1.9$ ppm. The additional signal splitting is caused by different neighboring units in the hyperbranched structure. Such dyad or triad effects are well-known for polymers and are also described for hyperbranched polymers.[9,27–29]

The spectrum of experiment 2 (Figure 3b) shows additional quaternary carbon signals at 49.50, 48.60, 47.43, and 46.78 ppm. Furthermore, a broad signal centered at 73.2 ppm appears in the methylene carbon region. The HMQC spectrum shows an one-bond correlation for this carbon signal to protons at 3.4 ppm. Both chemical shifts correspond well with the postulated ether structures. Hult et al.[30] give ^{13}C chemical shifts between 70 and 73 ppm for the ether carbon in a hb aliphatic polyether prepared from 3-ethyl-3-(hydroxymethyl) oxetane.

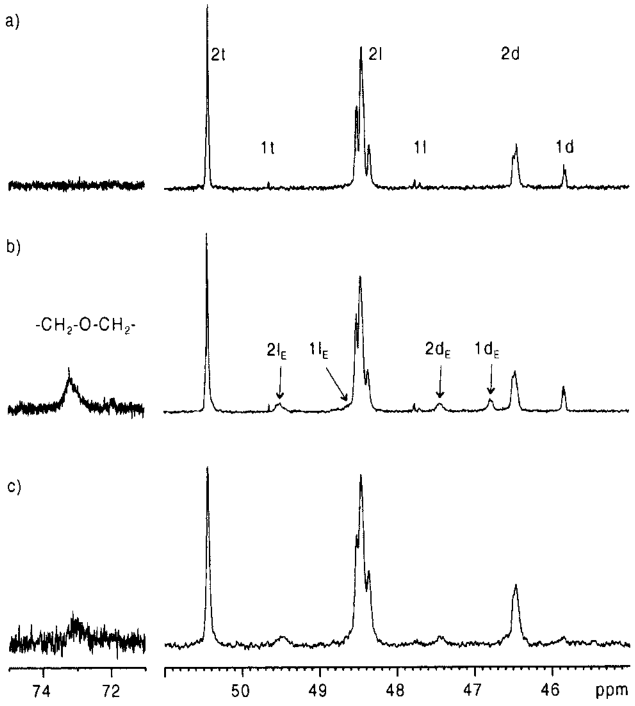


Figure 3. ^{13}C NMR spectra (regions of the quarternery and the ether OCH_2 carbons) for different poly(bis-MPA) samples: (a) experiment 3; (b) experiment 2; (c) experiment 7 (^{13}C HR-MAS spectrum) with signal assignment to structural units.

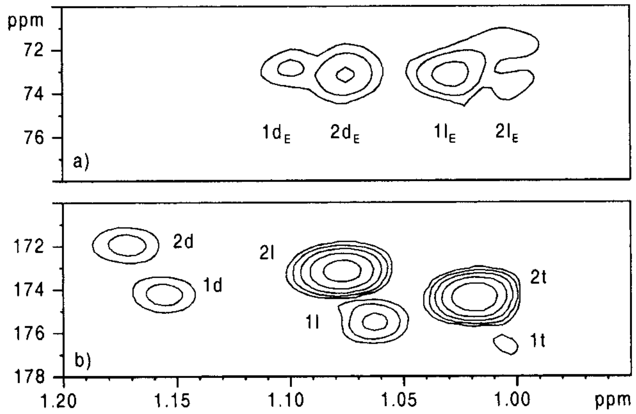
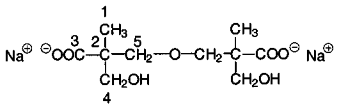


Figure 4. ^{1}H−^{13}C HMBC spectra showing a) the three-bond-correlation between methyl protons and ether carbons of units $\mathbf{1l_E}$, $\mathbf{2l_E}$, $\mathbf{1d_E}$, and $\mathbf{2d_E}$ and (b) the three-bond-correlation between methyl protons and carbonyl carbons of units **1t**, **1l**, **1d**, **2t**, **2l**, and **2d**.

The formation of ether bonds in a hb polycondensation of bis-MPA could unequivocally be proven by complete alkaline hydrolysis of the polyester, because under these conditions only ester bonds are cleaved. The presence of the sodium salt of 2-(1-carboxy-1-hydroxyethoxy)-2-hydroxypropionic acid (**I**) as product after hydrolysis can only be explained by ether bond formation. More details will be given in connection with the quantification of ether groups described in the following section.



$$Na^{\oplus}\ {}^{\ominus}OOC-\overset{CH_3}{\underset{CH_2OH}{C}}-CH_2-O-CH_2-\overset{CH_3}{\underset{CH_2OH}{C}}-COO^{\ominus}\ Na^{\oplus}$$

I

The four additional quaternary carbon signals of the polymer are low-field shifted by 1 ppm with respect to the four signals of **L** and **D** units. This ^{13}C chemical shift effect corresponds to the β-effect induced by replacing an ester group by an ether group.[31] Furthermore, the chemical shift differences between these four signals reflect the $\Delta\delta$ values determined for esterification of COOH and esterification of CH_2OH. Obviously, they can be assigned to structures $\mathbf{1l_E}$, $\mathbf{2l_E}$, $\mathbf{1d_E}$, and $\mathbf{2d_E}$ which all result in **I** after polymer hydrolysis. The ^{13}C chemical shifts of the quaternary carbons of $\mathbf{1d_{2E}}$ and $\mathbf{2d_{2E}}$ can be calculated from those of $\mathbf{1d_E}$ and $\mathbf{2d_E}$ assuming that replacing the second ester group by an ether group results in an additional low field shift of 1 ppm. These signals should appear at 47.8 ($\mathbf{1d_{2E}}$) and 48.4 ppm ($\mathbf{2d_{2E}}$). Whereas the first signal would be overlapped by the signal of **2l**, the signal of $\mathbf{2d_{2E}}$ is missing. Taking into account that in most samples the overall content of **I** is lower than 6 mol %, the content of double etherified units should be very low and could not be detected by ^{13}C NMR. Further ^{13}C NMR signals of ether-containing units are overlapped by signals of the main structure and could not be assigned. This is also valid for the ^{1}H NMR signals. The methyl protons of hb poly(bis-MPA) show a splitting due to different structural units which can be used to quantify these units and finally to calculate the DB. Therefore, the ^{1}H chemical shifts for the methyl protons of the four etherified units are of interest. The HMBC spectrum gives the desired information (Figure 4). Correlation between carbonyl carbons and methyl protons allow to assign the methyl groups of the six regular units. Additionally, three-bond-correlations are observed between ether carbons and two methyl proton regions at 1.09 and 1.02 ppm. The first one is assigned to the methyl groups of $\mathbf{1d_E}$/$\mathbf{2d_E}$ and the second one to $\mathbf{1l_E}$,/$\mathbf{2l_E}$. The consequence is that the content of **T** units is overestimated and the content of **D** units is underestimated. This is valid when the ether structures $\mathbf{1l_E}$ /$\mathbf{2l_E}$ are regarded as linear units and $\mathbf{1d_E}$/$\mathbf{2d_E}$ as dendritic units.

Two polymerization experiments using H_2SO_4 as catalyst resulted in gelled samples which cannot be investigated by common solution NMR. Following a careful extraction to remove residual soluble parts, the remaining solids were analyzed using HR-MAS NMR spectroscopy. This technique allows to analyze semisolid materials under high-resolution conditions[32] and opens new possibilities for structural characterization of swellable polymeric materials. As demonstrated in Figure 3c, the good swelling of the cross-linked samples in combination with magic angle spinning results in line widths for the ^{13}C NMR signals, which are comparable with those of the soluble samples. In this way, also the structure of these gels can be analyzed by quantification of structural units. The contents of different structural units determined by quantitative ^{13}C NMR are summarized for all experiments in Table 2.

Quantification of Ether Units. The amount of ether units can be determined from quantitative ^{13}C NMR spectra. Such measurements are time-consuming and the accuracy is limited due to the broad signal of the ether carbons. Nevertheless, they allow the determination of the absolute content of $\mathbf{1l_E}$, $\mathbf{2l_E}$, and $\mathbf{2d_E}$. The partial signal overlap of $\mathbf{1d_E}$ with **2l** limits the quantification of this ether unit. In most cases only the total content of the ether structures is of interest. For this reason, the polyesters are hydrolyzed under alkaline conditions in D_2O/NaOD and investigated by ^{1}H NMR. Within a few minutes the complete cleavage of the ester bonds was observed whereas the ether bonds were stable. Figure 5 depicts the methylene proton region of such a sample. Beside the strong signal of bis-MPA and its ^{13}C satellites six additional signals are observed. They are caused by two AB spin systems of the ether methylene protons of the *meso* and *racemic* form of **I**. Generally, eight signals should appear for two AB systems but the doublet at 3.47 ppm with double intensity is caused by both AB systems.

The hydroxymethylene proton signals of **I** coincide with the corresponding signal of the monomer bis-MPA. It should be mentioned that the high field ^{13}C satellite is overlapped by an additional signal which is assigned to a trace of 1,1,1-tris(hydroxymethyl)ethane (TME) in bis-MPA (0.75 mol %). Quantification of ether units is accomplished from the integral values of regions X and Y. Region X represents four protons of bis-MPA and six protons of **I**. Integral Y was corrected by the intensity of the ^{13}C satellite and TME determined from a sample of pure bis-MPA under the same conditions. It is still influenced in a minor extent by the base of the large monomer signal. This integral represents two ether methylene protons. It is not differentiated between the two diastereomers. They have the same concentration as it can be estimated from ^{13}C NMR. Figure 6 depicts regions from the ^{13}C NMR spectrum of hydrolyzed poly(bis-MPA). Pairs of signals with comparable intensity are observed due to both diastereomers.

Table 2. Content of Structural Units Determined from Quantitative ^{13}C NMR Spectra (in mol %), Degree of Branching According to Fréchet[6] (in %), and Content of Unreacted A Groups (in mol %) for Different Poly(bis-MPA) Samples

experiment	1	2	3	4	5	6g[a,b]	6s[b]	7[a]	8	9
catalyst	pTSA	pTSA	pTSA	pTSA	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	Ti(^{i}PrO)$_4$	Ti(^{i}PrO)$_4$
reaction temp (°C)	140	185	185	185	140	140	140	185	185	185
1l	1.3	1.2	1.3	1.2	1.5	0	0	0	1.8	1.5
1d	3.8	3.7	3.4	3.5	3.4	0.9	1.2	0.8	3.0	2.6
2t	22.3	21.4	23.9	23.5	23.7	21.8	20.6	19.6	22	21.8
2l + **1l$_E$**	55.4	52.2	57.8	57.7	55.2	53.2	55.2	53.1	50.6	52.9
2d	11.8	11.9	13.6	13.2	14.5	17.9	17.3	16.5	14.8	15.7
1d$_E$	1.8	3.6	0	0.6	0.7	0	2.8	0	2.3	1.7
2l$_E$	2.0	3.1	0	0	0.5	3.1	1.6	4.7	3.4	2.3
2d$_E$	1.6	2.9	0	0.3	0.5	3.1	1.3	5.3	2.1	1.5
etherified monomer units[c]	6	12.6	1	2.6	1	8.2	6.2	12.2	10	5.2
T	22.3	21.4	23.9	23.5	21.8	19.6	20.6	23.7	22.0	21.8
L	58.7	56.5	59.1	58.9	56.3	57.8	56.8	57.2	55.8	56.7
D	19.0	22.1	17.0	17.6	21.9	22.6	22.6	19.1	22.2	21.5
DB	41.3	43.5	40.9	41.1	43.7	42.2	43.2	42.8	44.2	43.3
unreacted A groups[d]	6.9	8.5	4.7	5.3	5.6	0.9	4.0	0.8	7.1	6.4

[a] Insoluble gel, content of structural units determined from quantitative ^{13}C HR-MAS NMR spectrum of the swollen sample. [b] Experiment 6 could be separated in an insoluble part (experiment 6g) and a soluble part (experiment 6s). [c] Determined from hydrolyzed samples taking into account that each ether molecule **I** contains two etherified monomer units. [d] Sum of **1l**, **1d**, and **1d$_E$**.[33]

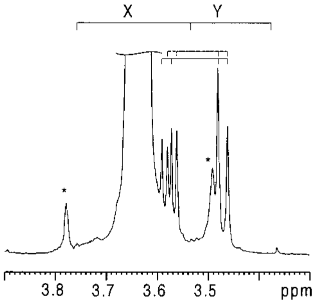


Figure 5. ^{1}H NMR spectrum (region of OCH_2 protons) of a hydrolyzed poly(bis-MPA) sample showing the integral regions used for quantitative determination of the content of **I** and the two AB spin systems of the $-CH_2-O-CH_2-$ group of *meso*- and *rac*-**I** (∗ indicate ^{13}C satellites).

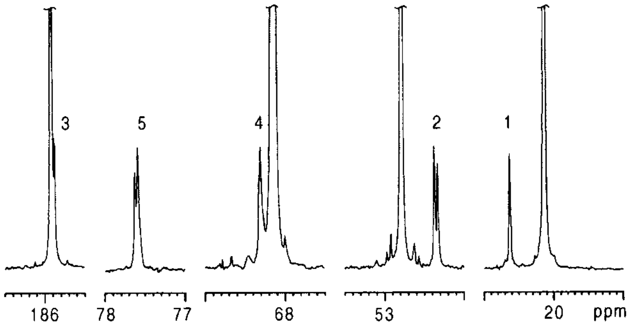


Figure 6. ^{13}C NMR spectrum of a hydrolyzed poly(bis-MPA) sample showing the signals of both diastereomers of **I** (truncated signals: bis-MPA).

Table 2 gives the molar content of ether units for different experiments determined by quantitative ^{13}C NMR and ^{1}H NMR.

Structure, Ether Group Formation and Gelation. Although this paper is focused on the proving of ether bonds, the overall structure of the synthesized polymers is also analyzed depending on the different catalysts. It could be shown that besides the well-known protic acids H_2SO_4 and pTSA also the Lewis acid Ti(^{i}PrO)$_4$ can be used as a catalyst for the polymerization of bis-MPA. On the basis of the assignments given in ref 8 and the assignments for ether units given in this paper, the content of different structural units was determined (Table 2). It is found that the content of **D** units is significantly lower than 25% for all catalysts, which would be the expected value for a random hyperbranched polycondensation of an AB_2 monomer. As proposed by Hult et al., the bulkiness of the hyperbranched structure and so differences in the accessibility for the reaction between **T** and **L** groups should result in the lowered content of **D** units.[8]

A degree of branching of 41−44% is calculated according to Fréchet considering the ether units also as **L** and **D** units depending on the number of unreacted hydroxyl groups. These values correspond well with data of Hult et al.[8] The content of unreacted A groups was calculated as sum of all focal units and varies from 4.7 to 8.5% for the soluble samples. For some experiments, the composition of the reaction mixture was also determined before purification. The conversion of the A groups varies from 89.4 to 93.6% with a remaining monomer content smaller than 1.5% which is comparable with data given by Hult at al.[24] For the gels, the content of unreacted A groups was calculated to be lower than 1%. Only a small signal of **1d** is observed.

Despite the fact that the content of ether units significantly scatters between the samples (Table 2) the results clearly prove that etherification is a side reaction in the hyperbranched polymerization of bis-MPA which cannot be neglected. Long reaction times and therefore higher rates of conversion promote the formation of ether groups but we are not able to correlate the ether content unambiguous with experimental conditions. However, it is obvious that the Ti catalyst favors ether formation. It seems that the formation of a large amount of ether groups does not result in a gelation if the degree of conversion is below 95−96%. Obviously, most ether groups are formed in intramolecular reactions resulting in rings similar to intramolecular esterification. As mentioned before, it is not possible to distinguish cyclic structures from esterification and etherification by their mass difference to the regular polymer in mass spectra. Both reactions result in the elimination of water. A quantitative determination of the content of cyclic ester structures using mass spectrometry[20] can be falsified by ether cycles.

Intramolecular cyclic ether and ester structures do not result in gelation but intermolecular ether formation leads to B_yA_x molecules which can act as a cross-linker. Obviously, the concentration of molecules with two or more A groups formed by intermolecular etherification remains low and the point of gelation is reached only at a very high degree of conversion. Both experiment 2 (soluble) and experiment 7 (gel) have a comparable high content of ether linkages (about 12%), but they differ significantly in their content of unreacted A groups. For the soluble sample (experiment 2) 8.5% of A groups is determined whereas the gel contains only 0.8%. The same relation between conversion and gel formation can be observed comparing the content of unreacted A groups of the soluble and insoluble part of experiment 6: 4% vs 0.9%.

Theoretically, the critical conversion leading to gelation occurs only at a conversion of A groups of 100% for a hb polycondensation of AB_2 molecules.[5] This point seems not to be reached for the insoluble samples as can be proven by detection of focal A groups in the HR-MAS NMR spectra. Instead, molecules with two or more A groups formed by etherification act as cross-linking agents. Multifunctional alcohols as core molecules in the polymerization of bis-MPA result in end-capping of free A functionalities. Therefore, the formation of cross-linking molecules and so gelation is suppressed when a core molecule is added.[8]

Conclusions

Hyperbranched polymers from bis-MPA were synthesized at 140 °C and 185 °C using different catalysts (*p*-toluenesulfonic acid, sulfuric acid, and $Ti(^iPrO)_4$). Etherification as side reaction was proven for all samples. Using NMR techniques, the ether structures were identified by characteristic ^{13}C NMR signals of the quarternary carbons and of the ether methylene carbons. Different substitution patterns of the ether units could be distinguished. The ether groups can be formed in both inter- and intramolecular reactions. Intramolecular etherification would lead to the formation of cycles. The intermolecular reaction results in molecules with two or more focal A groups that can act as cross-linker leading to cross-linked samples which were obtained in experiments using sulfuric acid as catalyst. The gels were characterized using the HR-MAS technique. The total amount of ether units could be determined from ^1H NMR spectra after hydrolyzing the polyester under alkaline conditions (D_2O/NaOD). Whereas all ester bonds were cleaved the ether bond was stable under these conditions. In this way, the content of the ether compound 2-(1-carboxy-1-hydroxyethoxy)-2-hydroxypropionic acid (sodium salt) could be determined beside the sodium salt of 2,2-bis(hydroxymethyl)-propionic acid. Depending on catalyst and temperature the amount of ether units varied from 1 to 12%. No correlation between catalyst and the amount of ether could be verified. However, long reaction times, higher reaction temperature, and higher rates of conversion seem to promote the formation of ethers. The titanium catalyst also seems to favor this side reaction. The knowledge of the ether side reaction is important for the calculation of the DB. Etherification may also result in the formation of cross-linked structures and subsequently in gelation which is crucial to avoid, especially industrially. Last but not least the existence of intramolecular cycles based on esterification *and* etherification can be proven by mass analyses because of obtained mass differences of 18 g/mol.

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References and Notes

(1) Fréchet, J. M. J.; Hawker, C. J. *React. Funct. Polym.* **1995**, *26*, 127.
(2) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.
(3) Hult, A.; Johansson, M.; Malmström, E. *Adv. Polym. Sci.* **1999**, *143*, 1.
(4) Voit, B. I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.
(5) Flory, P. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(6) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(7) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1999**, *32*, 4764.
(8) Magnusson, H.; Malmström, E.; Hult, A. *Macromolecules* **2000**, *33*, 3099.
(9) Schmaljohann, D.; Komber, H.; Barratt, J. G.; Appelhans, D.; Voit, B. I. *Macromolecules*, submitted for publication.
(10) Hölter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298.
(11) Yan, D.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024, 7034, and 7042.
(12) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7016.
(13) Schmaljohann, D.; Barratt, J. G.; Komber, H.; Voit, B. I. *Macromolecules* **2000**, *33*, 6284.
(14) Litvinenko, G. I.; Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 2418.
(15) Chu, F.; Hawker, C. J.; Pomery, P. J.; Hill, D. J. T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1627.
(16) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441.
(17) Feast, W. J.; Keeney, A. J.; Kenwright, A. M.; Parker, D. *Chem. Commun.* **1997**, 1749.
(18) Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180.
(19) Gong, C.; Miravet, J.; Fréchet, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3193.
(20) Dusek, K.; Somvarsky, J.; Smrckova, M.; Simonsick, Jr., W. J.; Wilczek, L. *Polym. Bull. (Berlin)* **1999**, *42*, 489.
(21) Burgath, A.; Sunder, A.: Frey, H. *Macromol. Chem. Phys.*, **2000**, *201*, 782.
(22) Bharathi, P.; Moore, J. S. *Macromolecules* **2000**, *33*, 3212.
(23) Ihre, H.; Johansson, M.; Malmström, E.; Hult, A. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press: Stamford, CT, 1996; Vol. 3, pp 1−25.
(24) Malmström, E.; Hult, A. *Macromolecules* **1996**, *29*, 1222.
(25) Vollhardt, K. P. C.; Schore, N. E. *Organische Chemie*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2000; p 354.
(26) Malmström, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, *28*, 1698.
(27) Schmaljohann, D.; Komber, H.; Voit, B. I. *Acta Polym.* **1999**, *50*, 196.
(28) Huber, T.; Böhme, F.; Komber, H.; Kronek, J.; Luston, J.; Voigt, D.; Voit, B. *Macromol. Chem. Phys.*, **1999**, *200*, 126.
(29) Eigner, M.; Komber, H.; Voit, B. *Macromol. Chem. Phys.*, **2001**, *202*, 245.
(30) Magnusson, H.; Malmström, E.; Hult, A. *Macromol. Rapid Commun.* **1999**, *20*, 453.
(31) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: Chichester, England, 1988; p 112.
(32) Lippens, G.; Bourdonneau, M.; Dhalluin, C.; Warrass, R.; Richert, T.; Seetharaman, C.; Boutillon, C.; Piotto, M. *Curr. Org. Chem.* **1999**, *3*, 147.
(33) Note: The content of free **A** functionalities is slightly underestimated if the sample contains $\mathbf{1l_E}$ units. The content of $\mathbf{1l_E}$ cannot be determined due to signal overlap with **2l** in the ^{13}C NMR spectrum.

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