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Cyclizations in Hyperbranched Aliphatic Polyesters and Polyamides

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Summary: Hyperbranched aliphatic polyesters of 2,2'-bis-(hydroxymethyl) propanoic acid and hyperbranched aliphatic polyamides obtained from new carboxy- and amino-functionalized caprolactams were studied by NMR spectroscopy and MALDI-TOF mass spectrometry. Ring-chain equilibria taking place through intramolecular hydroxy-ester, carboxy-amide or amine-amide interchanges and leading to the formation of cyclic branches or end-groups were found to exert a predominant influence on the molar mass of these hyperbranched polymers. A number of intra- or intermolecular side reactions, such as the formation of ethers in polyesters and the formation of anhydrides, imides, amidines and secondary amines in polyamides were also detected and resulted in polymer crosslinking on prolonged heating. The existence of such ring-chain equilibria and side-reactions make the control of hyperbranched polymer structure much more difficult than generally accepted.

Keywords: aliphatic polyamides, aliphatic polyesters, hyperbranched polymers, ring-chain equilibrium, side reactions

Introduction

The existence of intramolecular side reactions is a common feature of virtually all polycondensation or polyaddition reactions and results in the competitive formation of cyclic molecules along with linear polymer chains.[1] For most polycondensation polymers, the content in cyclics is generally low (a few %) and their presence plays only a minor role in polymer properties. The situation is somewhat different in AB_f-type hyperbranched condensation polymers, since intramolecular reactions result in the formation of ring-terminated hyperbranched macromolecules and limit the maximum attainable molar mass to values well below those predicted by Flory's theory, as shown by Monte-Carlo simulations.[2] The existence of intramolecular reactions has been detected in many hyperbranched polymers, such as polyesters[3,4] and polysiloxanes,[5] and are likely to exert an important influence on

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the properties of nearly all hyperbranched condensation polymers. The presence of cyclic branches or rings in AB_f-type hyperbranched polymers is generally assigned to the existence of A+B intramolecular reactions during the synthesis.[3] Since end-group concentration is very high in such polymers - ca. one B end-group per monomer unit for AB_2-type polycondensations - "back-biting" reactions, however, are likely to play an important role in the ring formation taking place in these polymers.

This work was devoted to the study of cyclization reactions taking place in hydroxy-terminated aliphatic hyperbranched polyesters and in amino- and carboxy-terminated aliphatic hyperbranched polyamides under ring-chain equilibrium conditions, i.e. thermodynamically controlled cyclizations rather than kinetically controlled ones.

Experimental

Hyperbranched Aliphatic Polyesters

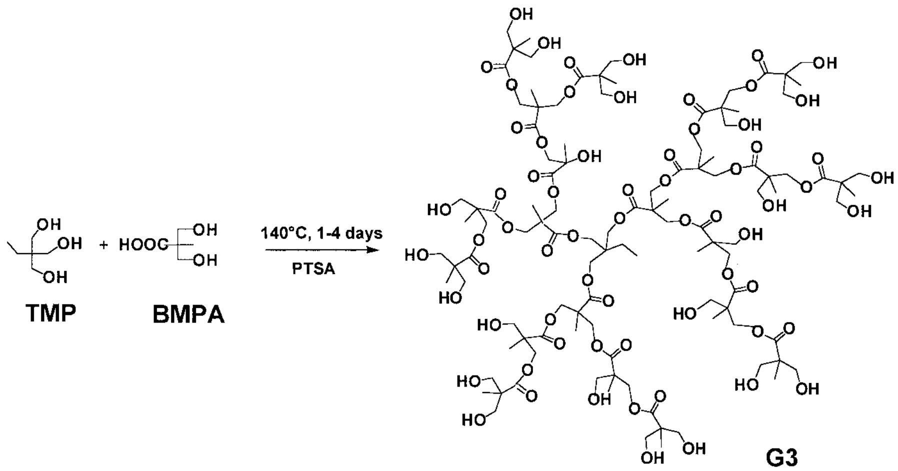
Trimethylolpropane (TMP) or pentaerythritol (PE) core molecules were reacted in the bulk with 2,2-bis(hydroxymethyl)propanoic acid (BMPA) at 140°C under nitrogen in the presence of 0.5 mass % p-toluenesulfonic acid (PTSA) catalyst[6]. Polyesters of pseudo-generation 2 or 3 (G2 or G3 respectively) were obtained using 1:9 or 1:21 TMP:BMPA mol ratio and 1:12 or 1:28 PE:BMPA mol ratio (Scheme 1).

γ-carboxyethyl-ε-caprolactam (1), γ-aminoethyl-ε-caprolactam (2) and 4-aminoethyl-1,7-heptanedioic acid (3)

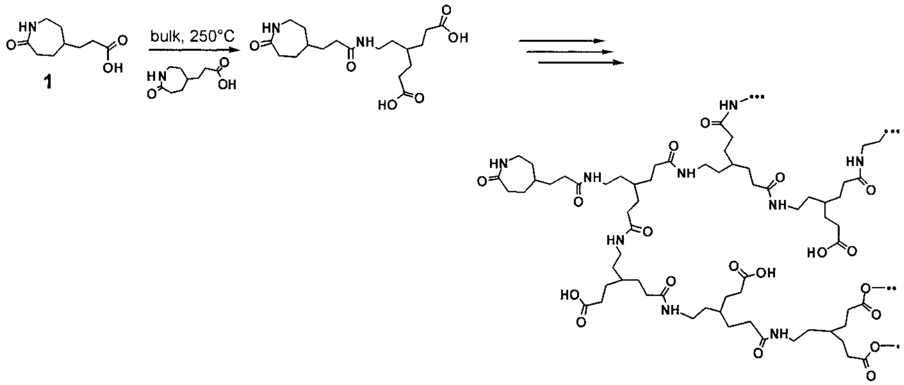
Carboxy- and amino-functionalized ε-caprolactams **1** and **2** were prepared by a multi-step synthesis starting from methyl 3-(4-hydroxyphenyl)propanoate and consisting of (i) hydrogenation of the phenyl group by H_2/Raney-Ni[7], (ii) CrO_3 oxidation of the resulting cyclohexanol to the corresponding cyclohexanone[7] and (iii) conversion of this compound to γ-carboxyethyl-ε-caprolactam **1** by reaction with O-sulfonic hydroxylamine in 95% formic acid (Schmidt-Beckmann reaction).[8] γ-Aminoethyl-ε-caprolactam **2** was synthesized by reacting **1** with sodium azide in a 2:1 vol $CHCl_3/H_2SO_4$ mixture.[8] 4-Aminoethyl-1,7-heptanedioic acid (**3**) was prepared by hydrolysis of **1** in refluxing 35% aqueous HCl.[8]

Hyperbranched Aliphatic Polyamides

Samples of **1** or **2** (100 mg) were placed in a 5mL tube and heated to 250°C under nitrogen for a predetermined reaction time (Scheme 2).



Scheme 1. Synthesis of TMP-BMPA hyperbranched polyester of generation 3.



Scheme 2. Synthesis of carboxy-terminated hyperbranched polyamides.

Results and Discussion

Hyperbranched Aliphatic Polyesters

Hyperbranched polyesters were synthesized according to the procedure described by Malmström et al.[6] by the reaction of 2,2-bis(hydroxymethyl)propanoic acid (BMPA) with pentaerythritol (PE) or trimethylolpropane (TMP) core molecules (Scheme 1). No carboxy end-groups were detected in the ^{13}C NMR spectra of the hyperbranched polyesters after 24 h reaction (Fig. 1) and the chemical titration of carboxy end-groups indicated that the conversion of COOH groups was above 98.7 %. The degree of branching (DB) was in the range 0.46-0.48 for all synthesized polyesters, close to the theoretical DB value (0.5) expected for hyperbranched AB$_2$ condensation polymers.

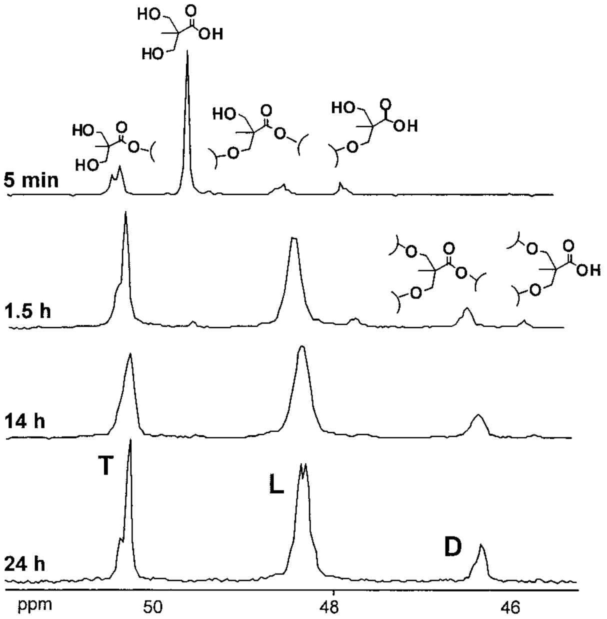


Fig. 1. ^{13}C NMR spectra (62.9 MHz, DMSO d-6) of G2-TMP:BMPA (1:9 mol ratio) polyesters after various reaction times (bulk reaction, 140°C, 0.5 mass % PTSA). T, D, L: terminal, dendritic and linear units, respectively.

The MALDI-TOF mass spectra of samples taken after 24 h reaction show, however, the presence of a series of small peaks at -18 Th from the main ones for either TMP- or PE-based hyperbranched polyesters, reflecting the existence of water-forming intramolecular side reactions. The 1250-1350 Th m/z region (DP = 11 oligomer molecules) of the mass spectrum of a G2 PE-based hyperbranched polyester obtained after 24 h reaction is given in Fig. 2.

The main peaks correspond to the expected core-unit-containing molecules (sodium cationized PE-M_x series where PE is the core unit and M_x monomer units) while the series of small M_x peaks corresponds to COOH-terminated molecules i.e. hyperbranched molecules that do not contain a core-unit. The presence of such molecules is not unexpected since conversion is not complete at this reaction time.

The (PE-M_x - 18) series is assigned to the formation of cyclic branches by intramolecular etherification - one cyclic branch per molecule. Etherification is a well-known side reaction of the synthesis of aliphatic and aliphatic-aromatic linear polyesters and results in the formation of a small proportion of oxyalkylene units. Due to the high OH functionality of PE-BMPA and TMP-BMPA hyperbranched polyesters, intramolecular etherification takes place to a much higher extent than in linear polyesters. On the other hand, intermolecular etherification cannot be discriminated from intermolecular esterification (the normal reaction) by mass spectrometry. The presence of an increasing amount of etherified units was observed at t > 24h in the ^{13}C NMR spectra of PE-BMPA hyperbranched polymers (Fig. 3). Since crosslinking was observed at t > 96 h, intermolecular etherifications should obviously be involved. It is worth mentioning that the presence of structures resulting from etherifications has been recently reported in similar polyester systems.[9]

The (M_x - 18) series is assigned to cyclic-terminated hyperbranched molecules resulting from intramolecular esterifications. Such reactions produce ring-containing molecules without core unit. Model cyclization studies were carried out on ester-, hydroxy- or carboxy-terminated linear aliphatic polyesters. The results obtained showed that the formation of cyclics is favored in hydroxy-terminated polyesters, and that hydroxy-ester interchange is the predominant reaction. The (M_x-18) series may be assigned, therefore, to compounds resulting from hydroxy-ester interchange or carboxy-hydroxy reaction. The hydroxy-ester equilibrium, well known in high temperature bulk polyesterifications, results in chain scission and in the formation of hyperbranched molecules containing one cyclic ester branch. The maximum attainable molar mass, therefore, depends on the cyclization equilibrium constant K (Scheme 3).

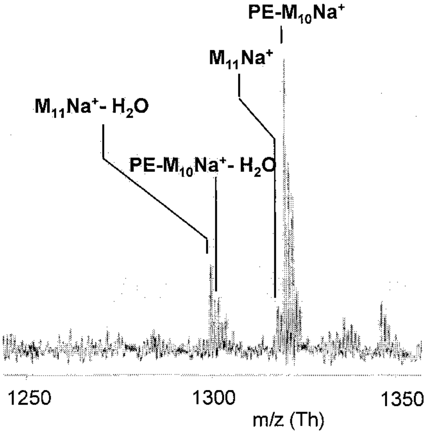


Fig. 2. MALDI-TOF MS spectrum (undecamer region) of G2-PE:BMPA (1:12 mol) polyester. Bulk reaction, 24 h, 140°C, 0.5 mass % PTSA.

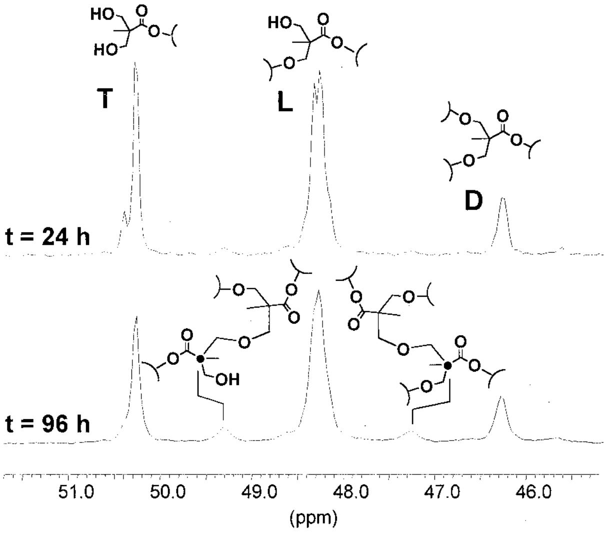
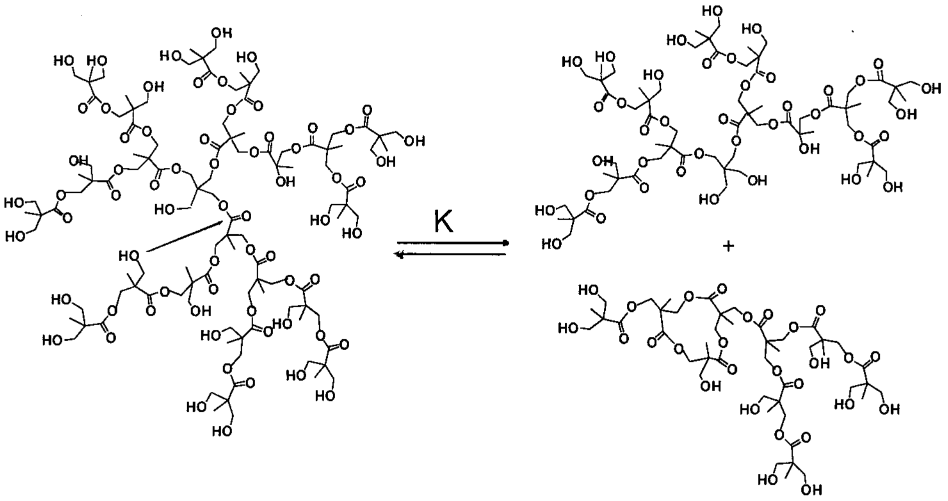


Fig. 3. ^{13}C NMR spectra (62.9 MHz, DMSO d-6) of G2 PE:BMPA (1:12 mol) polyester at 24h and 96h reaction. Bulk reaction, 140°C, 0.5 mass % PTSA.



Scheme 3

Hyperbranched Aliphatic Polyamides

Polymerization

Carboxy-terminated hyperbranched polyamides were obtained by polymerizing γ-carboxyethyl-ε-caprolactam **1** in the conditions of the acidolytic polyamide-6 synthesis (250°C, bulk reaction) (Scheme 2). The course of polymerization was followed by integrating the ^1H NMR resonances of caprolactam and polyamide CON$\underline{H}$ at 7.41 and 7.76 ppm respectively.

A rapid polymerization took place, but conversion reached a plateau value close to 0.53 after 3h reaction. The addition of polyamidation catalysts such as phosphorous and hypophosphorous acids (1 mass %) accelerated the first steps of reaction (t < 1h), but did not change the conversion plateau value (Fig. 4).

The NMR spectra of all samples fitted with the expected structure and exhibited resonances corresponding to both residual lactam and carboxylic acid end-groups. Similarly, the MALDI-TOF MS spectra were in agreement with the expected structure. Each hyperbranched molecule gives multiple peaks, assigned to H^+-Na^+ or H^+-K^+ exchanges taking place on COOH end-groups (Fig. 5). This confirms the high COOH functionality of these polyamides. According to these structural studies, it is obvious that the reaction did not stop because of reactive group consumption by possible side reactions. In the same way, kinetic factors cannot be involved since polyamidation catalysts did not change the conversion plateau value. The existence of the conversion limit can, therefore, be assigned to a ring-chain equilibrium, similar to the caprolactam-polyamide equilibrium taking place during the synthesis of linear polyamide-6. This equilibrium involves carboxy-amide interchange reactions (Scheme 4).

Similar observations were made during the polymerization of γ-aminoethyl-ε-caprolactam (**2**). Lactam CONH conversion rapidly reached a plateau value close to 0.57 after only 30 min reaction. This was assigned to a ring-chain equilibrium, analogous to that depicted in Scheme 4, in which amine end-groups are involved instead of carboxy end-groups.

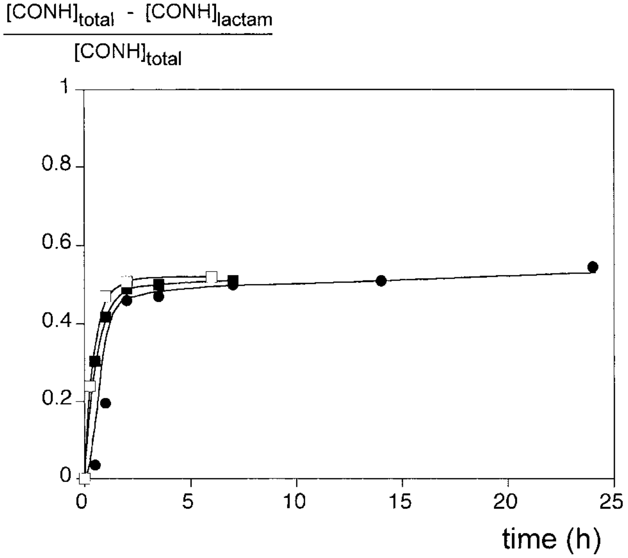


Fig. 4. Polymerization of caprolactam **1** (250°C): Variation of caprolactam CONH conversion versus reaction time for uncatalyzed (●), H_3PO_3- (■) and H_3PO_2-catalyzed(❑) reactions.

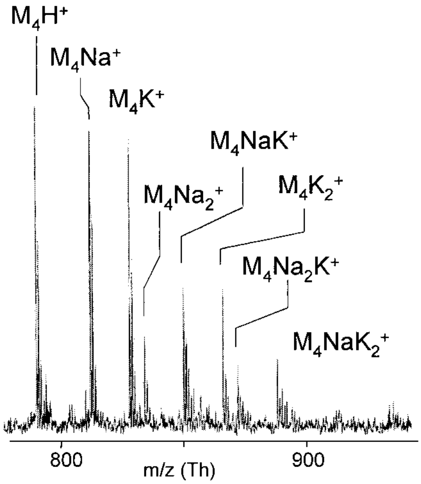
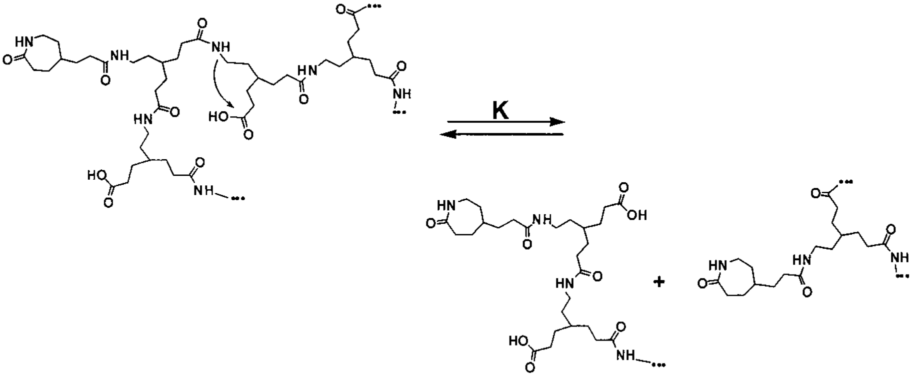


Fig. 5. Polymerization of capro-lactam **1** (250°C, 3.5h): MALDI-TOF MS spectrum of the 800-900 Th region.



Scheme 4

The polycondensation of 4-aminoethyl-1,7-heptanedioic acid, obtained from caprolactam **1** hydrolysis, was carried out at 170°C for 3h. It resulted in the formation of a lactam-terminated low-molar mass compound. Carboxy-amide interchange reaction is very slow at 170°C and cannot be involved in the formation of lactam end-groups during the polycondensation of this aminodiacid. In this case ring formation is clearly under kinetic control, which means that the intramolecular $COOH+NH_2$ reaction is faster than the intermolecular reaction.

Side reactions on prolonged heating

In both carboxy- and amino-terminated hyperbranched polyamides, the formation of an insoluble, crosslinked fraction was observed on prolonged heating, 48h for the carboxy system and 4 h for the amine system. Crosslinking clearly involves intermolecular side reactions of end-groups, amine or carboxy, which are present in large quantity in the hyperbranched polymers. In the case of carboxy-terminated hyperbranched polyamides, IR and NMR spectra indicated the probable formation of imide and anhydride linkages. MALDI-TOF MS study showed that multiple dehydration reactions take place on the same molecule, since peaks corresponding to the loss of one and two water molecules, respectively M_x - 18 and M_x - 36 series, are present in the spectra (Fig. 6). In the same way, multiple dehydrations were observed in the MS spectra of amino-terminated polyamides after prolonged heating (M_x - 18, M_x - 36 and M_x - 54 series). These dehydrations are attributed to amidine formation by reaction of -NH_2 end-groups on amide -CO-. Moreover, NH_3 loss reflecting the formation of secondary amines by deamination reaction of two amine end-groups was also observed in the spectra. The extent of these various side reactions is quite high since no peak corresponding to the expected series (M_x) can be seen in the spectra after 2h reaction (Fig. 7). In this case, mass spectrometry cannot discriminate intermolecular- from intramolecular dehydration or deamination side reactions. Since crosslinking is observed, intermolecular reactions must obviously take place, but the existence of intramolecular side reactions leading to the formation of cyclic branches cannot be excluded.

Study of ring-chain equilibrium

In order to examine the influence of a high reactive group concentration on the lactam/polymer equilibrium, model reactions were carried out on linear polyamide-6, namely (i) the acidolysis of high molar mass polyamide-6 by dodecanoic acid and (ii) the acidolytic polymerization of ε- caprolactam in the presence of dodecanoic acid. Both reactions were carried out in equimolar COOH:CONH ratio at 250°C, i.e. in reaction conditions similar to those used for the polymerization of γ-carboxyethyl-ε-caprolactam **1**. ε-Caprolactam concentration was monitored by ^{1}H NMR spectroscopy (Fig. 8). Caprolactam was consumed during the acidolytic polymerization, and formed during the acidolysis of polyamide-6. In both reactions, however, lactam concentration reached the same plateau value after a few hours of reaction, corresponding to lactam amide conversion = 0.75 or [lactam amide]/[total amide] = 0.25. This indicate that carboxyl groups, caprolactam amides and linear amides take part in a ring-chain equilibrium through amide-carboxylic acid interchange reactions (Scheme 5).

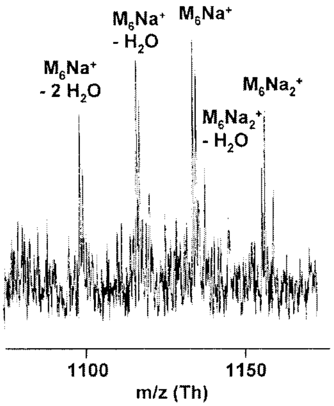


Fig. 6. MALDI-TOF MS spectrum (hexamer region, Na^+ cationization) showing the existence of dehydration reactions during carboxy-functionalized caprolactam **1** polymerization (250°C, 14 h).

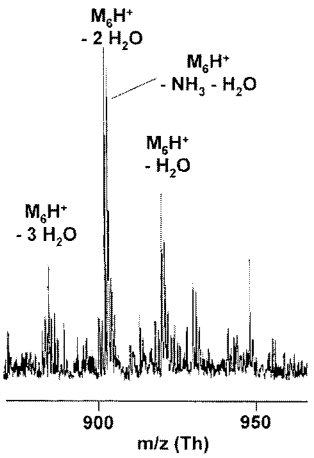
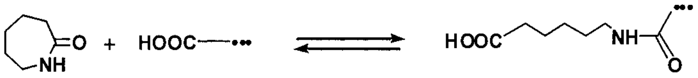


Fig. 7. MALDI-TOF MS spectrum (hexa-mer region, H^+ cationization) showing the existence of dehydration and deamination reactions during amino-functionalized caprolactam **2** polymerization (250°C, 2 h).



Scheme 5

The acidolytic polymerization of γ-carboxyethyl-ε-caprolactam **1** presents features quite similar to those of the linear polymerization (Fig. 8 and Scheme 4), the only noticeable difference being the lower conversion plateau value, 0.53 instead of 0.75 in the case of the linear polymerization. Such a large equilibrium lactam concentration, however, is not in agreement with Jacobson-Stockmayer's theory of ring-chain equilibrium for which the equilibrium concentration of a given cyclic species is a constant and does not depend on polymer or end-group concentrations. Since the equilibrium lactam conversion usually observed in linear polyamides is ca. 0.92, values of[lactam amide]/[total amide] close to 0.08 were expected instead of the value (0.25) found for the model linear polymerizations. The model reactions show that the formation of rings is favored in the presence of high end-group concentration. This may explain to a certain extent the high equilibrium [lactam amide]/[total amide] value (0.47) found in the acidolytic polymerization of carboxyethylcaprolactam **1**. Some other parameters should be considered to explain this value. The first one is the high "internal" concentration of pairs of reactive groups available for intramolecular reactions in hyperbranched polymers with respect to linear ones[10] and the second one is the lower polymerizability generally observed for substituted lactams with respect to non-substituted ones.[11]

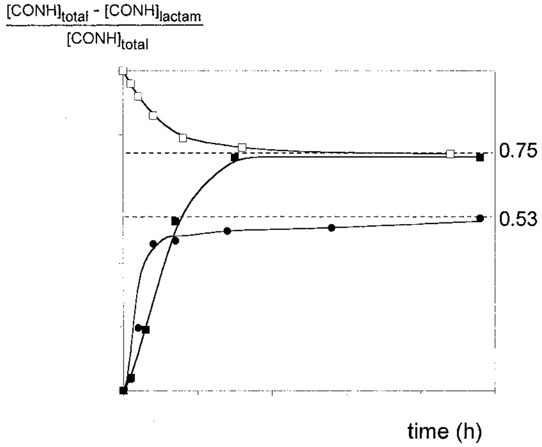


Fig. 8. Variation of lactam conversion versus time during polyamide-6 dode-canoic acid reaction (□), ε-caprolactam dodecanoic acid reaction (■) and γ-carboxyethyl-ε-caprolac-tam polymerization (●). (1:1 COOH: CONH mol ratio, bulk reaction, 250°C).

Conclusions

The synthesis of high molar mass aliphatic AB_f-type hyperbranched condensation polymers is hindered by the existence of a competition between cyclization and polymerization, which exert a predominant influence on polymer structure. Hydroxy-ester, carboxy-amide and amine-amide back-biting ring-forming reactions taking place during the synthesis result in the formation of cyclic branches or cyclic end-groups such as lactams, and lead to a noticeable lowering of the molar mass of final polymers. The preparation of high molar mass aliphatic hyperbranched polymers should, therefore, involve either a fractionation step to eliminate low molar mass oligomers or reaction conditions in which back-biting reactions are very slow, i.e. polymerization under kinetic control rather than thermodynamic control - although cyclizations have also been reported in hyperbranched polymer syntheses in these conditions.[12]

The presence of a large number of end-groups exert also a deleterious effect on polymer structure and properties. On prolonged heating, a number of side reactions, negligible in linear polymers due to very low end-group concentration at high conversion, become quite important and may result in the formation of crosslinked material: The formation of ethers was detected in hyperbranched polyesters, and the formation of anhydrides, imides, amidines and secondary amines in hyperbranched polyamides.

Ring-chain equilibrium and side-reactions make the control of hyperbranched polymer structure obviously much more difficult than generally accepted.

[1] H. R. Kricheldorf, S. Böhme, G. Schwarz, *Macromolecules* **2001**, *34*, 8879.
[2] C. Cameron, A. H. Fawcett, C. R. Hetherington, R. A. W. Mee, F. V. McBride, *Macromolecules* **2000**, *33*, 6551
[3] A. Burgath, H. Sunder, H. Frey, *Macromol. Chem. Phys.* **2000**, *201*, 782.
[4] D. Parker, W. J. Feast, *Macromolecules* **2001**, *34*, 2048.
[5] C. Gong, J. Miravet, J. M. J. Fréchet, *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 3193.
[6] E. Malmström, A. Hult *Macromolecules* **1995**, *28*, 1698.
[7] F. Leyendecker, G. Mandville, J. M. Conia *Bull. Soc. Chim.* **1970**, 556.
[8] X. Arnaud, C. Guillermain, M. Tessier, A. Fradet, *to be published.*
[9] H. Komber, A. Ziemer, B. Voit, *Macromolecules* **2002**, *35*, 3514.
[10] S. B. Roos-Murphy, R. F. T. Stepto, "*Macromolecular Cyclizations*" in "*Large Ring Macromolecules*", Vol. 1., *Macrocyclic Coupounds*, Ed. J. A. Semlyen, Wiley, New-York (1996).
[11] R. C. P. Cubbon *Makromol. Chem.* **1964**, *80*, 44.
[12] L. Vakhtangishvili, G. Schwarz, H. R. Kricheldorf, Poster P56, "Polycondensation 2002", Hamburg, Sept. 2002.