Cyclic Hyperbranched Poly(ether ketone)s Derived from 3,5-Bis(4-fluorobenzoyl)phenol[†]

Hans R. Kricheldorf,*,[‡] Lali Vakhtangishvili,[‡] Gert Schwarz,[‡] and Ralph-P. Krüger[§]

Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, D-20146 Hamburg, Germany, and BAM, Unter den Eichen 87, D-12205 Berlin, Germany

Received December 31, 2002; Revised Manuscript Received April 22, 2003

ABSTRACT: 3,5-Bis(4-fluorobenzoyl)phenol was polycondensed under various reaction conditions. Low molecular weights were obtained (M_n < 8000 Da), and MALDI−TOF mass spectrometry indicated that the chain growth was limited by cyclization. In the best mass spectra the cyclic, hyperbranched poly(ether ketone)s were detectable up to masses around 14 000 Da. When 4,4′-difluordiphenyl sulfone was added, star-shaped polymers having a diphenyl sulfone star center were formed, but cyclization was not completely suppressed. The results were compared to those obtained from "linear polycondensations" based on 4,4′-difluorobenzophenone (DFBP) and 4-*tert*-butylcatechol or bisphenol A. The poly(ether ketone)s of DFBP had also low molecular weights and contained high fractions of cycles. It is concluded that also in the case of hyperbranched polymers cyclization competes with propagation at any stage of the polycondensation at any concentration. Therefore, the fundamental trend of any "ab$_n$" polycondensation is the formation of star-shaped polymers having a cyclic core and hyperbranched star arms.

Introduction

The course of a polycondensation involving "ab$_n$" monomers was for the first time discussed by Flory,[1] although without any experiments. In his so-called "cascade theory", Flory did not consider a significant influence of cyclization reactions in close analogy to his original treatment of "linear polycondensations".[2] Furthermore, the cascade theory did not distinguish between kinetically controlled (KCP) and thermodynamically controlled polycondensations (TCPs). Later, Jacobson and Stockmayer[3] demonstrated for TCPs of "ab" and "aa" + "bb" monomers that the equilibration reactions involve the formation of cycles via "backbiting degradation". However, the cascade theory was not modified with regard to an influence of cyclization reactions.

During the past 5 years, several research groups[4−8] reported about the formation of cyclic hyperbranched oligomers in polycondensations of "ab$_2$" monomers. The syntheses of hyperbranched polyesters[6−8] most likely involved transesterification reactions, so that the formation of cycles can be explained by "backbiting degradation". However, two research groups[4,5] reported on partial cyclization of hyperbranched aromatic polyethers under conditions certainly obeying the definition of KCPs (absence of any equilibration reactions). Quite recently, we have demonstrated[9−11] that in KCPs of linear monomers ring closure competes with propagation at any concentration and at any stage of the polycondensations. Therefore, all reaction products are necessarily cycles at 100% conversion when side reactions are absent. The present work had the purpose to discuss how KCPs of "ab$_n$" monomers are correlated with our recent theory of "linear polycondensations". The experimental work is based on polycondensations of the "ab$_2$" monomer **1** (Scheme 1) and a comparison with the "linear polycondensations" formulated in Scheme 2. Two polycondensations of the sodium salt of **1** have already been reported by Miller et al.[12] and the possibility of cyclization was discussed, but the formation of cycles has not been investigated. Hyperbranched poly(ether ketone)s of different structure were also reported by other research groups,[13−15] but in those cases the formation of cyclic structures was not considered.

Experimental Section

Materials. Hexamethyldisilazane (HMDS), 5-hydroxyisophthalic acid, fluorobenzene, bisphenol A, 4-*tert*-butylcatechol, 4,4′-difluorobenzophenone (DFBP), and 4,4′-difluorodiphenyl sulfone (DFDPS) were purchased from Aldrich Co. (Milwaukee, WI) and used as received. Dimethyl sulfoxide (DMSO), sulfolane, and *N*-methylpyrrolidone (NMP) were purchased from E. Merck KG (Darmstadt, Germany). DMSO was used as received, whereas sulfolane and NMP were distilled over P_4O_{10} in vacuo.

Monomers. 3,5-Bis(4-fluorobenzoyl)phenol[12] (**1**) was prepared from 5-hydroxyisophthalic acid and 5-methoxyisophthalic acid via Friedel−Crafts acylation of fluorobenzene with 5-methoxyisophthaloyl chloride. After recrystallization from toluene (twice), monomer **1** had a melting point of 152−153 °C.

Polycondensations of 1 (Table 1). Monomer **1** (20 mmol) and dry K_2CO_3 (21 mmol) were weighed into a 150 mL three-necked flask, and DMSO (80 mL) and toluene (20 mL) were added. This mixture was stirred at a bath temperature of 140 °C, whereby the toluene was slowly distilled off. The loss of toluene was compensated from a dropping funnel. After 6 h, the reaction mixture was cooled and precipitated into water. The isolated polymer was intensively washed with hot water and dried at 100 °C in vacuo. In a second experiment, xylene was used to remove the water, and the bath temperature was fixed around 170 °C.

Analogous experiments were performed in sulfolane or NMP instead of DMSO. For the polymer isolated from the sulfolane/toluene mixture (no. 3, Table 1) elemental analyses were performed:

Analyses calcd for $C_{20}H_{11}F_1O_3$ (317.3): C, 75.23; H, 3.79; F, 5.95. Found: C, 75.61; H, 3.50; F, 5.93%.

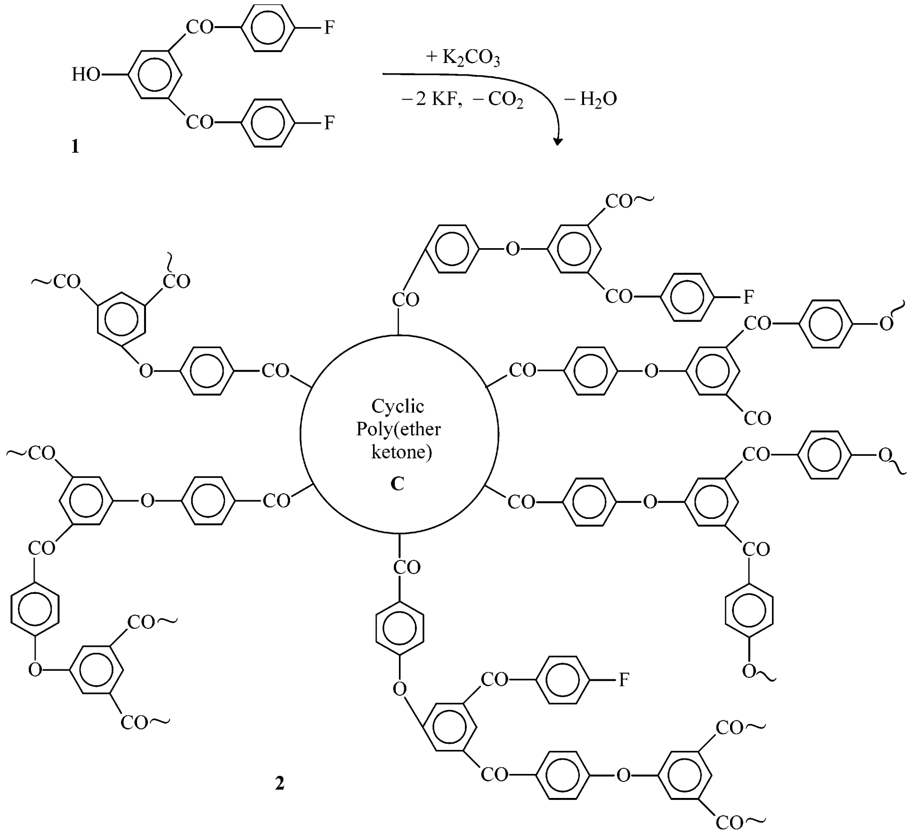
[†] "Macrocycles" Part 24.

[‡] Institut für Technische und Makromolekulare Chemie.

[§] BAM.

10.1021/ma021799x CCC: $25.00

Scheme 1



Scheme 2

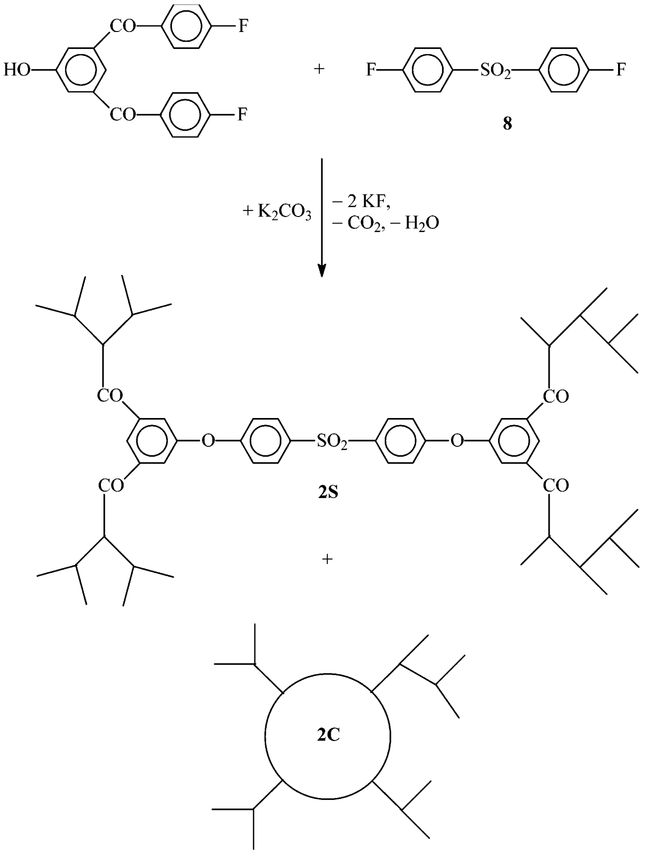


Table 1. K_2CO_3-Promoted Polycondensations of Monomers 1

exp no.	monomer	reaction medium	temp[a] (°C)	yield (%)	η_{inh}[b] (dL/g)
1	**1**	DMSO + toluene	140	96	0.08[c]
2	**1**	DMSO + xylene	170	97	0.10[d]
3	**1**	NMP + toluene	150	96	0.08
4	**1**	NMP + xylene	180	97	0.09[e]
5	**1**	sulfolane + toluene	160	71	0.07[f]
6	**1**	sulfolane + xylene	190	93	0.07[f]

[a] Reaction time: 6 h. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] $M_n = 6500$, $M_w = 10\,000$ Da (PS-calibrated SEC). [d] $M_n = 8000$, $M_w = 12\,500$ Da (PS-calibrated SEC). [e] $M_n = 7500$, $M_w = 11\,500$ Da (PS-calibrated SEC). [f] $M_n = 3000$, $M_w = 7000$ (PS-calibrated SEC).

Table 2. K_2CO_3 Copolycondensations[a] of Monomer 1 and 4,4′-Difluorodiphenyl Sulfone (DFDPS)

exp no.	monomer **1a**[b]/DFDPS	monomer **1a**[b]/K_2CO_3	yield (%)	η_{inh}[c] (dL/g)
1	1.0:0.0	1.0/1.0	97	0.10
2	1.0:0.025	1.0/1.025	98	0.09
3	1.0:0.05	1.0/1.05	98	0.08
4	1.0:0.10	1.0/1.10	98	0.06

[a] In DMSO/xylene 170 °C/6 h. [b] Molar ratios. [c] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

Copolycondensation of 1 and DFDPS (No. 3, Table 2). Monomer **1** (20 mmol), DFDPS (**8**, 1 mmol), and K_2CO_3 (22 mmol) were weighed into a 150 mL three-necked flask, and DMSO (80 mL) and xylene (20 mL) were added. This mixture was stirred at 170−175 °C over a period of 6 h. The xylene was slowly distilled off and replaced from a dropping funnel. After cooling, the reaction mixture was worked up as described above.

Polycondensations of DFBP (**3**). (*A*) *With 4-tert-Butylcatechol* (Table 3). 4-*tert*-Butylcatechol (**4**, 20.0 mmol), DFBP (**3**, 20.2 mmol), and K_2CO_3 (21 mmol) were weighed into a 150 mL three-necked flask equipped with a flat-blade stirrer. Sulfolane (80 mL) and toluene (20 mL) were added, and this mixture was stirred at 150−155 °C, whereby the toluene was slowly distilled off. The loss of toluene was replaced from a

Table 3. Polycondensations of 4-*tert*-Butylcatechol and 4,4′-Difluorobenzophenone (DFBP)

exp. no.	excess of DFBP	reaction medium	temp[a] (°C)	yield (%)	η_{inh}[b] (dL/g)
1	0	DMSO + toluene	140−145	96	0.08
2	0	NMP + toluene	150−155	87	0.10
3	0	sulfolane + toluene	150−155	98	0.08
4	0	sulfolane + xylene	170−175	98	0.14
5	1	sulfolane + toluene	150−155	97	0.08[c]
6	1	sulfolane + xylene	170−175	97	0.10[d]

[a] Reaction time: 6 h. [b] Measured at 25°C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [c] $M_n = 3000$, $M_w = 13\,000$ from PS-calibrated SEC measurements. [d] $M_n = 3000$, $M_w = 17\,000$ from PS-calibrated SEC measurements.

Table 4. Polycondensations of Bisphenol-A and 4,4′-Difluorobenzophenone (DFBP)

exp. no.	reaction medium	temp[a] (°C)	yield (%)	η_{inh}[b] (dL/g)
1	DMSO + toluene	140−145	98	0.20
2	NMP + toluene	150−155	98	0.23
3	sulfolane + toluene	150−155	97	0.21[c]

[a] Reaction time: 6 h. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [c] $M_n \sim 4500$, $M_w \sim 20\,000$ Da.

dropping funnel. After 6 h the reaction mixture was cooled and precipitated into water. The precipitated polymer **6** was intensively washed with hot water and dried at 100 °C in vacuo.

In an analogous polycondensation toluene was replaced by xylene or sulfolane was replaced by DMSO or NMP.

(B) With Bisphenol A (Table 4). Bisphenol A (**5**, 20.0 mmol), DFBP (**3**, 20.0 mmol), and K_2CO_3 (21 mmol) were polycondensed as described for (A).

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The DSC measurements were performed on a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min in aluminum pans under nitrogen.

The MALDI−TOF mass spectra were recorded on a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). An acceleration voltage of 20 kV was used, and 150−250 scans were accumulated. The radiation targets were prepared from tetrahydrofuran and chloroform solutions with dithranol as matrix and potassium trifluoroacetate as dopant.

The SEC curves were recorded with a homemade SEC apparatus at 23 °C using THF as eluent. A combination of three PSS-SDV mix-bed columns was used along with an UV and RI detector. Commercial PS standards served for calibration. The number-average (M_n) and weight-average (M_w) values given in the footnotes of Tables 1, 3, and 4 were calculated from the main distribution curves without considering the well-resolved peaks of cyclic oligomers. When the separate peaks of cyclic oligomers were taken into account, the M_ns were 40−50% lower.

Results and Discussion

Syntheses of Hyperbranched Poly(ether ketone)s. The trifunctional monomer **1**[12] was prepared from fluorobenzene and 5-hydroxyisophthalic acid via 5-methoxyisophthalic acid and 5-methoxyisophthaloyl chloride. The K_2CO_3-promoted polycondensations of **1** were conducted in three different solvents: DMSO, NMP, and sulfolane. The liberated water was removed by azeotropic distillation either with toluene or with xylene. These six experiments and their results are summarized in Table 1. DMSO was used as reaction medium for the first pair of experiments because this solvent is known to give optimum results when poly(ether sulfone)s are prepared from diphenols and DFDPS. However, the molecular weight of the poly(ether ketone) **2** obtained from the first polycondensation was low. When toluene was replaced by xylene, the reaction temperature rose by 30 °C, and a somewhat higher molecular weight was achieved (no. 2, Table 1). The MALDI−TOF mass spectra indicated the formation of cycles as the predominant reaction products, at least in the mass range below 4000 and 6000 Da, respectively (Figure 1). They also indicate a higher fraction of cycles in the sample with the higher molecular weight. At this point it should be mentioned that the symbols **C5**, **C10,** etc. used in Figures 1 and 2 indicate a cyclic structure and the total number of repeat units. It should also be mentioned that the total number of repeat units does not necessarily parallel the ring size (see discussion below).

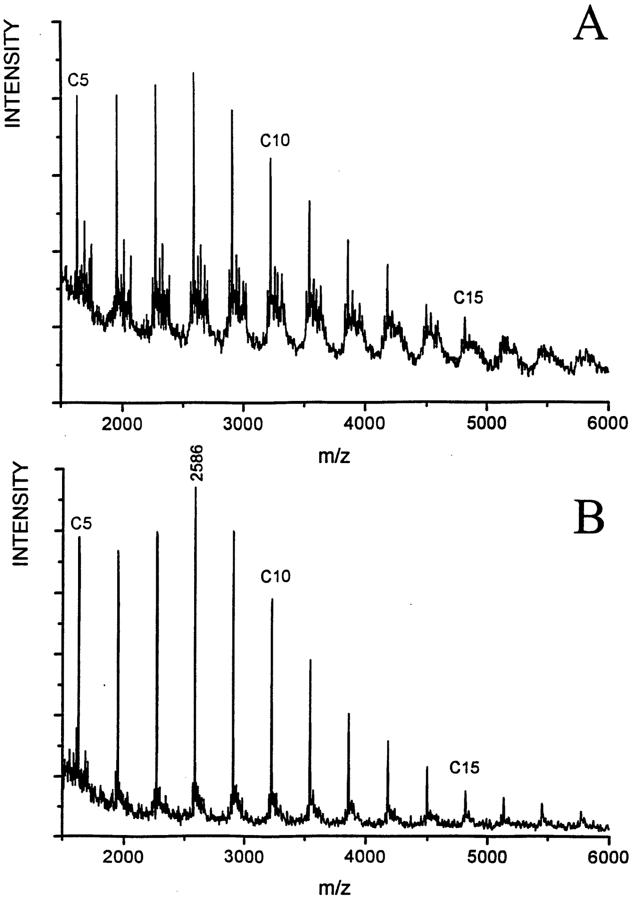


Figure 1. MALDI−TOF mass spectra of the hyperbranched poly(ether ketone) **2**, no. 1, Table 1 (A) and no. 2, Table 1 (B).

In NMP the molecular weights of the poly(ether ketone)s (nos. 3 and 4) were slightly lower than those obtained in DMSO. MALDI−TOF mass spectroscopy indicated a predominant formation of cyclic poly(ether ketone)s in both samples in the mass range below 6000 Da. Again, the content of cycles increased slightly with the higher molecular weights.

With sulfolane the temperatures could be raised to 150−155 and 170−175 °C, respectively, but the lowest molecular weights of this work were obtained in this solvent (nos. 5 and 6, Table 1). Particularly interesting proved the MALDI−TOF mass spectra of these samples. As illustrated in Figure 2, the polycondensations performed in sulfolane involved less side reactions than all other methods and reaction conditions studied in this work. Furthermore, the highest signal-to-noise ratio was

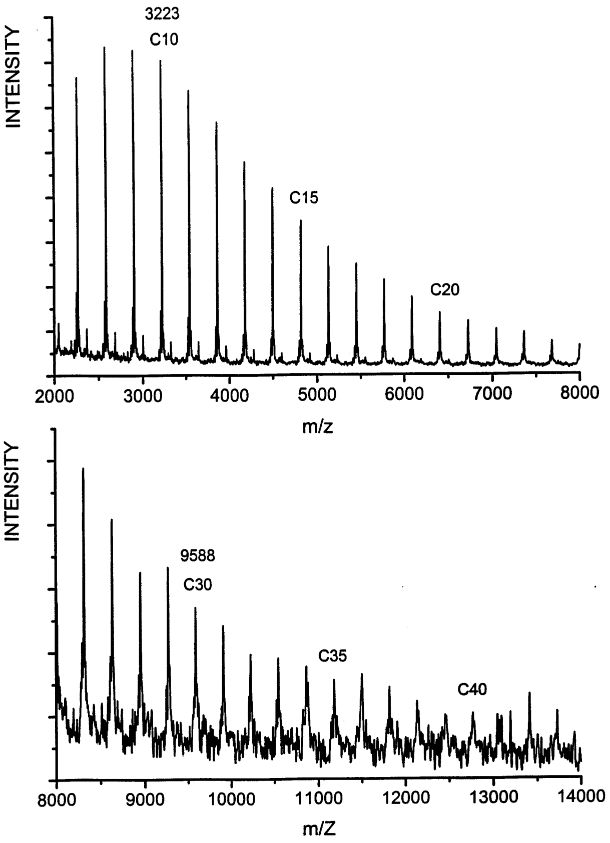


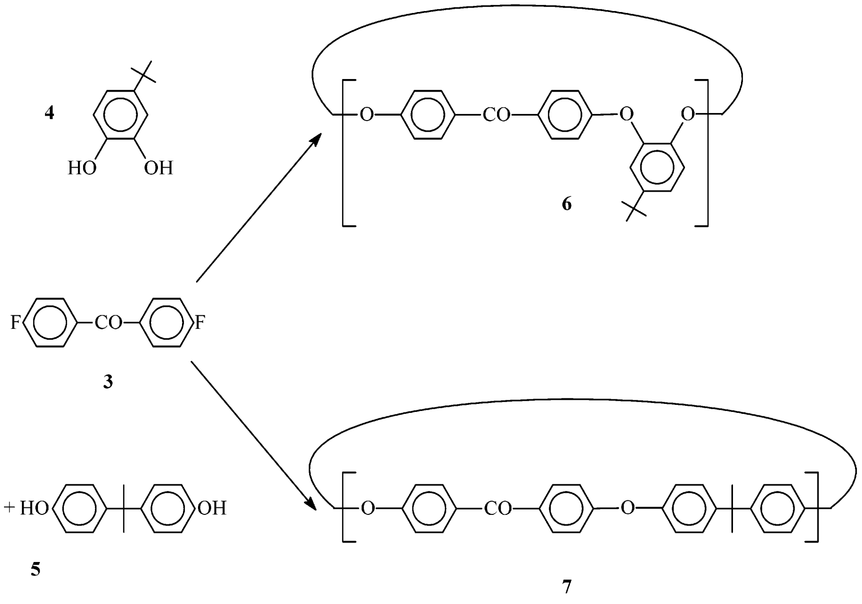
Figure 2. MALDI−TOF mass spectrum of the hyperbranched poly(ether ketone) **2**, no. 5, Table 1.

achieved allowing for the detection of cycles up to 14 000 Da. Considering the low molecular weights of these samples, these results allow two important conclusions. First, cyclization reactions were decisive for the limitation of the chain growth. Second, almost all reaction products have cyclic structure as formulated in Scheme 1.

In this context, it should be mentioned that the M_n and M_w values listed in the footnotes of Table 1 were evaluated from the main curve of the chromatogram, whereby the well-resolved two or three peaks of cyclic oligomers were not taken into account. These molecular weight data are not highly accurate anyway because linear polystyrene standards were used for the calibration of cyclic and hyperbranched poly(ether ketone)s, which certainly possess a lower hydrodynamic volume. Miller et al.[12] reported M_n values of 7410 and 9040 Da with M_w values of 11 300 and 19 100 Da which were also derived from polystyrene-calibrated SEC measurements. These values are slightly higher than those found in this work but fall into the same order of magnitude. It is remarkable that in all cases a high molecular weight tail is lacking in the elution curves with the consequence of relatively low polydispersities, when compared to the prediction of Flory's cascade theory.

Three more experiments were conducted in such a way that small amounts of 4,4′-difluorodiphenyl sulfone (DFDPS) were added to **1**. Since DFDPS is more reactive than fluoroketones, its addition should have two consequences. First, it modifies the structure in direction of star-shaped polymers containing a diphenyl sulfone center as illustrated in Scheme 2. Second, DFDPS should act as chain terminator and allow for a control of the average molecular weight via the feed ratio. This effect has previously been demonstrated in syntheses of hyperbranched polyesters and poly(ester amide)s.[16−18] Because of the low molecular weights obtained in the absence of any chain terminator (no. 2, Table 2), a strong propagation controlling effects of DFDPS was, of course, not expected in this study. Nonetheless, the viscosity data listed in Table 2 indicate the expected trend. However, the main purpose of this study was to find out (A) if the MALDI−TOF mass spectra prove the formation of the star-shaped polymers of structure **S** (Scheme 3) and (B) if the addition of DFDPS suppresses the formation of cycles. As exemplarily illustrated by the mass spectrum of Figure 3, the hyperbranched polymers of structure **S** were, indeed, the main reaction products, and the formation of cycles was not completely prevented even with the highest feed ratio of DFDPS. These MALDI−TOF spectra also indicated incomplete conversion and more than expected side reactions.

Scheme 3



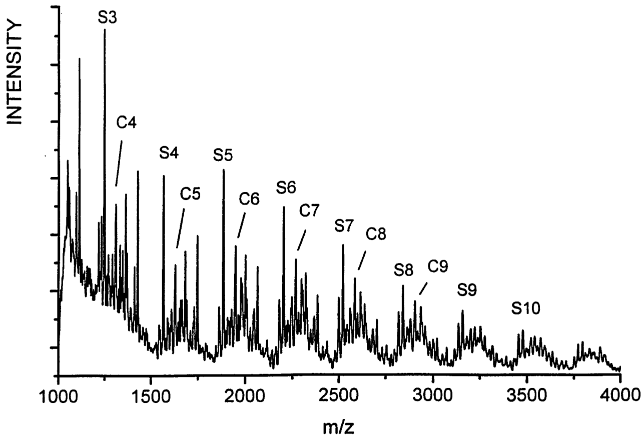


Figure 3. MALDI−TOF mass spectrum of the poly(ether ketone) **2**, no. 4, Table 2.

Polycondensations of DFBP (**3**). For the “linear polycondensations” of DFBP two different diphenols were used as comonomers to study the influence of their structure on cyclization tendency and chain growth (Scheme 3). 4-*tert*-Butylcatechol was selected because a high cyclization tendency was expected and because the resulting poly(ether ketone)s **6** should have a good solubility in nonacidic organic solvents. Bisphenol A was used because it is a technical monomer and because a significantly lower cyclization tendency was expected, together with a good solubility of the poly(ether ketone)s **7** in organic solvents.

The same reaction conditions were used as for the polycondensations of monomer **1**. The results obtained from 4-*tert*-butylcatechol are summarized in Table 3. When the stoichiometry was varied in such a way that DFBP was used in an excess of 1 mol %, slightly lower molecular weights were obtained. Nonetheless, the viscosity and molecular weight data were nearly the same as those measured for the hyperbranched polymers **1**. With bisphenol A higher viscosities and molecular weights were obtained, as expected (Table 4). No significant difference between the three reaction media was found.

The MALDI−TOF mass spectra of the poly(ether ketone)s **6** displayed nothing but the peaks of cycles, when exactly stoichiometric quantities of both monomers were used. The peaks of the cycles were observable up to 11 000 Da (Figure 4). However, when a 1 mol % excess of DFBP was used (nos. 5 and 6, Table 3), weak peaks of linear chain having two C−F end groups were detectable. These findings prove again[18] that MALDI−TOF mass spectra measured up to 10^4 Da or beyond are sensitive to slight changes in the stoichiometry. Analogous results were obtained from bisphenol A. The mass spectra of the poly(ether ketone)s **7** exclusively displayed mass peaks of cycles up to 10^4 Da. These observations indicate close analogy between the polycondensations of di- and trifunctional monomers. In both cases cyclization played a key role for the limitation of the chain growth and thus for the structure of the reaction products.

A remarkable observation concerns the doping of the cyclic poly(ether ketone)s. In all spectra of polymers **6** and **7** the strong peaks resulted from H-doping, although K trifluoroacetate was added when the irradiation targets were prepared. Only weak peaks of Na and K-doped cycles were detectable in the mass range below 5000 Da (Figure 4). In contrast, only K-doped peaks were observed for the hyperbranched cycles of structure **2**.

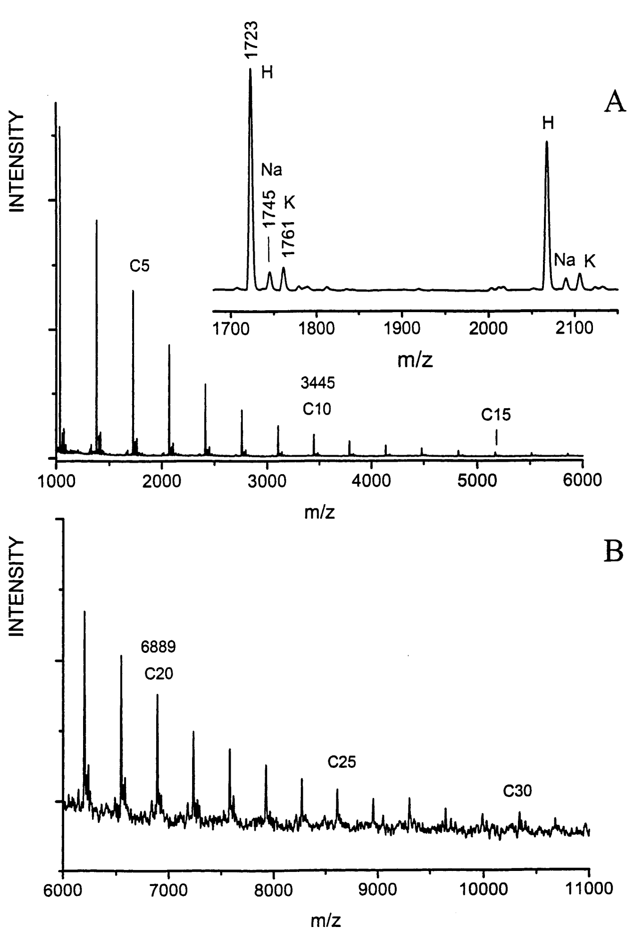


Figure 4. MALDI−TOF mass spectrum of the poly(ether ketone) **6**, no. 6, Table 3.

With regard to all polycondensations discussed above it should be mentioned that a kinetically controlled course was assumed for the following reasons. First, Carlier et al.[19] have studied the influence of KF on the stability of poly(ether sulfone)s and poly(ether ketone)s with respect to transetherification and “backbiting degradation”. Below 280 °C no cleavage of the polyether chains was found. Equilibrations of poly(ether ketone)s and poly(ether sulfone)s at temperatures around 160 ± 10 °C were studied by Colquhoun and co-workers.[20,21] Yet, only CsF has proven to be a sufficiently active catalyst. As will be reported elsewhere in more detail, we have found that the cyclic poly(ether ketone)s nos. 3, 5, and 6, Table 1, undergo ring-opening polymerization when treated with CsF in NMP at 180 °C. This finding clearly proves that these cycles do not represent a thermodynamically controlled reaction product.

Finally, the molecular weight distributions deserve a short discussion. In Flory’s classical theory of linear polycondensations and in his cascade theory both the frequency distribution and the mass distribution are monomodal.[2,22] The fraction of linear oligomers or of hyperbranched oligomers tends toward zero when this conversion approaches 100%. Polydispersities around 2.0 were calculated for linear polycondensates and polydispersities up to infinity for hyperbranched polymerizations.[22] However, in KCPs of linear or “ab_2” monomers the cyclic oligomers do not vanish with increasing conversion, and thus, bimodal mass distribu-

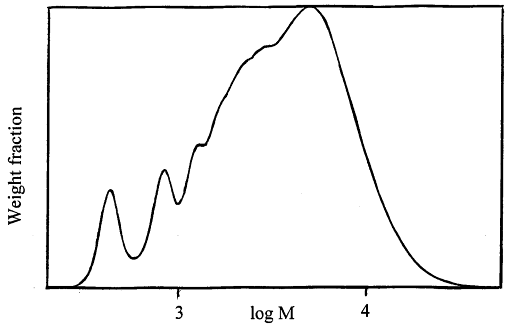


Figure 5. SEC elution curve of the cyclic hyperbranced poly(ether ketone), no. 6, Table 1.

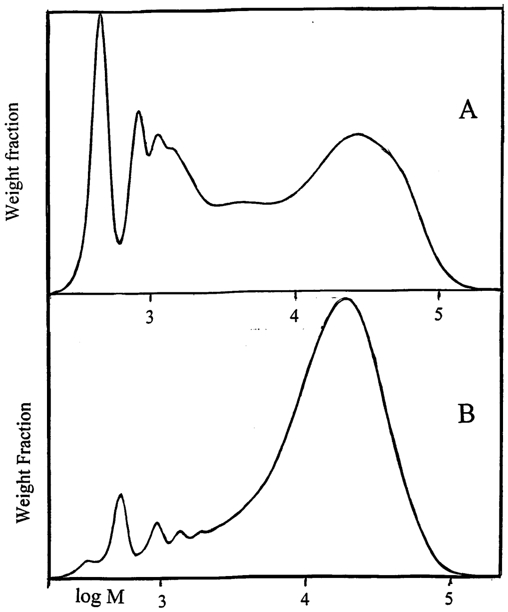


Figure 6. SEC elution curves of (A) the poly(ether ketone), no. 6, Table 3, derived from 4-*tert*-butylcatechol, and (B) the poly(ether ketone), no. 3, Table 4, derived from bisphenol A.

tion should result with a first maximum at the cyclic dimer (or tetramer, when the cyclization of the dimer is for steric reasons unfavorable). The intensity of this first maximum depends, of course, on the cyclization tendency, i.e., on the V_p/V_c ratio in eq 1.

$$\overline{\mathrm{DP}} = \frac{1}{1 - p\left(1 - \frac{1}{X^{\alpha}}\right)} \tag{1}$$

where X = constant > 1.0 and $\alpha = V_p/V_c$, with V_p and V_c being the propagation and cyclization rates. In fact, bimodal mass distributions of hyperbranched polymers have been reported[15] without satisfactory explanation. We have recently demonstrated for poly(ether sulfone)s[23] and poly(bisphenol A carbonate)s[24] that a high tendency of cyclization results in bimodal mass distributions. The SEC curves obtained in this work agree with these previous results and their interpretations. Figure 5 illustrates the broad but still monomodal mass distribution of a cyclic hyperbranched poly(ether ketone) obtained in sulfolane which is representative for all cyclic poly(ether ketone)s listed in Table 1. Figure 6 displays the mass distributions of poly(ether ketone)s derived from 4-*tert*-butylcatechol or bisphenol A, illustrating the tendency toward a bimodal mass distribution. (The resolution of individual cyclic oligomers is not taken into account for the definition of bimodality.) These examples also demonstrate that the large difference between polydispersities of linear and hyperbranched polymers predicted by Flory is reduced under the influence of cyclization. Cyclization may enhance the PD of "a-a" + "b-b" polymers to values above 10,[23,24] whereas the PDs of hyperbranched polymers may be limited to lower values by cyclization. More detailed studies of the influence of cyclization on molecular weight distributions of polycondensates are certainly desirable but were beyond the scope of this work.

Discussion

When the work of Miller et al.[12] is considered together with the syntheses presented in this work, the hyperbranched poly(ether ketone)s derived from monomer **1** have been prepared in four different reaction media. Furthermore, the temperature and the HF acceptor used for the polycondensations of **1** were varied. Interestingly, all these syntheses have in common that a maximum M_n in the range 8000−9000 Da was obtained. Furthermore, the comparison of the experiments nos. 1 and 2 in Table 1 indicates that the fraction of cycles increases with higher molecular weights (i.e., with higher conversion). Therefore, these results suggest that a KCP of "ab$_n$" monomers obey eq 1 analogous to a KCP of "ab" monomers (linear case). This means that (I) cyclization competes with propagation at any stage of the polycondensation, (II) cyclization limits the chain growth, and (III) at 100% conversion all reaction products are cyclic (having hyperbranched side chains in the "ab$_n$" case). Although the influence of cyclization reactions on linear polycondensations and "ab$_n$" polycondensations is qualitatively the same, there are characteristic differences which will shortly be discussed. For this purpose, it is useful to compare the effect of increasing conversion in both cases. The molar concentration of noncyclic active species $[\mathrm{S_{ac}}]$ (including all monomers) decreases with higher conversions according to eq 2.

$$[\mathrm{S_{ac}}]_p = [\mathrm{S_{ac}}]_0(1 - p) = [\mathrm{a}]_0(1 - p) \tag{2}$$

In both the linear and hyperbranched case, the definition of $\mathrm{S_{ac}}$ is based on the presence of "a" groups, and thus, $[\mathrm{a}]_p$ shows the same dependence on p as the concentration of $\mathrm{S_{ac}}$ molecules. Equation 2 indicates a characteristic and important property of any kind of step-growth polymerization, namely the "self-dilution" of the active species with increasing conversion. This steady dilution of the active species lowers the V_p/V_c ratio and favors the formation of cycles as outlined in eqs 3−5 for linear polycondensations

$$V_{\mathrm{pl}} = k_{\mathrm{pl}}[\mathrm{S_{ac}}]^2(1 - p)^2 \tag{3}$$

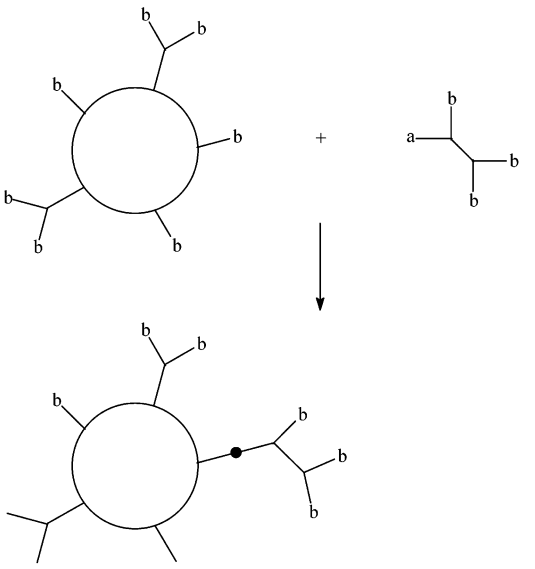
$$V_{\mathrm{cl}} = k_{\mathrm{cl}}[\mathrm{S_{ac}}] \tag{4}$$

$$V_{\mathrm{pl}}/V_{\mathrm{cl}} = k_{\mathrm{pl}}/k_{\mathrm{cl}}[\mathrm{S_{ac}}]_0(1 - p)$$

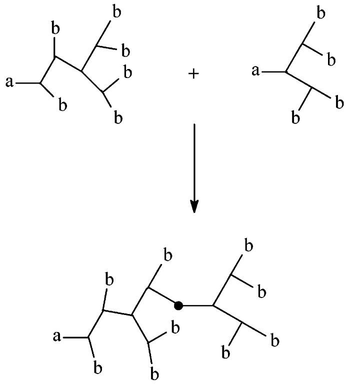
where the indices "pl" and "cl" mean propagation or cyclization of the linear species.

A similar trend, but with different kinetics, exists in the hyperbranched case. Whereas in linear polyconden-

Scheme 4



Scheme 5



sation the "b" groups disappear together with the "a" groups (eq 6)

$$[S_{ac}]_p = [a]_p = [b]_p \tag{6}$$

only 50% of the "b" groups will disappear at 100% conversion in the hyperbranched case (eq 7).

$$[b]_p = [S_{ac}]_0(1 - p) + [S_{ac}]_0 \tag{7}$$

This marks an important difference between "ab" and "ab$_n$" polycondensations with the following consequences. All cycles formed in a linear polycondensation are dead species from the viewpoint of chemical reactions and just play the role of solvent. However, in the hyperbranched case the cycles are reactive species due to their "b" groups (although they are not included in the definition of S$_{ac}$). Therefore, they can react with monomers and oligomers of the S$_{ac}$ type, whereby the DP of the entire molecule increases, whereas the ring size remains unchanged (Scheme 4). This type of coupling steps prevents the S$_{ac}$ species from cyclization, and it also represents a normal propagation step because it enhances the DP. However, this type of propagation reaction enhances the molar ratio of hyperbranched polymers having a cyclic core vs those having a tree-shaped structure (S$_{ac}$), in contrast to the propagation reaction formulated in Scheme 5. Therefore, "ab$_n$" polycondensations involve two types of propagation reactions in contrast to linear polycondensations, and the exponent "α" in eq 1 may be more precisely defined by eq 9.

$$N_b = DP + 1 \quad \text{in noncyclic hyperbranched polymers} \tag{8a}$$

$$N_b = DP \quad \text{in cyclic in a hyperbranched polymers} \tag{8b}$$

$$\alpha = (V_{pc} + V_{pt})/V_c \tag{9}$$

where V_{pc} = propagation rate according to Scheme 3 and V_{pt} = propagation rate according to Scheme 4. Particularly interesting is again the influence of increasing conversion. Whereas the molar concentration of the tree-shaped S$_{ac}$ molecules rapidly decreases at higher conversions, the number of cyclic species slowly increases. Therefore, increasing conversion enhances the V_{pc}/V_{pt} ratio. The importance of the chain growth formulated in Scheme 4 should be illustrated by the following hypothetical experiment. Assuming that only one single cyclization reaction occurs in an early stage of an "ab$_n$" polycondensation, 100% conversion will necessarily yield one giant hyperbranched polymer having a cyclic core. Therefore, one single cyclization suffices to satisfy point III in the above outlined hypothesis.

Another aspect of the propagation formulated in Scheme 4 concerns the ring size distribution. In linear polycondensations, high conversions favor the formation of large cycles. Yet, the chain growth according to Scheme 4 hinders the formation of big tree-shaped polymers which can form large cycles. Therefore, the average DPs of the cyclic cores ($\overline{DP}_{cc}$) in hyperbranched polymers will be lower than the $\overline{DP}$s of cycles in linear systems ($\overline{DP}_{cc} < \overline{DP}_{cl}$).

Furthermore, the influence of the conversion on the rate constants k_p and k_c needs a short discussion. If diffusion effects are neglected, k_p should be almost independent of the conversion, regardless if "ab" or "ab$_n$" monomers are polymerized. However, k_c depends on the distance between a and b groups (d_{ab}), which increases with the DP and, thus, with the conversion. In the linear case, it has been shown for flexible chains,[3] where the chain ends obey a Gaussian statistic, that k_c decreases with DP$^{-3/2}$. The exponents will tend to infinity for rigid chains and tend toward 0 for "monomers" with high cyclization tendency. In any case, each new monomer attached to an oligomer or polymer will influence the chain length by a constant value Δl which does not depend on DP and conversion. In the "ab$_n$" case, any new monomer has the choice between all "b" groups of an oligomer or polymer. The number of "b" groups in hyperbranched polymers is given by eq 8a or 8b, and thus, the net effect of a new monomer on Δl of a noncyclic hyperbranched polymer decreases with 1/(DP + 1). In other words, a hyperbranched polymer is more compact than linear chains, it has shorter "ab" distances than linear chains, and this difference increases with DP and conversion. Hence, higher conversions favor cyclization of hyperbranched polymers via k_c more than cyclization of linear chains. All these considerations indicate that the influence of cyclization reactions on the course of "ab$_n$" polycondensations should be higher than in the linear case and certainly not lower in agreement with the experimental results presented above.

Moreover, the effect of chain terminators/star centers should be discussed. In eq 10

$$\overline{\mathrm{DP}} = \frac{1+r}{2r(1-p)+1-r} - 1 \qquad (10)$$

with $r = [\mathrm{a}]$ of $[\mathrm{b}]_0$; $[\mathrm{b}]_0$ includes the "b" groups of the chain terminator. Flory[2] has formulated the influence of a bifunctional chain terminator on the polycondensation of "aa" + "bb" monomers. An excess of the "bb" monomer has the same consequence. Taking into account a permanent competition of cyclization and propagation, eq 10 should be substituted by eq 11.

$$\overline{\mathrm{DP}} = \frac{1+r}{2r\left[1-p\left(1-\dfrac{1}{X^{\alpha}}\right)\right]+1-r} - 1 \qquad (11)$$

This equation indicates that the influence of the chain terminator on the molecular weight increases with higher V_p/V_c ratios, and it vanishes in systems with high cyclization tendency. Furthermore, the chain terminator cannot completely suppress ring closure reactions (unless it prevents any propagation), in agreement with the above experimental results.

In this context, it should be mentioned that Dusek and co-workers[6] developed a mathematical model of "ab$_2$" polycondensations including cyclization reactions. However, this mathematical model was presented in connection with a thermodynamically controlled synthesis of a hyperbranched polyester, and the postulated high fraction of cycles with high conversion ($p \geq 0.95$) was not proven. More recently, Galina and co-workers[25,26] reported on a different mathematical modeling of "ab$_2$" polycondensations comparing courses with and without cyclization. Yet, this computer modeling was performed without any relationship to concrete experiments. In contrast to the experimental results presented in this work and by other authors, it was concluded that large hyperbranched molecules are particularly prone to cyclization due to the larger number of "b" functional group. It seems that at the current state of affairs both sufficient experimental information about cyclization and a satisfactory theoretical model are still lacking.

Conclusion

The results of this work combined with those of other research groups[4−6,12] clearly demonstrate that cyclization reactions play a decisive role in polycondensations of "ab$_n$" monomers. Although kinetic details of "ab" and "ab$_n$" polycondensations are different, the influence of cyclization reactions on both types of KCPs shows interesting analogies. First, cyclization competes with propagation at any concentration and at any stage of the polycondensation. Second, the formation of cycles limits the chain growth. Third, at 100% conversion all reaction products have a cyclic structure. In the case of hyperbranched polymers, the structure of the endproduct is best described as star-shaped polymers having a cyclic core and hyperbranched star arms. The tree-shaped oligomers and polymers depicted in numerous publications (including those of the first author) represent an intermediate state and indicate incomplete conversions (or side reactions) quite analogous to the linear chains in a polycondensation of "ab" or "aa + bb" monomers.

Finally, it should be emphasized that a nearly quantitative cyclization of polycondensations of "ab$_n$" monomers at high conversions has two interesting consequences. First, such polycondensations allow for syntheses of star-shaped molecules with cyclic core and pendant functional groups in a "one-pot procedure". Second, it is obvious from the results of this work and from other publications[4−6] that Flory's cascade theory may at best be considered as a small segment of the entire reaction pathway underlying a polycondensation of "ab$_n$" monomers. The cascade theory is not an adequate description of the entire polycondensation process, and in several aspects, such as the structure of the reaction products or the unlimited chain growth and the unlimited growth of the polydispersity, it is even misleading when applied to real polycondensations.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter IX.

(2) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.

(3) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.

(4) Martinez, C. A.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

(5) Gooden, J. K.; Gross, M. C.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180.

(6) Dusek, K.; Somvarsky, J.; Smrckova, M.; Simonsick, W. J., Jr.; Wilczek, L. *Polym. Bull. (Berlin)* **1999**, *42*, 489.

(7) Park, D.; Feast, W. J. *Macromolecules* **2001**, *34*, 2048.

(8) Burgath, A.; Sunder, A.; Frey, H. *Macromol. Chem. Phys.* **2000**, *201*, 782.

(9) Kricheldorf, H. R.; Rabenstein, M.; Maskos, M.; Schmidt, M. *Macromolecules* **2001**, *34*, 713.

(10) Kricheldorf, H. R.; Böhme, S.; Schwarz, G. *Macromolecules* **2001**, *34*, 8879.

(11) Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Krüger, R.-P.; Schulz, G. *Macromolecules* **2001**, *34*, 8886.

(12) Miller, T. M.; Neenan, T. Y.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356.

(13) Chu, F.; Hawker, C. J. *Polym. Bull. (Berlin)* **1993**, *30*, 265.

(14) Hawker, C. J.; Chu, F. *Macromolecules* **1995**, *29*, 4370.

(15) Back, J.-B.; Quin, H.; Mather, P. T.; Tan, L.-S. *Macromolecules* **2002**, *35*, 4951.

(16) Kricheldorf, H. R.; Stöber, O.; Lübbers, D. *Macromolecules* **1995**, *28*, 2118.

(17) Kricheldorf, H. R.; Löhden, G. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 1915.

(18) Kricheldorf, H. R.; Stukenbrock, T. *Polymer* **1997**, *38*, 3373.

(19) Carlier, U.; Devaux, J.; Legras, R.; McGrail, P. T. *Polymer* **1993**, *34*, 167.

(20) Ben-Houda, A.; Baxter, I.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Williams, D. J. *Chem. Commun.* **1997**, 1533.

(21) Baxter, I.; Ben-Haida, A.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Williams, D. J. *Chem. Commun.* **1998**, 2213.

(22) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter VIII.

(23) Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Krüger, R.-P.; Schulz, G. *Polymer*, in press.

(24) Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Schultz, C.-L. *Macromol. Rapid Commun.* 2002.

(25) Galina, H.; Lechowicz, J. B.; Kazzmarski, K. *Macromol. Theory Simmul.* **2001**, *10*, 174.

(26) Galina, H.; Lechowicz, J. B.; Walczak, M. *Macromolecules* **2002**, *35*, 3253.

MA021799X