Multicyclic Poly(ether ketone)s Obtained by Polycondensation of 2,6,4′-Trifluorobenzophenone with Various Diphenols

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ABSTRACT: 2,6,4′-Trifluorobenzophenone (TFB) was polycondensed with silylated 4,4′-dihydroxybiphenyl (DHBP) or silylated bisphenol A in *N*-methylpyrrolidone by means of K_2CO_3 as catalyst and HF acceptor. At constant concentration (0.08 mol/L) the feed ratio was varied from 1.0/1.0 to 1.0/1.5. For polycondensations of DHBP cross-linking was observed for feed ratios above 1.0/1.1, whereas no gelation occurred with bisphenol A regardless of the feed ratio. The MALDI−TOF mass spectrometry proved the formation of cyclic, bicyclic and multicyclic oligomers and polymers in all cases. At a feed ratio of 1.00/1.48, multicyclces free of functional (end)groups were the only reaction products. However, gelation was only avoided when the initial concentration of TFB was lowered to 0.04 mol/L. Under these optimized conditions three more diphenols resembling bisphenol A were polycondensed with TBP and multicycles free of functional groups were again obtained as predominant reaction products. SEC measurements proved the formation of broad, at least bimodal molecular weight distributions containing a high molar mass fraction in the range of 10^6−10^9 Da.

Introduction

Three-dimensional polycondensations (Flory's nomenclature) or "$a_2 + b_3$" polycondensations are stage-growth polymerizations of difunctional (a_2) and trifunctional (b_3) monomers. A first systematic experimental and theoretical study of such polycondensations was presented by Flory,[1,2] including the earlier work of Kienle et al..[3,4] Flory's work concentrated on the influence of the conversion on the gelation point using equifunctional monomer mixtures ($a_2/b_3 = 1.5/1.0$). More recently "$a_2 + b_3$" polycondensations found increasing interest as source of hyperbranched polymers.[5−20] To avoid gelation despite high conversions (> 99%), equimolar monomer mixtures or stoichiometries close to this feed ratio were studied. However, most authors did not care about the influence of cyclization reactions.

Recently we have started a broader study of "$a_2 + b_3$" polycondensations yielding aromatic polyethers.[21−24] Difunctional or trifunctional activated chloro- or fluoroaromats were used as reaction partners of di- or triphenols. The feed ratio of a_2/b_3 monomers was varied from 1.0/1.0 to 1.5/1.0 to detect the dependence of the gelation point on the stoichiometry under conditions allowing for a quantitative reaction of the underrepresented functional groups. MALDI−TOF mass spectrometry (MS) revealed in all cases the presence of large amounts of cyclic, bicyclic, and even multicyclic oligomers and polymers. In systems with high cyclization tendencies, almost no hyperbranched or cross-linked polymers were formed. To elucidate the influence of the monomer structure on the cyclization tendency, the chemical structures of both holoaromats and phenols need to be varied over a broad range. In this context the present work was aimed at studying polycondensations of 2,6,4′-trifluorobenzophenone (TFB) with three silylated diphenols (**1**, **2**, and **3**). These diphenols were selected with the expectation that the cyclization tendency increases with decreasing "linearity" and, thus, increases in the order **1** < **2** < **3**. Furthermore, the results of this work should be compared with those of a parallel study in which 1,3,5-tris(4-fluorobenzoyl)benzene, TFBB, was used as reaction partner of **1** and **3**. A particular interesting aspect of these studies are the syntheses of multicyclic polymers (with or without functional end groups) which represent a novel polymer architecture.

Experimental Section

Materials. 2,6-Difluorobenzoyl chloride, fluorobenzol, 4,4′-dihydroxybiphenyl, bisphenol A, α,α-bis(4-hydroxyphenyl)-ethylbenzene, and 1,1-bis(4-hydroxyphenyl) cyclohexane were purchased from Aldrich Co. (Milwaukee, WI) and used as received. Potassium carbonate p.a. was purchased from Merck KF (Darmstadt, Germany) and dried at 150 °C in vacuo. *N*-Methylpyrrolidone (NMP) was twice distilled in vacuo.

2,6,4′-Trifluorobenzophenone (TFB). 2,6-Difluorobenzoyl chloride (0.2 mol) was dissolved in fluorobenzene (400 mL) and aluminum chloride (0.3 mol) was added portionwise with cooling. The reaction mixture was stirred overnight at 20 °C and refluxed for 2 h. The reaction mixture was then concentrated, part of the fluorobenzene was distilled off and the remaining concentrated solution was diluted with dichloromethane (400 mL). This solution was washed successively with 5% aqueous NaOH, 5% hydrochloric acid, and twice with water. Finally, it was dried with Na_2SO_4 and concentrated in vacuo. Portionwise addition of ligroin under cooling with ice caused crystallization of the product which was completed in a refrigerator overnight. Yield 65%; mp 62−64 °C.

Anal. Calcd for $C_{13}H_7F_3O$ (236.2): C, 66.11; H, 2.94; F, 24.13. Found: C, 65.81; H, 3.14; F, 24.60.

The IR spectrum (KBr) displays 10 sharp bands of nearly equal intensity at 797, 852, 929, 1005, 1235, 1283, 1465, 1600, 1624, and 1665 cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.01$ (t, 2H), 7.16 (t, 2H), 7.46 (quintett, 1H), 7.90 (t, 2H) ppm.

Silylation of Diphenols. All diphenols were silylated by heating with a 50 mol % excess of hexamethyldisilazane in refluxing xylene for 24 h. Afterward, the reaction mixtures were concentrated in vacuo, and the products were isolated by distillation over a short path apparatus in a vacuum of 10^{-2} mbar. All silylated diphenols were described in the literature. Their structure and purity were checked by ^1H NMR spectroscopy.

Polycondensations. A. Equimolar Monomer Mixture. Silylated bisphenol A (4.0 mmol), TFB (4.0 mmol), and dry

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Table 1. Polycondensations of TFB with Silylated 4,4′-Dihydroxybiphenyl (1, DHBP) in NMP at 160−165 °C

expt no.	TFB/DHBP(**1**)	yield[a] (%)	η_{inh}[b] (dL/g)	reaction products (MALDI−TOF)
1	1.0/1.0	98	0.20	**CN**, **B_1CN**
2	1.0/1.1	97	0.38	**B_1CN**, **B_2CN**, **B_3CN**
3	1.0/1.2	partially cross-linked		
4	1.0/1.3	cross-linked	cross-linked	

[a] After reprecipitation. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

Table 2. Polycondensations of TFB with Silylated Bisphenol-A (3) in NMP at 160−165 °C/48 h

expt no.	TFB/**3**	TFB/NMP	yield (%)	η_{inh}[a] (dL/g)	reaction products[b] (MALDI−TOF)
1	1.0/1.00	4/50	88	0.12	**CN**, **B_1CN**
2	1.0/1.05	4/50	92	0.13	**CN**, **B_1CN**, **B_2CN**
3	1.0/1.10	4/50	96	0.13	**CN**, **B_1CN**, **B_2CN**, **B_3CN**
4	1.0/1.20	4/50	100	0.14	**CN**, **B_1CN-B_4CN**
5	1.0/1.30	4/50	100	0.17	**B_1CN−B_5CN**
6	1.0/1.40	4/50	100	0.44	**B_1CN−B_7CN**, **B_nC2n**
7	1.0/1.48	4/50		0.53[c]	**B_nC2*n***, **B_nC(2*n*−1)−OH**,[c] **B_nC(2*n*+1)**
8	1.0/1.50	4/50		0.50[c]	**B_nC2*n***, **B_nC(2*n*−1)−OH**[c]
9[d]	1.0/1.48	4/100	100	0.18	**B_nC2n**, **B_nC(2n-1)**-OH, **B_nC(2*n*+1)**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 8:1). [b] **CN** means simple cycles, **B_1CN** means bicycles, **B_nCN** means multicycles with **N** = number of repeat units. [c] Soluble fraction. [d] 48 h at 180−185 °C.

K_2CO_3 (5.0 mmol) were weighed (under dry nitrogen) in a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet and gas-outlet tubes. Dry NMP (50 mL) was added, and the reaction vessel was placed into an oil bath preheated to 100 °C. The temperature was rapidly raised to 160 °C and maintained for 48 h. The liberated hexamethyldisiloxane was removed with a slow stream of dry nitrogen. After cooling, the reaction mixtures were poured into water, the polymers were isolated by filtration and dried at 120 °C in vacuo.

Analogous polycondensations were conducted with increasing amounts of silylated bisphenol A and K_2CO_3 (see Table 2). The polycondensations of other silylated diphenols were performed analogously.

B. Equifunctional Monomer Mixtures. Silylated bisphenol A (6.0 mmol), TFB (4.0 mmol), and K_2CO_3 (7.0 mmol) were weighed on a cylindrical glass reactor and dry NMP (100 mL) was added. The polycondensation was performed at 160−165 °C for 48 h. Afterward, part of the NMP was removed in vacuo, and the remaining reaction mixture was worked up as described above.

Measurements. The inherent viscosities were measured in a dichloromethane/trifluoroacetic acid mixture (volume ratio 8:1) using an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes. The 100,4 MHz ^{13}C NMR spectra were recorded on the same NMR spectrometer in 10 mm o.d. sample tubes. $CDCl_3$ containing TFA (volume ratio 8:1) and TMS served as solvent and shift reference. The MALDI−TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and K−trifluoroacetate as dopant. For the SEC measurements two different procedures were applied. For procedure I, an apparatus of Polymer Laboratories containing RI detector "Shodex RI 101" was used. A combination of three PL mixed-bed-columns allowing for the resolution of molar masses up to 7×10^6 Da was used. Chloroform served as eluent and commercial polystyrene standards for calibration. For procedure II, a Hewlett-Packard HP 1050 apparatus was used with CH_2Cl_2 as eluent. A combination of five Merck columns (trade number 4, 40, 400, 4000, 40000) was used, and the elution curves were evaluated with a triple detector TDA-301.

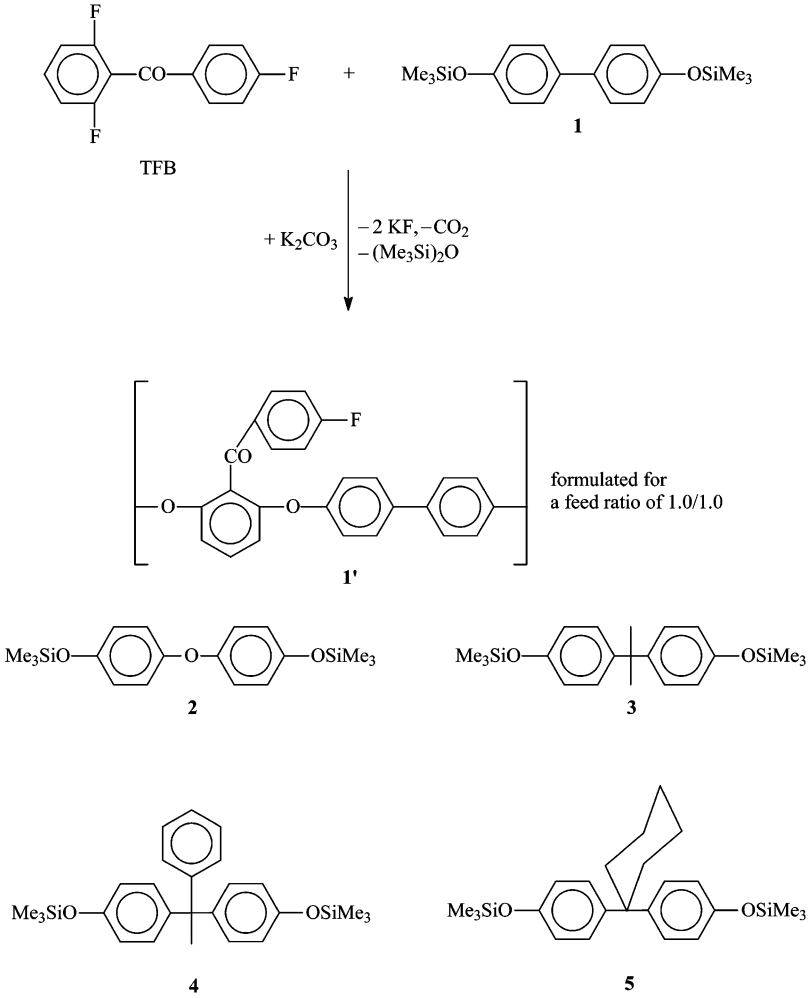
Results and Discussion

Polycondensations of Silylated 4,4′-Dihydroxybiphenyl (Scheme 1). 4,4′-Dihydroxybiphenyl is the most rigid and linear diphenol used in this work, and thus, the lowest cyclization tendency was expected for its polycondensations with TFB. On the basis of previous studies of linear polycondensations the reaction conditions were selected, so that quantitative conversions were obtained. The feed ratio was varied in steps of 10 mol % excess of the silylated diphenol (**1**) starting out from an equimolar monomer mixture (Table 1). Gelation was observed, when an excess of **1** above 10 mol % was applied. Characterization of the soluble polyethers showed that the molecular weights increased with higher feed ratios of **1**. Unfortunately, the MALDI−TOF mass spectra (MS) had poor signal-to-noise ratios. None the less, these MS proved a considerable cyclization tendency, because all species which were clearly detectable in the spectra of sample no. 2 were cycles, bicycles, or higher multicycles. Characterization by NMR spectra proved to be useless, because both ^{1}H and ^{13}C NMR signals were broad due to the presence of numerous species with slightly different structure. In the case of ^{1}H NMR spectra even end group signals (protons neighboring C−F) were not detectable. In the ^{13}C NMR spectra end group signals were detectable due to the typical C−F coupling. Yet, as demonstrated in Scheme 2 four different types of C−F will exist in these polyethers, so that a clear-cut identification requires cumbersome syntheses of model compounds. However, even after identification broad end group signals do not say anything about number and structure of the (multi)-cyclic species.

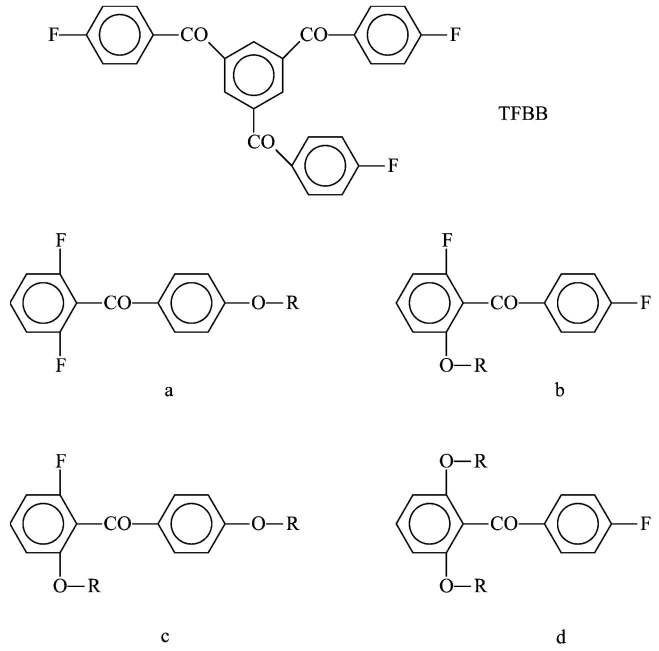
Since these polyethers were neither completely soluble in THF nor in chloroform or dichloromethane SEC measurements were not not feasible. However, for polymers with compact architecture an inherent viscosity of 0.38 dL/g indicates a relatively high M_w as discussed below for polyethers **3′** (Table 6).

At this point the terminology used in this work (and in previous studies) should be explained. The structures of bicycles and multicyclic oligomers or polymers are symbolized by the formula **B_nCN**. In this formula **N** denotes the degree of polymerization, and **C** stands for cycle. **B** means "bridge unit" and subscript ***n*** indicates the number of "bridge units" in a multicyclic molecule. The "bridge units" result from the incorporation of

Scheme 1



Scheme 2



additional “a_2” monomers (i.e., diphenols in this work). The schematic structural formulas presented in Schemes 3 and 4 should illustrate this terminology. When the feed ratio of b_3/a_2 monomers was higher than 1.0/1.5 (a_2/b_3 ratio below 1.5/1.0) the cyclic and multicyclic species contained one or more reactive C−F groups. Incorporation of more and more “bridge units” (resulting from a larger excess of diphenols) consumed C−F groups and created more cycles. In the case of an equifunctional polycondensation (theoretical a_2/b_3 ratio: 1.0/1.5) multicycles free of functional groups (Scheme 4) should be the only reaction products. However, it should be kept in mind that all cyclic and multicyclic species may consist of several isomers. As outlined in Scheme 5 even the simple cyclic species, **C2**, can theoretically exist in the form of four isomers. Since the MALDI−TOF mass spectrometry does not distinguish between isomers, the role of isomers will not be discussed here in more details.

Polycondensations of Silylated Bisphenol A. Since bisphenol A is an important technical monomer and far less expensive than 4,4′-dihydroxydiphenyl ether most polycondensations involving a nonlinear diphenol were conducted with silylated bisphenol A. At the same concentration already used for the polycondensations of **1** (0.08 mol TFB/L) the feed ratio was varied from 1.0/1.0 to 1.0/1.5, but in contrast to polycondensations of monomer **1**, partial gelation was only observed at the feed ratio of 1.0/1.48 and 1.0/1.5 (nos. 7 and 8, Table 2). When the monomer concentration was lowered by a factor of 2 (no. 9), cross-linking was completely avoided. These results clearly indicated that bisphenol A imparted a far higher cyclization tendency than 4,4′-dihydroxybiphenyl. The inherent viscosities showed a clear upward trend with increasing feed ratio of silylated bisphenol A, whereas the influence of the

Table 3. Masses of K^+-Doped Cyclic and Multicyclic Poly(ether ketone)s[a] (in Da) Resulting from Polycondensations of TFB and Silylated Bisphenol-A

N	CN	B_1CN	B_2CN	B_3CN	B_4CN	B_5CN	B_6CN	B_7CN	B_8CN
2	888.1	1076.4							
3	1312.6	1500.9							
4	1737.1	1925.4	2113.7						
5	2161.6	2349.9	2538.2						
6	2586.1	2774.4	2962.7	3151					
7	3010.6	3198.9	3387.2	3575.5					
8	3435.1	3623.4	3811.7	4000	4188.3				
9	3859.6	4047.9	4236.2	4424.5	4612.8				
10	4284.1	4472.4	4660.7	4849	5037.3	5225.6			
11	4708.6	4896.9	5085.2	5273.5	5461.8	5650.1			
12	5133.1	5321.4	5509.7	5698	5886.3	6074.6	6262.9		
13	5557.6	5745.9	5934.2	6122.5	6310.8	6499.1	6687.4		
14	5982.1	6170.4	6358.7	6547	6735.3	6923.6	7111.9	7300.2	
15	6406.6	6594.9	6783.2	6971.5	7159.8	7348.1	7536.4	7724.7	
16	6831.1	7019.4	7207.7	7396	7584.3	7772.6	7960.9	8149.2	8337.5
17	7255.6	7443.9	7632.2	7820.5	8008.8	8197.1	8385.4	8573.7	8762
18	7680.1	7868.4	8056.7	8245	8433.3	8621.6	8809.9	8998.2	9186.5
19	8104.6	8292.9	8481.2	8669.5	8857.8	9046.1	9234.4	9422.7	9611
20	8529.1	8717.4	8905.7	9094	9282.3	9470.6	9658.9	9847.2	10035.5

[a] Mass of the repeat unit = 424.5 Da.

Table 4. Polycondensations of TFB with Various Silylated Diphenols

expt no.	diphenol	TFB/diphenol	concn[a] (mmol/mL)	yield (%)	η_{inh}[b] (dL/g)	reaction products[c] (MALDI−TOF)
1	**2**	1.0/1.3	4/50		0.45	**CN**, **B_1CN−B_3CN**, **B_nC2n**
2	**2**	1.0/1.4	4/50	part. cross-linked		
3	**2**	1.0/1.5	4/50	part. cross-linked		
4	**2**	1.0/1.5	4/100		0.17	**B_nC2n**, **$B_nC(2n+1)$**
5	**4**	1.0/1.4	4/50		0.24	**B_1CN-$BnCN$**, **B_2CN**, **B_2C2n**
6	**4**	1.0/1.5	4/50	part. cross-linked		
7	**4**	1.0/1.5	4/100		0.14	**B_nC2n**, **$B_nC(2n+1)$**
8	**5**	1.0/1.4	4/50		0.49	**B_1CN-B_4CN**, **$BnC2n$**
9	**5**	1.0/1.5	4/50	part. cross-linked		
10	**5**	1.0/1.5	4/100		0.13	**B_2C2n**, **$B_nC(2n+1)$**

[a] Initial concentration of TFB. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 8:1). [c] CN means simple cycles, **B_1CN** means bicycles, **B_nCN** means multicycles with N = number of repeat units.

Table 5. Masses (Da) of H^+- or K^+-Doped Multicycles of Structure B_nC2n Prepared from TFB and Silylated Diphenols

	diphenol **2**		diphenol **4**		diphenol **5**	
DP	H^+	K^+	H^+	K^+	H^+	K^+
2	960.00	998.0	1256.4	1294.4	1158.0	1196.0
4	1918.0	1957.0	2511.8	2549.8	2315.0	2353.0
6	2878.0	2916.0	3707.2	3805.2	3472.0	3451.0
8	3837.0	3875.0	5022.6	5060.6	4629.0	4668.0
10	4796.0	4834.0	6278.0	6316.0	5786.0	5824.0

feed ratio on the yields was negligible.

The MALDI−TOF MS revealed the following trends. Even at the low feed ratio of 1.0/1.0, all species found in the MS had a cyclic or multicyclic structure as illustrated in Figure 1. This result underlines the high cyclization tendency of TFB, because in all $a_2 + b_3$ polycondensations of other monomers studied so far, linear and branched species free of cyclic elements were detectable, when a feed ratio of 1.0/1.0 was applied. A comparison of Figures 1, 2, and 3 also demonstrated that with higher feed ratios of monomer **3**, the simple cycles (**CN** in Tables 1 and 2) gradually disappeared and more complex multicycles containing one or more bridge units were formed. An increasing number of bridge units ($B_1 \rightarrow B_7$) also means a higher number of cycles in one multicyclic molecule. The total number of cycles N_c which may be found in a two-dimensional formula equals $B_n + 1$ as illustrated by the schematic formulas in Schemes 3 and 4. The calculated masses of these cycles and multicycles are summarized in Table 3.

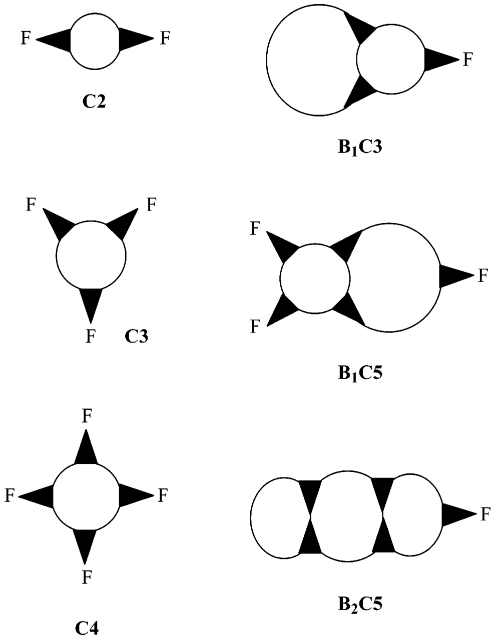
At a feed ratio of 1.0/1.4, a particularly interesting species of multicycles appears, which may be symbolized by the formula **B_nC2n**. These multicycles are bare of any functional group (Scheme 4). They represent 100% conversion of the functional groups inside the molecule, and due to their three-dimensional structure they may be considered as the low molar mass counterparts of an infinite network. With a further increase of the feed ratio toward the equifunctional stoichiometry (1.0/1.5, no. 8, Table 2), the **B_nC2n** multicycles became the dominating reaction products as evidenced by the MS of Figure 5. In the case of perfect stoichiometry in the reaction mixture and 100% conversion these multicycles should amount to 100%. However, the MS of the 1.0/1.5 polyether also evidenced the presence of multicycles having free OH groups (Scheme 6). This observation indicates that a small part of the C−F groups (1−2 mol %) was lost by side reactions. A loss of 1−2 mol % of the electrophilic monomer was observed for almost all polycondensations reported previously, and thus, is nothing unusual or special in the case of TFB. For an additional experiment with a feed ratio of 1.0/1.48 (no. 7), the MS proved indeed an almost perfect stoichiometry, but part of the product was again cross-linked and the MS indicated again incomplete conversion. Both, multicycles having C−F groups (**$B_nC(2n+1)$**, Scheme 3) and those having OH-groups (**$B_nC(2n-1)$—OH**, Scheme 6) were present. Finally, another polycondensation with a feed ratio of 1.0/1.48 was performed at a lower concentration to avoid gelation and at a higher temperature to favor a higher conversion

Table 6. SEC Measurements of Poly(ether ketone)s Derived from Bisphenol-A (3′)

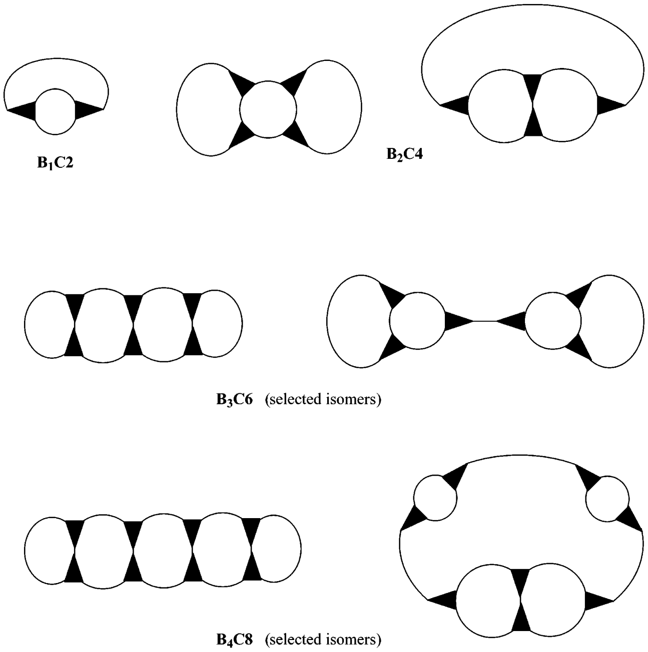
sample no. of Table 2	η_{inh}[b] (dL/g)	I. PS calibration[a] in $CHCl_3$ M_n (Da)	M_w (Da)	II. PC calibration[b] in CH_2Cl_2 M_n (Da)	M_w (Da)	triple detection[c] in CH_2Cl_2 M_w (Da)
1	0.12	3150	11500	1550	5500	
				1600[d]	15500[d]	17000 ± 1000
4	0.14	4800	24000	2300	100000	42000 ± 2000
7	0.51	8500	110000	6000	8000000	2500000

[a] Commercial polystyrene standards were used. [b] Poly(bisphenol A) carbonate standards of Bayer AG were used. [c] Including LS measurements. Each value represents the average of three measurements (margin of error ± 5%). [d] The high molar mass tail (10^5−10^7 Da) was taken into account.

Scheme 3



Scheme 4



(no. 9). Cross-linking was indeed avoided, but the MS indicated that the conversion was not significantly higher than in the case of polycondensations nos. 7 and 8. In other words, ideal conditions allowing for nearly 100% conversion without cross-linking were not found.

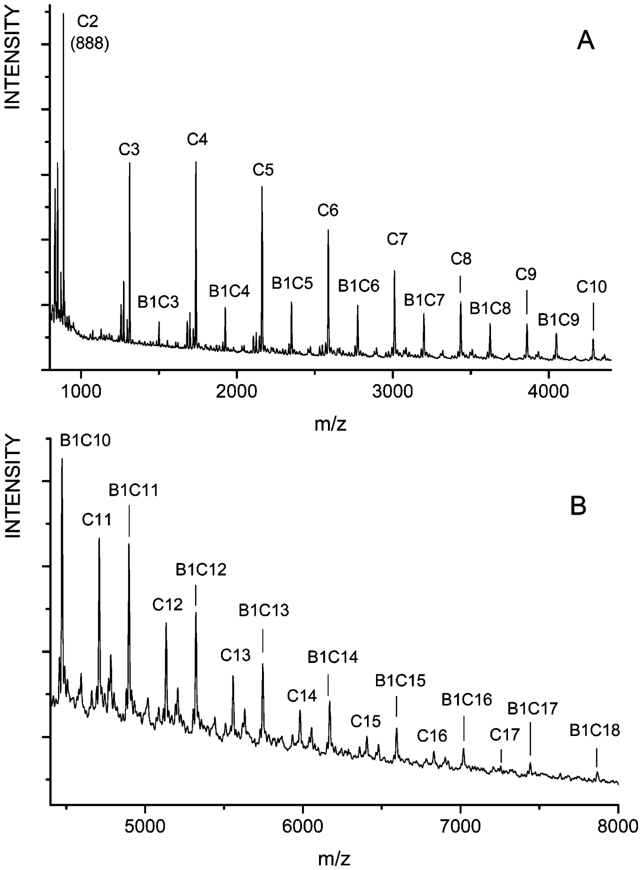
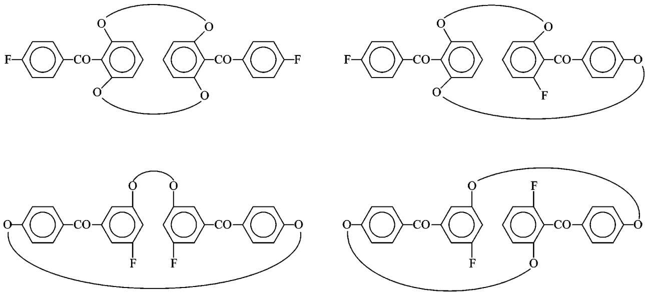


Figure 1. MALDI−TOF mass spectrum of the poly(ether ketone) **3′** prepared with equimolar feed ratio of TFB and **3** (no. 1, Table 2).

Scheme 5



When ^1H and ^{13}C NMR spectra of the poly(ether ketone)s **3′** were recorded again broad signals were found as discussed for **1′**. However, in the ^1H NMR spectra of **3′** an “end group” signal (i.e., protons neighboring a C−F group) was detected at 6.8 ppm (signal X in Figure 5). By comparison with the spectra of 2,6,4′-TFB and 4,4′-difluorobenzophenone signal “X” was tentatively assigned to the protons in ortho position of the F atom which is in 4′-position relative to the CO-

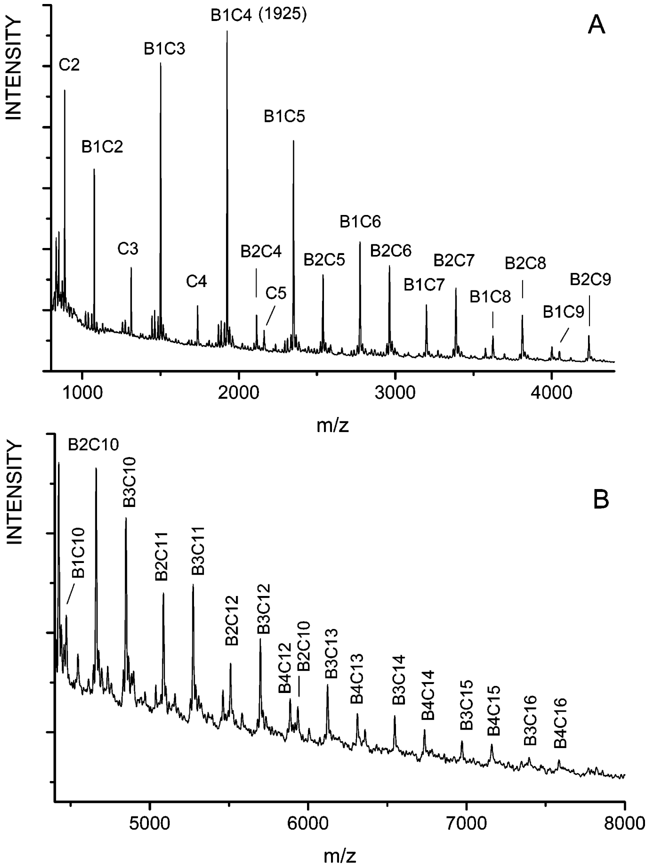


Figure 2. MALDI–TOF mass spectrum of the poly(ether ketone) **3′** prepared with 20 mol % excess of **3** (no. 4, Table 2).

group (formulas b and d in Scheme 2). The intensity of signal X decreased and the intensity of the phenyl ether signal at 6.7 ppm increased with higher feed ratios of bisphenol A. Two C–F groups were also detected in the ^{13}C NMR spectra at 164.95/162.20 ppm (I = 275 Hz) and 161.76/159.01 ppm (I = 250 Hz). Their intensity decreases with higher feed ratios of **3** confirming again the expected influence of the stoichiometry on the conversion. However, detection and quantification of C–F end group signals does not say anything about number and structure of (multi)cyclic species.

Polycondensations of Various Silylated Diphenols. On the basis of the results obtained from silylated bisphenol A, the only few polycondensations were conducted with **2**, **4**, and **5**. The feed ratios and results were compiled in Table 4. In the case of **2**, a completely soluble product was obtained at a feed ratio 1.0/1.3 (no. 1), whereas cross-linking occurred at ≥1.0/1.4. However, when the concentration was halved at the feed ratio 1.0/1.5, again a soluble polycondensate was formed (no. 4). From the silylated diphenols **4** and **5**, perfectly soluble products were isolated at a feed ratio of 1.0/1.4, whereas gelation occurred at 1.0/1.5. Lowering the concentration had the consequence of soluble products. In summary, the silylated diphenols **4** and **5** showed about the same cyclization tendency as silylated bisphenol A.

The MALDI–TOF MS provided the expected mass patterns. Noncyclic branched species or simple cycles (**CN**) were not detectable. As exemplarily illustrated in Figure 6, the multicycles **B$_n$C2n** were the predominant reaction products in the mass range below 4000 Da, even at a feed ratio of 1.0/1.4 (their H$^+$ and K$^+$-doped masses are listed in Table 5). However, the MS of the polycondensates prepared at a lower concentration with

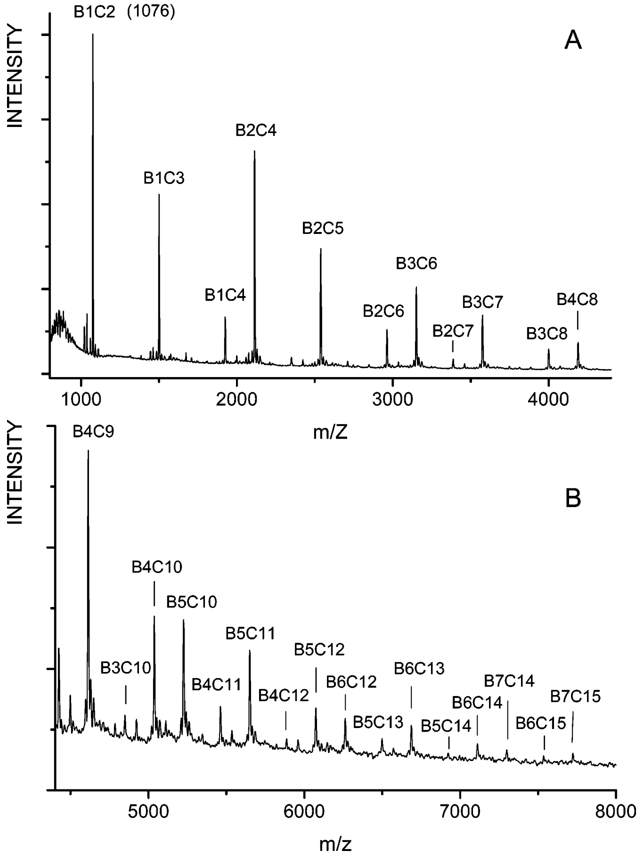


Figure 3. MALDI–TOF mass spectrum of the poly(ether ketone) **3′** prepared with 40 mol % excess of **3** (no. 6, Table 2).

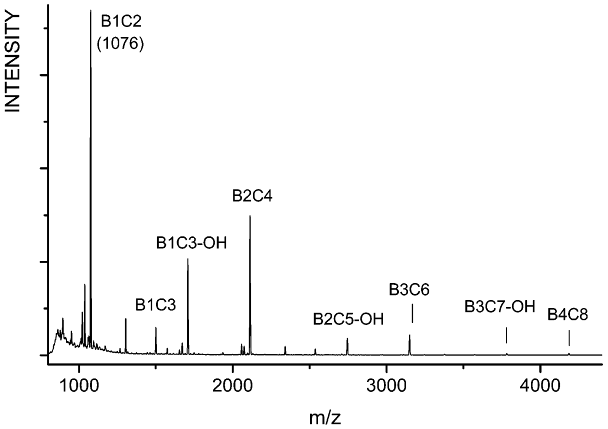


Figure 4. MALDI–TOF mass spectrum of the poly(ether ketone) **3′** prepared with 50 mol % excess of **3** (no. 8, Table 2).

a feed ratio of 1.0/1.5 also proved that the conversions of C–F groups (e.g., **B$_2$C5**, Scheme 2) and C–OH groups (Scheme 6) were not quantitative. These results and the analogous results obtained from **3** can be rationalized by taking into account that in TFB, all three F atoms are activated by only one CO group. When two C–F groups have reacted, the resulting C–O bonds deactivate the last C–F bond by their +M effect. Furthermore, an efficient formation of **B$_n$C2n** multicycles may be affected by steric hindrance.

SEC Measurements. Three samples of poly(ether ketone) **3′** prepared with 0, 20, or 50 mol % excess of silylated bisphenol A were subjected to SEC measurements. Two different procedures (labeled I and II) were applied to elucidate how sensitive the molecular weight data and the molecular weight distribution are to a

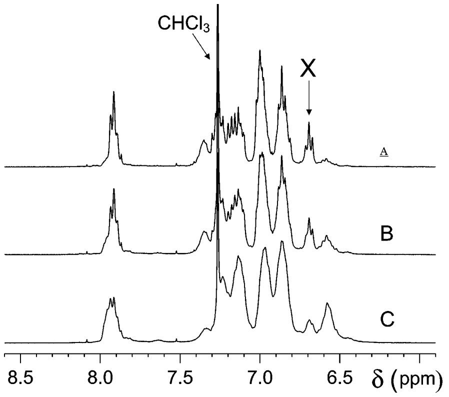


Figure 5. 400 MHz ^{1}H NMR spectra of the poly(ether ketone)s **3′**, samples nos. 1, 3, and 5, Table 2.

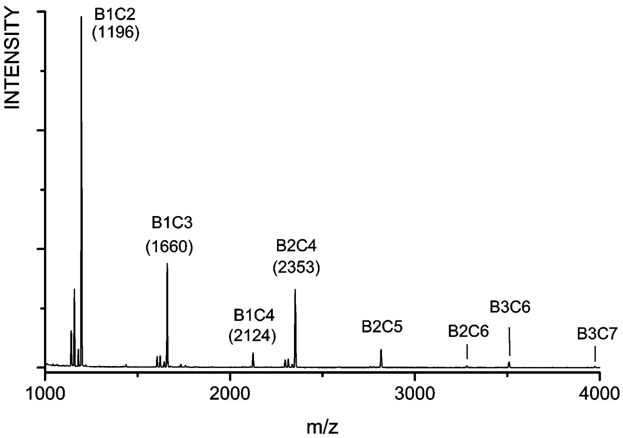
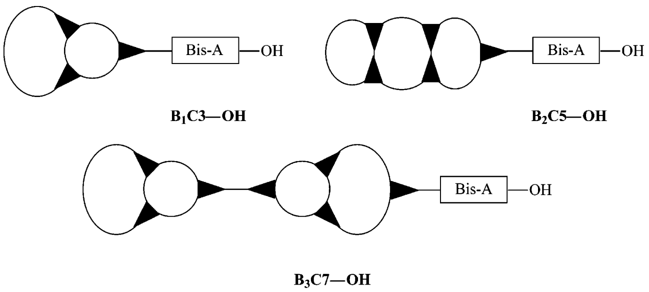


Figure 6. MALDI−TOF mass spectrum of the poly(ether ketone) **5′** prepared with 40 mol % excess of 5 (no. 8, Table 4).

Scheme 6



variation of the experimental parameters. In a previous publication[25] dealing with hyperbranched aromatic polyesters, three different column combinations, two different solvents and three detectors were used. The resulting number-average molecular weights (M_n's) varied by a factor of 2 and the weight-average molecular weights (M_w's) by a factor of 4. For the multicyclic polymers of this work similarly broad molecular weight distributions were expected.

Procedure I was based on a combination of three PL mixed-bed columns allowing for the resolution of molecular weights up to 10^6 Da. Chloroform served as eluent, a refractometer for detection and commercial polystyrene standards for calibration. In this way the elution curves presented in Figure 7 were obtained. These elution curves evidenced the expected broad mass distribution with a high content of oligomers and low molar mass polymers. The polydispersities varied between 3.5 and 12.5 and widened with increasing molecular weights (Table 6). Considering the shape of the elution curves and the MALDI−TOF MS the M_n values obtained by procedure I seem to be reasonable.

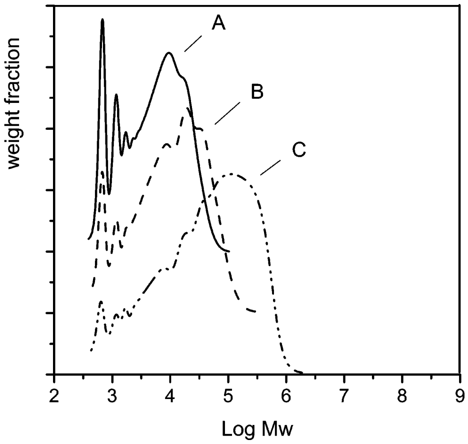


Figure 7. SEC elution curves (procedure I) of poly(ether ketone) **3′** prepared from **3**: A) feed ratio 1.0/1.0 (no. 1, Table 2), B) feed ratio 1.0/1.2 (no. 4, Table 2), C) feed ratio 1.0/1.5 (no. 7, Table 2).

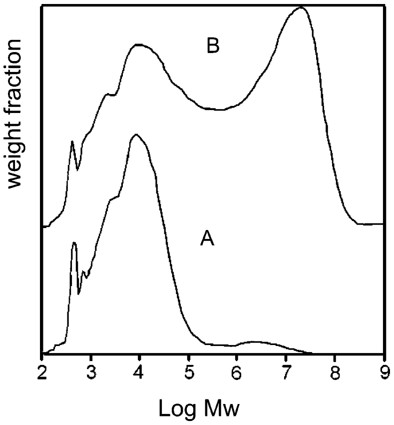


Figure 8. SEC elution curves (procedure II) of poly(ether ketone) **3′** prepared from **3**: A) with feed ratio 1.0/1.2 (no. 4, Table 2); B) with feed ratio 1.0/1.5 (no. 7, Table 2).

Procedure II was based on a combination of columns enabling a resolution of molar masses up to 100 × 10^6 Da. Dichloromethane served as eluent, a RI detector was used for the evaluation of the eluted material, and the calibration was performed with poly(bisphenol A carbonate), PC. The Mark−Houwink−Sakurada equation of PC was known from the literature (e.g., from ref 26). Furthermore, the M_w values of all three samples were determined via triple detection using light scattering as an “absolute method” (last column of Table 6). The most important difference between procedure I and II is the detection of a high molar mass fraction between 10^6 and 10^9 Da in the case of II (Figures 7 and 8). If this fraction was not taken into account the elution curves obtained via procedure I and II were quite similar. However, the detection of the high molar mass fraction has the consequence that the entire elution curve of sample no. 7 (B in Figure 8) looks quite different from that obtained by procedure I (C in Figure 7). In the case of sample no. 1 the high molar mass fraction was so low that it was not detected via the refraction index, but clearly indicated by the LS detector. When this high molar mass tail was included in the calibration with PC the resulting M_w value was in acceptable agreement with the M_w data obtained via triple detection. When it was not included, M_w was lower by a factor of 3. However, the evaluation of the high molar mass fraction did not have a significant influence on M_n.

In the case of samples nos. 4 and 7 the M_w values resulting from PC calibration were far higher than those obtained via triple detection. The values based on the LS detector are certainly more reliable and accurate. Considering the entire elution curves and the MALDI−TOF MS it is also obvious that PC calibration underestimates the real M_n values. In other words, the PC calibration seems to produce large errors when high molecular weight multicyclic poly(ether ketone)s should be characterized. These SEC measurements also demonstrate that it is particularly difficult to obtain reliable and accurate M_n or M_w data of multicyclic polymers. The only satisfactory method is obviously the determination of M_w (but not M_n) values via triple detection including a LS detector.

Conclusions

The results obtained in this study allow for a couple of interesting conclusions. When the trifunctional TFB is polycondensed with various silylated diphenols in NMP, a nearly quantitative conversion of the siloxy groups can be achieved if an excess of C−F groups is present (feed ratios ≤1.0/1.4). For equifunctional feed ratios (1.0/1.5), a quantitative conversion was not reached, even at a temperature of 180 °C. With silylated bisphenols **2**−**5**, gelation was circumvented at an equifunctional feed, when the initial concentration of TFB was lowered to 0.04−0.05 mol/L. Under these conditions, multicycles of the formula $\mathbf{B}_n\mathbf{C2}n$ (free of functional groups) became the main products. However, cyclic and multicyclic species were formed at all feed ratios and noncyclic branched molecules were never detected, regardless of the structure of the diphenol. These findings indicate an unusually high cyclization tendency for all monomer combinations. Nonetheless, differences were also detectable, so that the cyclization tendency increases with decreasing linearity of the diphenol, i.e., in the order: **1** < **2** < **3** ∼ **4** ∼ **5**.

The SEC measurements demonstrate that multicycles with high molar mass can be obtained. The relatively low solution viscosities are typical for compact globular molecules and were also observed for hyperbranched polymers. High polydispersities and a tendency toward bimodal mass distributions which were also found, are characteristic for all polycondensates having a high content of cycles. However, M_n and M_w measurements of multicyclic polymers are particularly difficult, because they are highly sensitive to any variation of the experimental conditions.

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References and Notes

(1) Flory, P. J. *Chem. Rev.* **1996**, *39*, 137.
(2) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter III and VIII.
(3) Kienle, R. H.; van der Meulen, F. A.; Fetke, F. E. *J. Am. Chem. Soc.* **1939**, *61*, 2258.
(4) Kienle, R. H.; Fetke, F. E. *J. Am. Chem. Soc.* **1941**, *63*, 481.
(5) Aharoni, S. M.; Murthy, N. S.; Zerr, K.; Edwards, S. F. *Macromolecules* **1990**, *23*, 2533.
(6) Aharoni, S. M. *Macromolecules* **1991**, *24*, 235.
(7) Jikei, M.; Chon, S. H.; Kakimoto, M.; Kawauchi, S.; Imase, I.; Watanabe, J. *Macromolecules* **1999**, *32*, 2061.
(8) Russo, S.; Boulares, A.; DaRen, A. *Macromol. Symp.* **1999**, *143*, 309.
(9) Fang, J.; Kita, H.; Okamoto, M. *Macromolecules* **2000**, *33*, 4639.
(10) Komber, H.; Voit, B.; Monticelli, O.; Russo, S. *Macromolecules* **2001**, *34*, 5487.
(11) Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendidri, R.; Pilto, V.; Tabuani, P.; Russo, S. *High Perform. Polym.* **2001**, *13*, 545.
(12) Ambrosio, K. C.; Jeffries-El, M.; Tarkha, R. M. *Polym. Mater. Sci. Eng.* **2001**, *518*, 84.
(13) Hao, J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2002**, *35*, 5372.
(14) Chen, H.; Yin, J. *J. Polym. Sci., Part A, Polym. Chem.* **2002**, *40*, 3804.
(15) Liu, Y.; Chung, T. S. *J. Polym. Sci., Part A, Polym. Chem.* **2002**, *40*, 4563.
(16) Hao, J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2003**, *36*, 3519.
(17) Chen, H.; Yin, J. *Polym. Bull. (Berlin)* **2003**, *50*, 303.
(18) Czupik, N.; Fossum, E. *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* **2003**, *44*, 861.
(19) Lusic, H.; Fossum, E. *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* **2003**, *44*, 858.
(20) Lin, Q.; Long, T. E. *Macromolecules* **2003**, *36*, 9809.
(21) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.
(22) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. *Macromolecules* **2003**, *36*, 4337.
(23) Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G. *J. Polym. Sci., Part A, Polym. Chem.* **2004**, *42*, 5725.
(24) Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G. *Macromolecules*, in press.
(25) Kricheldorf, H. R.; Hobzowa, R.; Schwarz, G.; Schultz, C.-L. *J. Polym. Sci., Part A Polym. Chem.* **2004**, *42*, 3751.
(26) Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Schultz, C.-L. *Macromol. Rapid Commun.* **2002**, *23*, 803.

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