Multicyclic Poly(ether sulfone)s of Phloroglucinol Forming Branched and Cross-Linked Architectures

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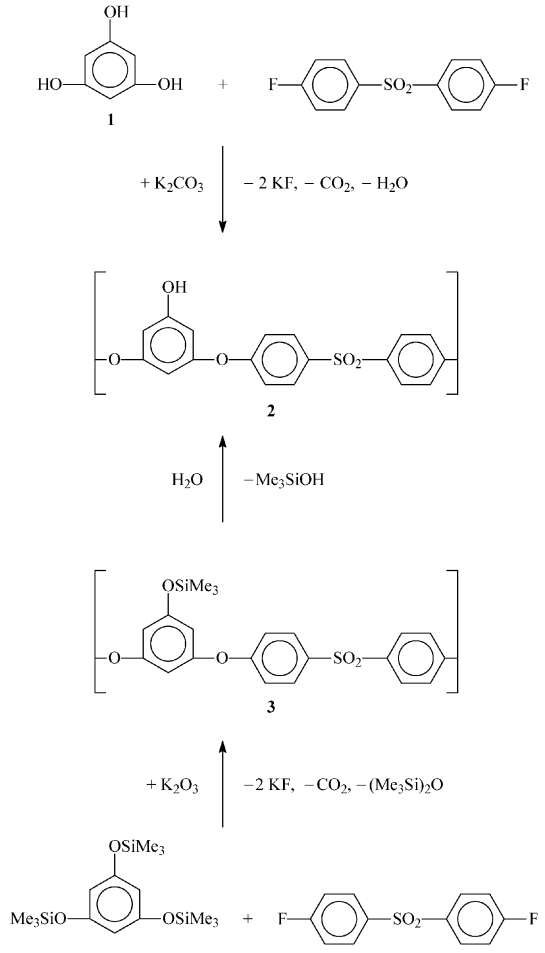
ABSTRACT: K_2CO_3-promoted polycondensations of phloroglucinol and 4,4′-difluorodiphenyl sulfone (DFDPS) in DMSO yielded mixtures of linear oligomers due to numerous side reactions. In contrast, polycondensations of silylated phloroglucinol under similar conditions were not plagued by such side reactions but involved various cyclization reactions with high efficiency. The MALDI−TOF mass spectra revealed the formation of various cyclic, bicyclic, and multicyclic species of complex structure up to 12 000 Da. Therefore, cross-linking only occurred when a large excess (+30 mol %) of DFDPS was added. The resulting branched and cross-linked polymers mainly consisted of cyclic building blocks. Attempts to introduce sulfonic acid groups by alkylation of pendant OH groups with sultones gave only a moderate degree of substitution, due to the high degree of cyclization. For comparison two polycondensations of silylated 5-methylresorcinol were studied.

Introduction

The original purpose of this work was synthesis and functionalization of branched poly(ether sulfone)s based on phloroglucinol (structure **1**). Either free phloroglucinol or silylated phloroglucinol should be polycondensed with 4,4′-difluorodiphenyl sulfone, DFDPS (Scheme 1). Finally, sulfonic acid groups should be introduced to obtain polymers which might be used as acidic membranes or catalysts. Yet, because of unexpected side reactions and extensive cyclizations, the course of the polycondensations became the main focus of this study.

Whereas in the classical theory of polycondensation[1,2] cyclizations do not play a significant role, Stockmayer and co-workers[3,4] have demonstrated 5 decades ago that cyclic oligomers are formed by "backbiting degradation" in thermodynamically controlled polycondensations involving efficient equilibration reactions. Quite recently we have demonstrated[5−7] for a variety of kinetically controlled polycondensations, KCPs, (no equilibration reactions), that cyclization competes with propagation at any concentration and at any stage of the polymerization process. K_2CO_3-promoted polycondensations of free or silylated diphenols with DFDPS at temperatures ≤ 140 °C belong to the group of KCPs.[7] The influence of cyclization reactions on the structure and properties of networks has also been discussed in recent theories of network formation.[8] However, cyclization was mainly discussed as an origin of loops resulting from the high concentration of functional groups in large branched polymers shortly before or during the gelation process. The results obtained from polycondensations of silylated phloroglucinol in this work present another scenario. For better understanding, the results obtained from polycondensations of silylated 5-methylresorcinol, a stereochemical equivalent of phloroglucinol, will be discussed first.

Scheme 1



Experimental Section

Materials. Hexamethyldisilazane, phloroglucinol, 5-methylresorcinol, fluorobenzene, and chlorosulfonic acid were purchased from Aldrich Co. (Milwaukee, WI) and used as received. 4,4′-Difluorodiphenyl sulfone, DFDPS, was synthesized as described in the literature.[9] K_2CO_3 p.a. grade was purchased from Merck KG (Darmstadt, Germany) and dried at 65 °C over P_4O_{10} in vacuo. *N*-Methylpyrrolidone (NMP, a gift of Bayer AG, Leverkusen, Germany) was twice distilled over P_4O_{10} in vacuo.

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Silylation of Phloroglucinol. Phloroglucinol (0.3 mol) and hexamethyldisilazane (0.5 mol) were refluxed in toluene for 20 h and concentrated in vacuo. The product was isolated by distillation in a vacuum of 0.02 mbar. Yield: 82%. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.25$ (s, 27 H), 6.01 (s, 3 H) ppm.

5-Methylresorcinol (0.2 mol) was silylated analogously with 0.3 mol hexamethyldisilazane. Yield: 91%. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.29$ (s, 18 H), 6.18 (m, 1 H), 6.32 (m, 2 H) ppm.

Polycondensation of Silylated 5-Methylresorcinol. (A) With Equimolar Stoichiometry. Silylated resorcinol (20 mmol), DFDPS (20 mmol), K_2CO_3 (20 mmol), and dry NMP (50 g) were weighed under dry nitrogen into a 150 mL three-necked flask equipped with flat-blade stirrer, gas-inlet tube, and drying tube. Under a slow stream of dry purified nitrogen, the reaction mixture was stirred for 48 h at 140 °C. After cooling, the reaction mixture was poured into water (500 mL), and the precipitated polymer was filtered off, washed intensively with warm water, and dried at 80 °C in vacuo. Yield: 86%. $\eta_{inh} = 0.43$ dL/g (with $c = 2$ g/L at 20 °C in CH_2Cl_2).

(B) With Excess DFDPS. Silylated resorcinol (20 mmol), DFDPS (22 mmol), and K_2CO_3 (22 mmol) were polycondensed as described above. Yield: 81%. $\eta_{inh} = 0.16$ dL/g (with $c = 2$ g/L in CH_2Cl_2).

Polycondensations of Phloroglucinol (Table 1). Phloroglucinol (20 mmol), DFDPS (20 mmol), and K_2CO_3 (21 mmol) were weighed into a 150 mL three-necked flask equipped with flat-blade stirrer and distillation head. DMSO (100 mL) and xylene (30 mL) were added. The reaction mixture was stirred for 6 h at a bath temperature of 170 °C, whereby most of the xylene and liberated water were distilled off. Finally, the reaction mixture was poured into water, and the precipitated polymer was filtered off, intensively washed with warm water, and dried at 80 °C in vacuo.

Polycondensations of Silylated Phloroglucinol (Table 2). Silylated phloroglucinol (20 mmol), DFDPS (20 mmol) K_2CO_3 (20 mmol), and dry NMP (25 g) were weighed under dry nitrogen in a 150 mL three-necked flask equipped with flat-blade stirrer, gas-inlet tube, and drying tube. The reaction mixture was stirred at 140 °C for 48 h under a slow stream of dry N_2. After cooling, the reaction mixture was poured into water, and the precipitated polymer was isolated by filtration, intensively washed with water, and dried at 80 °C in vacuo.

Polycondensations via the Pseudo-High-Dilution Method (Table 3). Silylated phloroglucinol (20 mmol) dissolved in dry NMP (50 mL) and DFDPS (20 mmol) dissolved in dry NMP (50 mL) were added dropwise and simultaneously to a stirred suspension of dry K_2CO_3 (20.2 mmol) in dry NMP (50 mL) at 140−145 °C. The time required for complete addition was 1 h. Stirring at 145 °C was continued for 3 h. The cold reaction mixture was then precipitated into water, and the precipitated polymer was filtered off, washed with water, and dried at 80 °C in vacuo.

Alkylation with Sultones. Silylated phloroglucinol (10 mmol), DFDPS (11 or 12 mmol), K_2CO_3 (11 or 12 mmol), and dry NMP (60 g) were weighed into a 150 mL three-necked flask and polycondensed at 140 °C for 24 h. After the temperature was lowered to 100 °C, 1,4-butane sultone (11 mmol) and K_2CO_3 (11 mmol) were added, and the reaction mixture was stirred at 100 °C for 24 h. The resulting slurry was then poured into water, and the precipitated polymer was filtered off, washed with water, and dried at 80 °C in vacuo. The dry polymer was dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid (1:1 by volume) and precipitated into methanol.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C (Tables 1−3) or 25 °C (Table 4).

The MALDI−TOF mass spectra were recorded with a Bruker Biflex III equipped with a nitrogen laser in the reflectron mode. An acceleration voltage of 20 kV was used, and a cutoff range of 500, 1000, or 3000 Da. The irradiation targets were prepared from chloroform solution, with dithranol as matrix and K−trifluoroacetate as dopant.

The VPO measurements were conducted in DMF at 95 °C with an "OSMOMATE 070" apparatus of Genotec GmbH. Benzil was used for calibration. The SEC measurements were performed with a SK-18V6 column combination of Polymer Standard Service GmbH having an inner diameter of 4.6 mm.

DMF containing NH_4 acetate served as eluent. A combination of a RI detector (Jasco, Japan) and a viscosity detector (WGE, Dr. Bures GmbH) was used for the evaluation via universal calibration based on polystyrene standards (WINGPC software 6.01 of PSS was also used).

The light-scattering measurements were performed with a triple-angle light-scattering detector "mini DAWN" from Wyatt Technology in combination with ASTRA 4.70 chromatography software.

Table 1. Polycondensations of Phloroglucinol and DFDPS in DMSO/Xylene[a]

expt no.	molar excess of DFDPS and K_2CO_3	yield (%)	η_{inh}[b] (dL/g)
1	0	76	0.08
2	10	70	0.08
3	20	78	0.08
4	30	90	0.07
5	40	78	0.07
6	50	88	0.07
7	60	95	0.08
8	70	97	0.08
9	80	90	0.09

[a] Time: 6 h. Bath temperature: 170 °C. [b] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1).

Table 2. Polycondensations of Silylated Phloroglucinol and DFDPS in NMP at 140 °C

expt no.	molar excess of DFDPS and K_2CO_3	time (h)	yield (%)	η_{inh}[a] (dL/g)	M_n(VPO)[b] (Da)	M_w(LS)[c] (Da)
1	0	24	79	0.15	1900	49 000
2	0	48	81	0.15	2000	65 000
3	10	24	81	0.17		
4	10	48	82	0.17	2200	100 000
5	20	24	93	0.19	2500	250 000
6	20	48	94	0.20	2400	200 000
7	30	24	cross-linked			
8	30	48	cross-linked			

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

Table 3. Polycondensations of Silylated Phloroglucinol and DFDPS by the Pseudo High Dilution Method[a]

expt no.	molar excess of DFDPS and K_2CO_3	yield (%)	η_{inh}[b] (dL/g)
1	0	77	0.14
2	10	79	0.20
3	20	91	0.23
4	30	cross-linked	

[a] In NMP at 140 °C, total reaction time 24 h [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1)

Results and Discussion

Polycondensations of 5-Methylresorcinol. Silylated 5-methylresorcinol was polycondensed with DFDPS in *N*-methylpyrrolidone at 140 °C over a period of 48 h. These reaction conditions were found in a previous study[7] dealing with silylated bisphenol A to allow for nearly quantitative conversion and to avoid side reactions and equilibrations almost completely. Two different feed ratios were used for comparison with analogous polycondensations of phloroglucinol. The first experiment was performed with exactly equimolar amounts of both monomers, and a poly(ether sulfone), PES, with an inherent viscosity of 0.43 dL/g was isolated. For the second polycondensation, a 10 mol % excess of DFDPS was used, and the resulting PES had the low viscosity

Table 4. Masses of Cyclic Species (Including One K Ion) Identified in the MALDI−TOF Mass Spectrum of Figures 4 and 5 (PES No. 1, Table 3)

deg of polymerization of the cycles[a]	C	B_1C	B_2C	B_3C	B_4C	B_5C	B_6C	B_7C	B_8C
2	719.8								
3	1060.2	1224.2							
4	1400.5	1614.8							
5	1740.9	1955.1	2169.3						
6	2081.2	2295.5	2509.7						
7	2421.6	2635.8	2850.1	3064.3					
8	2761.9	2976.2	3190.4	3404.5					
9	3102.3	3316.6	3530.8	3745.0					
10		3656.9	3871.5	4085.5	4299.5				
11		3997.3	4211.5	4425.8	4639.8				
12		4337.6	4551.9	4766.1	4980.2				
13		4877.9	4892.3	5106.4	5320.5	5534.8			
14			5232.6	5446.8	5660.9	5875.1			
15			5572.9	5786.1	6001.3	6215.5			
16			5913.2	6126.4	6341.6	6555.8	6770.2		
17			6255.6	6466.7	6681.9	6896.1	7110.5		
18				6807.0	7022.2	7236.4	7451.3		
19				7147.3	7362.5	7576.8	7791.7		
20				7487.6	7072.0	7917.1	8132.0	8346.2	
21					8042.0	8257.4	8472.3	8686.5	
22					8382.3	8597.8	8812.6	9026.9	
23					8722.6	8938.1	9153.0	9367.2	
24					9063.0	9278.4	9493.3	9707.5	
25						9618.8	9833.6	10047.9	10262.1
26						9959.1	10174.0	10388.2	10602.5
27						10299.4	10414.3	10728.5	10942.8
28							10754.6	11068.9	11283.2
29							11095.0	11408.2	11623.5
30							11435.3	11748.6	

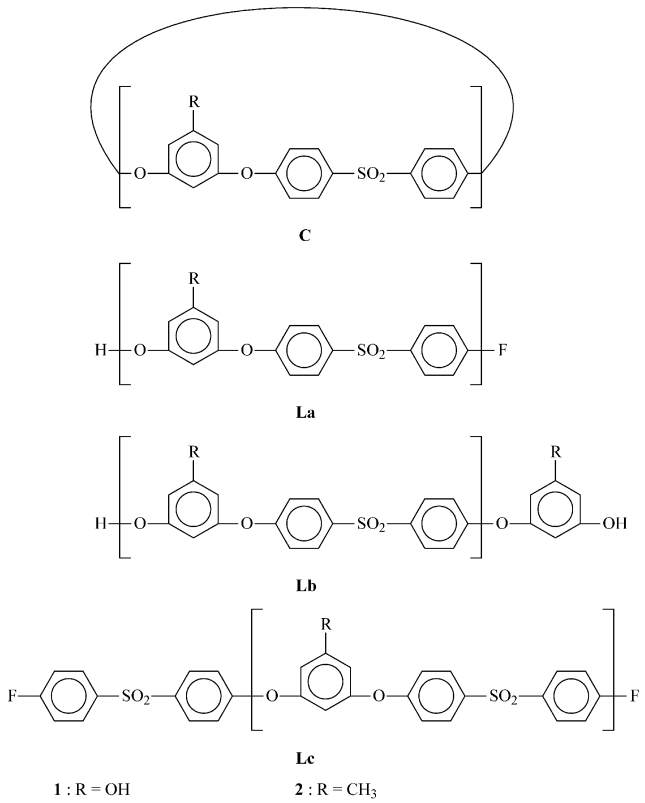
[a] This DP includes OH-terminated side chains, such as those of BC3′ in Scheme 1 or B_2C8 and B_3C11 in Scheme 2.

of 0.16 dL/g as expected of a significant imbalance of the stoichiometry.

The MALDI−TOF mass spectrum (MS) of the high molar mass sample displayed the peaks of cyclic oligomers and polymers (**2C** in Scheme 1) as the predominant species up to 10 000 Da (Figure 1). At higher masses, linear chains of structure **2La** or **2Lb** (Scheme 2) were prevailing. The absence of **2Lc** chains together with the presence of **2Lb** chains indicates that the stoichiometry in the reaction mixture was not perfect, possibly due to a minor side reaction of DFDPS. This observation agrees well with our previous results concerning bisphenol A,[7] where the most perfect stoichiometry, the highest molecular weights, and the largest extent of cyclization were obtained with a slight excess (∼ 1 mol %) of DFDPS in the feed. The MALDI−TOF MS of the low molar mass sample revealed again the formation of cycles, but only the peaks of the trimer and tetramer (**2C**3 and **2C**4) were predominant and the peaks of larger cycles vanished above 4000 Da. As expected from the excess of DFDPS in the feed, the **2Lc** chains were now the predominant species above 1500 Da (Figure 2).

In summary, the MS showed the pattern of reaction products expected for a normal kinetically controlled polycondensation with one exception. The peak of the cyclic dimer was barely detectable in contrast to analogous polycondensations of silylated bisphenol A or silylated 4-*tert*-butylcatechol (to be reported in a future publication). Obviously, the cyclization of the linear dimer is for sterical and entropical reasons unvaforable.

Scheme 2



Polycondensations of Free Phloroglucinol. For the preparation of branched PES derived from phloroglucinol (**1**), two synthetic methods were compared (Scheme 1) to study the influence of the reaction condition on the onset of gelation. The polycondensation of free diphenols in DMSO combined with an aromatic solvent for the azeotropic removal of water is the standard method for the preparation of PES, which is also used for the technical production of PES. When

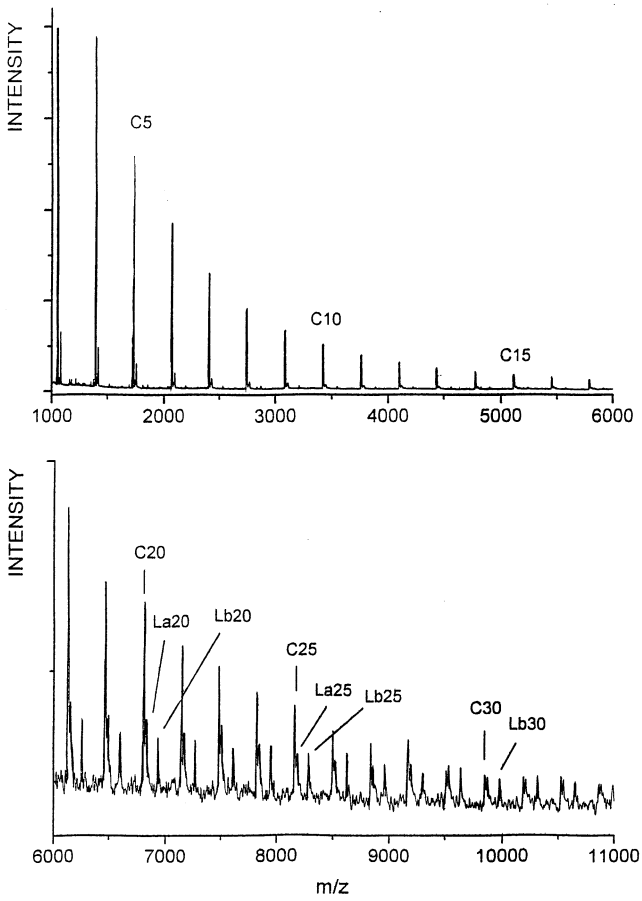


Figure 1. MALDI−TOF mass spectrum of the PES prepared from equimolar quantities of silylated 5-methylresorcinol and DFDPS.

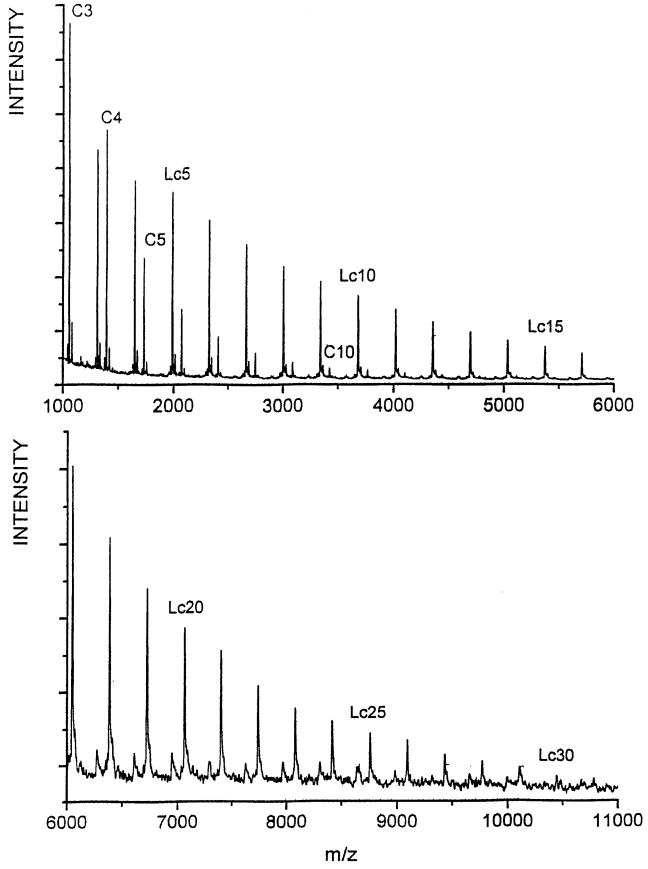


Figure 2. MALDI−TOF mass spectrum of the PES prepared from silylated 5-methylresorcinol with a 10 mol % excess of DFDPS.

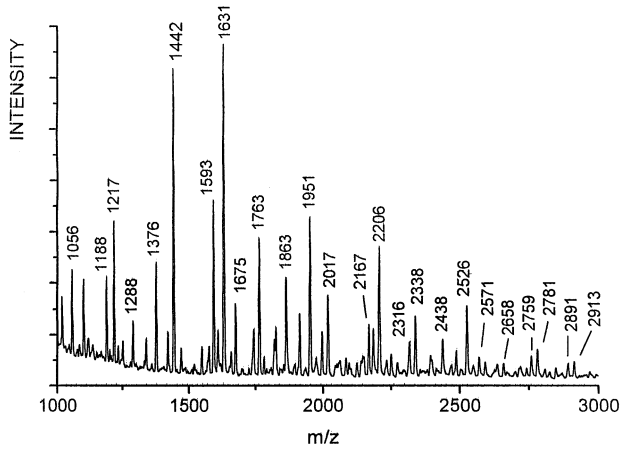


Figure 3. MALDI−TOF mass spectrum of a PES prepared from phloroglucinol with a 30 mol % excess of DFDPS (no. 4, Table 1).

polycondensation of phloroglucinols in DMSO were conducted in the presence of toluene, only low molar masses were obtained (η_{inh} < 0.1 dL/g). Therefore, toluene was replaced by xylene, hoping that a higher reaction temperature (see Table 1) will result in higher conversions and higher molar masses. However, the viscosities listed in Table 1 demonstrate that this modification of the reaction conditions was successless. Yet, the most surprising result was that increasing excess of DFDPS did neither enhance the molecular weights nor generate cross-links. The MALDI−TOF MS of all samples listed in Table 1 (examplarily demonstrated in Figure 3) displayed the same peaks, only the intensity ratios varied. The expected linear or cyclic species were not found, and a comparison of the masses summarized in Figure 3 with those listed in Table 4 for PESs prepared from silylated phloroglucinol did not show any overlapping. In other words, the successless polycondensations of free phloroglucinol in DMSO were a consequence of intensive side reactions, which were not analyzed in detail.

Polycondensations of Silylated Phloroglucinol. Whereas polycondensations of bisphenol A and silylated bisphenol A with DFDPS gave nearly identical results, the present work proved that polycondensations of free and silylated phloroglucinol take a completely different course. The molecular weights of PES samples prepared from silylated phloroglucinol were about three times higher and gelation occurred at certain feed ratios (Table 2). Surprising was in this case that no cross-linking took place at a 1.0:1.0 feed ratio despite almost 100% conversion of the C−F groups (as evidenced by MALDI−TOF MS). Even an excess of 10 or 20 mol % of DFDPS did not suffice for gelation. When four polycondensations were repeated using the pseudo-high-dilution method, the results were similar to those obtained at high concentration (Table 3). Obviously, the condensation steps were too slow at 140 °C, so that the concentration increased upon monomer addition over a period of 1 h. Again no cross-linking occurred with an excess of 10 or 20 mol % of DFDPS, but the increase of the molecular weight was steeper. The MALDI−TOF MS of the PES samples listed in Table 2 differed from those of Table 3 insofar as weak peaks of noncyclic species were detectable up to masses above 5000 Da,

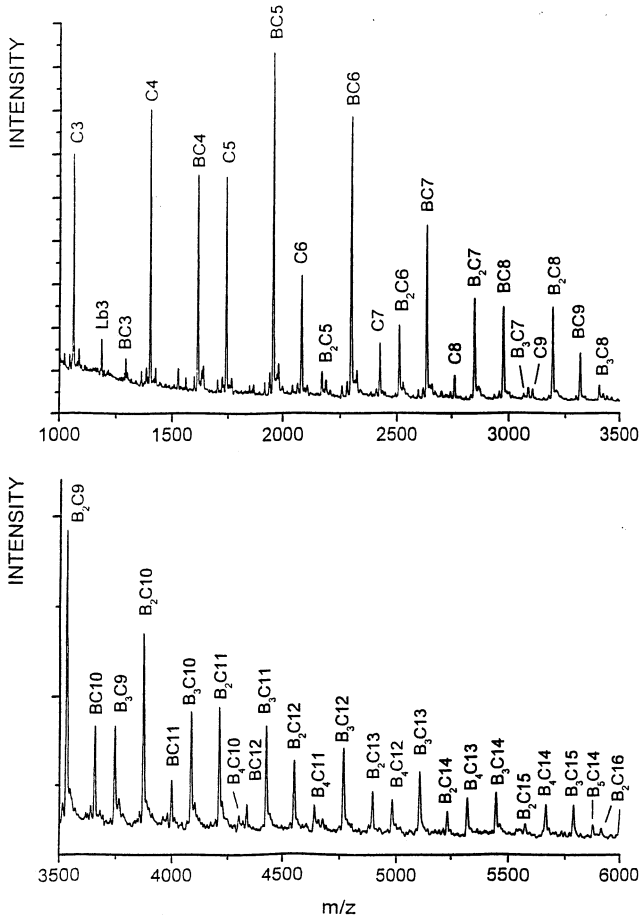


Figure 4. MALDI−TOF mass spectrum (lower mass range) of a PES prepared from silylated phloroglucinol with a feed ratio of 1.0:1.0 via the "pseudo-high-dilution method" (no. 1, Table 3).

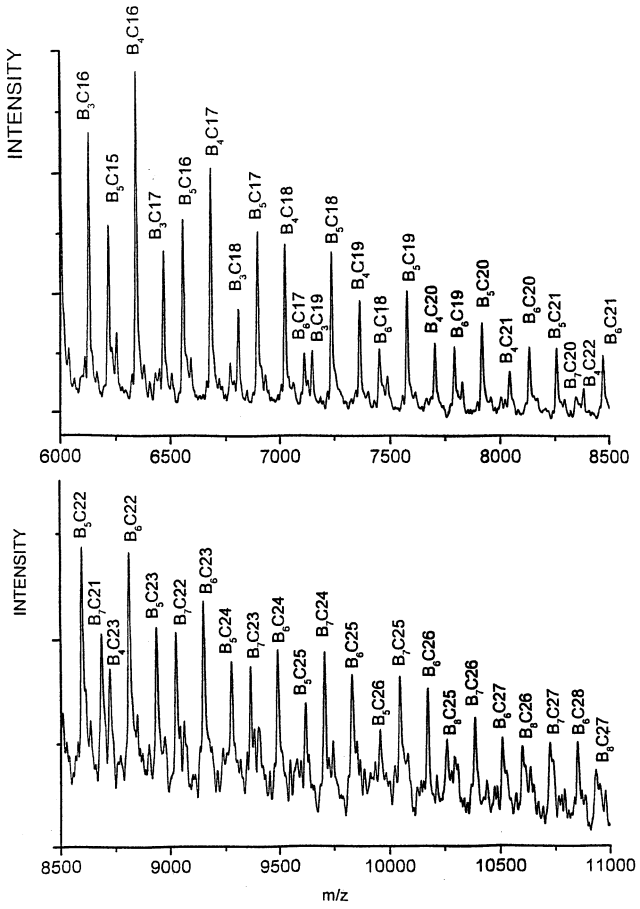


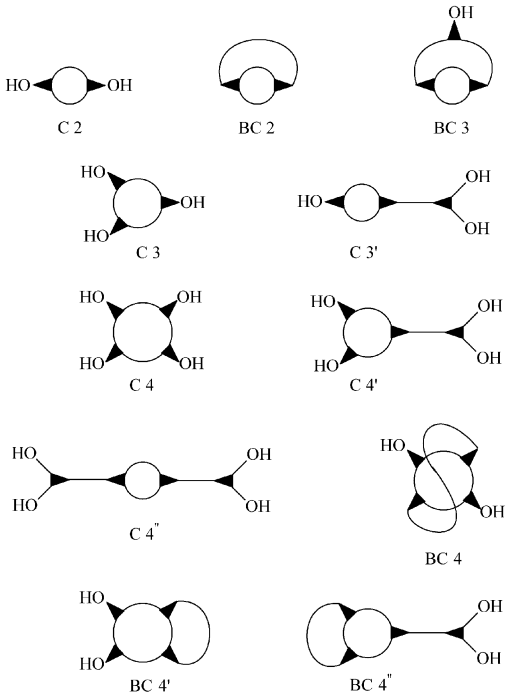
Figure 5. MALDI−TOF mass spectrum (higher mass spectrum) of a PES prepared from a silylated phloroglucinol with a feed ratio of 1.0:1.0 via the "pseudo-high-dilution method" (no. 1, Table 3).

whereas such peaks were almost absent in the MS of the products listed in Table 3. All mass peaks of cyclic species in both series of PES samples were identical; only the intensity ratio varied as discussed below.

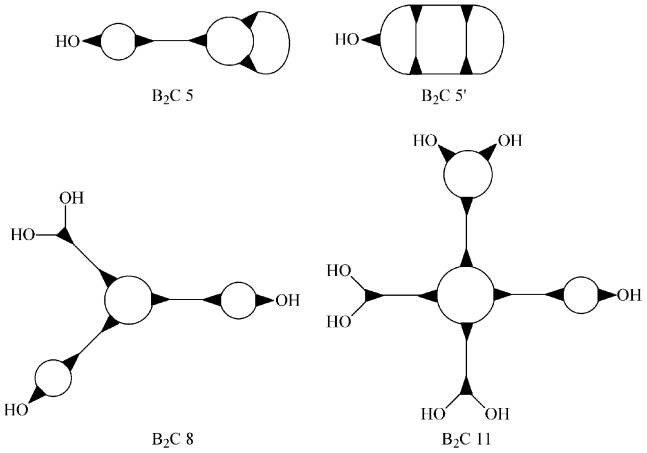
The MALDI−TOF MS of sample no. 1, Table 3, had the best signal-to-noise ratio of all samples (mass peaks up to 12 000 Da were detectable), and therefore, this spectrum is exemplarily discussed in more detail. All mass peaks were assigned (Table 4) and Figures 4 and 5 display 92 assignments. Only two weak peaks of linear species, namely the dimer and trimer of structure **1Lb** were found (see **Lb** in Figure 4). All other mass peaks originated from species containing at least one cycle. Since no C−F terminated species were detected in the MS of Figures 4 and 5, these MS prove an almost quantitative conversion of the C−F groups. Therefore, the isomeric structures presented in Schemes 3 and 4 are exclusively based on OH functionalities. The role of diphenyl sulfone units is 3-fold. First, they form the linear or cyclic repeating units, second, they connect to cycles (intermolecular bridge) or they form a bridge across a cycle (intramolecular bridge). Therefore, the nomenclature $\mathbf{B}_x\mathbf{C}Y$ was selected to count the total number of "bridge units" (x) and the total number of repeating units (Y). All the mass peaks assigned in this way are listed in Table 4.

Interestingly, the peaks of the cyclic dimer (**C**2) and of the bicyclic dimer **BC**2 (bridged cyclic dimer, Scheme 3) were barely detectable. This finding agrees with the low concentration of the cyclic dimer in the polycondensations of silylated 5-methylresorcinol. Therefore, it needs to be emphasized that the peak of **BC**3, the bridged cyclic trimer (see Scheme 3), was clearly detectable in all MS The peak intensity of **BC**3 was relatively

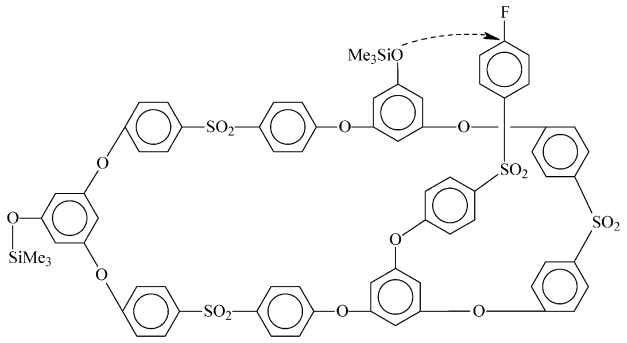
Scheme 3



Scheme 4



Scheme 5



low in Figure 4, but it increased significantly with higher DFDPS feeds. For the bicyclic structure of **BC**3, no isomer exists. Therefore, the structure of **BC**3 proves that the formation of dimeric cycles is much more favorable when bridging of a preformed cycle is involved (Scheme 5) compared to the formation of **C**2 from the linear dimer. Another important aspect of **BC**3 is its monofunctional character. This means that the normal cyclization reactions competing with the propagation in polycondensations of silylated phloroglucinol automatically produce chain terminators, even when side reactions destroying functional groups are absent.

Scheme 3 also includes the various isomers based on **C**4 units. Here it is noteworthy that two **BC**4 species may exist (**BC**4 and **BC**4′) which in contrast to **BC**3 can react as difunctional building blocks. In the case of cycles containing two bridge units (Scheme 4) two aspects are of interest. For **B$_2$C**5, two isomers can be formulated which have two structural features in common. First, they contain rings corresponding to cyclic dimers, and second, both are monofunctional. This means that in addition to **BC**3 cyclic species containing two or more bridge units, such as **B$_2$C**5, **B$_3$C**7, or **B$_4$C**9, may also play the role of chain stoppers. The formulas **B$_2$C**8 and **B$_2$C**11 in Scheme 4 should illustrate that three- and higher-membered rings may act as star centers having further rings in their star arms. When the feed of DFDPS is increased beyond the 1.0:1.0 ratio, the formation of bridged cycles including bicycles is highly favored. The MS of PES no. 5, Table 2 (Figure 6), demonstrates exemplarily that the **BC**3/**C**3, **BC**4/**C**4, and **BC**5/**C**5 ratios together with the content of **B$_2$C**5 have significantly increased.

The comparison of Figure 6 with Figure 2 illustrates the striking difference between polycondensations of

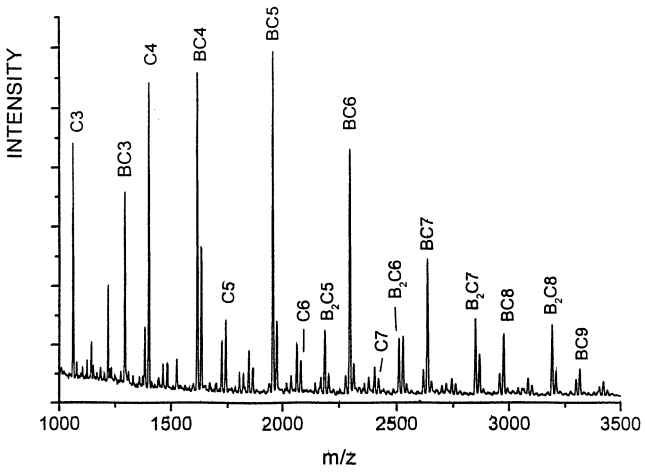


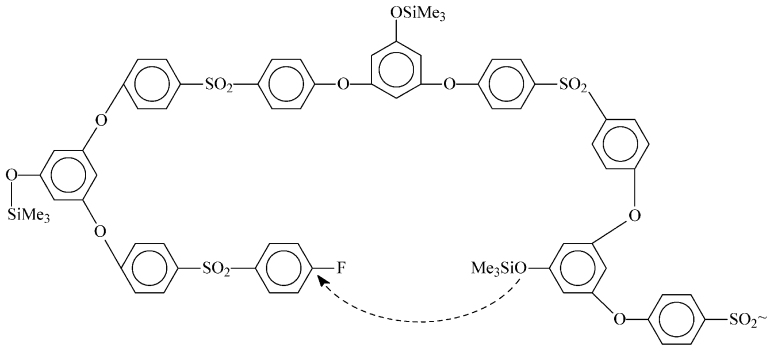
Figure 6. MALDI−TOF mass spectrum of a PES prepared from silylated phloroglucinol with a 1.0:1.2 feed ratio (no. 5, Table 2).

silylated 5-methylresorcinol and phloroglucinol. In the former case, the excess of DFDPS considerably reduces the extent of cyclization and yields chains terminated by two C−F groups, whereas in the case of phloroglucinol the excess of DFDPS intensifies ring closing reactions favoring the formation of bridged cycles.

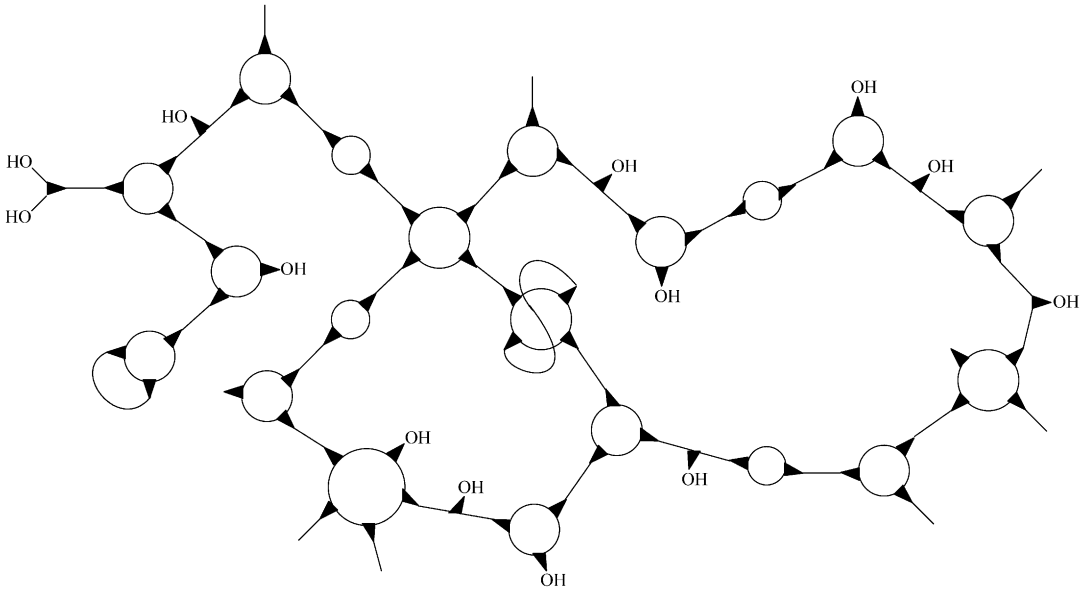
For the proper understanding of the entire polymerization process, it should be emphasized that formation of small cycles results from two different processes. The first one is the direct formation of cycles from end-to-end reactions of oligomers. Most of these cycles was detected up to **C**9 in the MALDI−TOF MS (Table 4 and Figures 4 and 5). The second process yielding cyclic building blocks is the "backbiting" of C−F chain ends as illustrated in Scheme 6. This kind of "backbiting" neither cleaves the chain nor intercepts the polycondensation process, because the resulting cycles may still contain OH groups. The coexistence of both cyclization pathways explains the high concentration of cyclic species in all PES isolated from polycondensations of silylated phloroglucinol. The consequence for the structure of the resulting branched or cross-linked PESs is illustrated in Scheme 7. Most building blocks are small macrocycles.

Molecular Weight Measurements. Three analytical methods were used to obtain reliable information on the molar masses of the PESs listed in Table 2, but the results were not satisfactory. Polystyrene, even using the universal calibration, is not a trustworthy standard for the unusual structure of the PES samples under investigation. However, the SEC measurements revealed at least the expected high polydispersities (PDs) which fell into the range of 4 (no. 1) to 10 (no. 6). Vapor pressure osmometry (VPO, see Table 2) gave very low number-average molecular weights (M_ns). These low values certainly underestimate the real M_ns, possibly because the OH groups of the PESs bind water via H bonds which survives a normal drying process. Light scattering (LS, see Table 2) gave extremely high weight-average molecular weights (M_ws), which clearly overestimate the real values. One reason for the overestimation results from the fact that numerous oligomers present in these samples do not scatter light. Association via H bonds may be another source of errors. However, the PS-calibrated SEC measurements in NH_4 acetate DMF solutions gave similarly high M_w values

Scheme 6



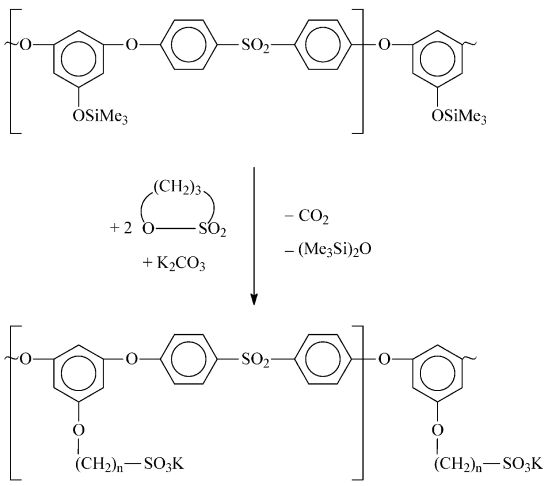
Scheme 7



as the LS measurements, although the NH_4 acetate should break up the H bonds. Yet, these high M_w values disagree with the low solution viscosities, which are more closely correlated with M_w than with M_n. The MALDI−TOF MS of polymers having a broad molecular weight distribution do not give any useful information on M_n or M_w, unless a sample is fractionated into numerous narrow fractions. In summary, the comparison of five series of measurements (incl. viscosities) demonstrates that it is rather difficult to obtain a satisfactory description of molecular weights and molecular weight distributions of this type of polymers.

Alkylation with Sultones. According to the original purpose of this work, namely functionalization of branched PESs with sulfonate groups, the alkylation with sultones was studied. On the basis of the experience with alkylation of other aromatic polyethers,[10,11] the direct alkylation of the trimethylsilyl-protected crude reaction products (structure 3) seemed to be most promising (Scheme 8). The reaction conditions and results obtained from 1,3-propane sultone and 1,4-butane sultone are summarized in Table 5. PESs prepared with a 10 and 20 mol % excess of DFDPS were compared. The degrees of substitution (DS) determined by means of ^1H NMR spectroscopy were calculated on the basis of $OSiMe_3$ groups available after complete conversion of all DFDPS. The following trends were found. 1,4-Butane sultone may give higher DS values than the propane sultone. An excess of sultone reduces the DS instead of enhancing it. This result is difficult

Scheme 8



to understand but reproducible. Even in the best case, not more than 70% of the theoretically available $OSiMe_3$ groups were alkylated. This limitation is most likely a consequence of steric hindrance. The relatively high viscosity values have a dual origin. First, a fractionation took place upon precipitation into methanol. Second, the charged polymers certainly possess and show the typical solution properties of polyelectrolytes. In summary, the introduction of sulfonate groups via sultones was in principle successful, whereas treatment with concentrated sulfuric acid at 20−25 °C caused cross-linking

Table 5. Syntheses of Poly(ether sulfone)s[a] from Silylated Phloroglucinol and Alkylations with Sultones[b]

expt no.	excess of[c] DFDPS (mol %)	sultone	excess of[c] sultone (mol %)	yield (%)	η_{inh}[d] (dL/g)	DS[e]
1	10	1,3-propane-	10	77	0.65	55
2	10	1,3-propane-	20	76	0.67	50
3	20	1,3-propane	10	83	1.17	55
4	20	1,3-propane	20	85	1.18	46
5	20	1,3-propane	50	88	1.30	45
6	10	1,4-butane-	10	74	0.58	68
7	10	1,4-butane-	20	76	0.62	63
8	20	1,4-butane-	10	75	1.22	58
9	20	1,4-butane-	20	76	1.28	45
10	20	1,4-butane-	50	82	1.30	45

[a] In NMP at 140 °C/48 h. [b] In NMP at 100 °C/24 h. [c] Relative to silylated phloroglucinol. [d] Measured at 25 °C with $c = 2$ g/L in DMSO. [e] Degree of substitution as determined by ^{1}H NMR spectroscopy.

and treatment with trimethylsilyl chlorosulfonate at 20−25 °C did not effect any substitution.

Conclusion

Under conditions favoring a nearly quantitative reaction of the C−F bonds, the polycondensations of silylated 5-methylresorcinol and silylated phloroglucinol showed the expected high cyclization tendencies. However, in both cases, the formation of cyclic dimers proved to be unfavorable. Somewhat unexpected but characteristic for the polycondensations of silylated phloroglucinol was the bridging of preformed cycles (yielding bicycles and possibly multicycles) and the formation of cyclic building blocks by "backbiting" of C−F groups. As a consequence of this high cyclization tendency, the resulting branched PESs and networks mainly consist of cyclic and bicyclic oligomers as building blocks (Scheme 7).

In the classical experiments and theories of Flory concerning the gelation in polycondensations of $a_3 + b_2$ monomers, equivalent mixtures (a = b) were studied and the minimum conversion was determined leading to gelation. In a clean polycondensation free of cyclization and side reactions, gelation should occur at 71 ± 1% conversion. The experimental results obtained by Kienle[12] and Flory[2,13] from various polyester syntheses were gelation points around 77 ± 2%, and Flory interpreted this difference as due to the influence of a few cyclization steps. However, Flory ignored other side reactions, such as the formation of ether and vinyl groups, which may also occur in acid-catalyzed (poly)esterification reactions at high temperatures. Therefore, no reliable information about cyclization existed at that time. More advanced theories of networks and gelation[8] also include the formation of a few loops before and during the gelation process. These modern theories were designed to improve the understanding of physical and mechanical properties of loose networks (e.g., synthetic rubbers). They were not based on MALDI−TOF analyses of the sol phase and were not designed to analyze $a_2 + b_3$ polycondensation.

The approach of the present work is an alternative to Flory's method. It is based on reaction conditions allowing for more than 99% conversion with variation of the a_2/b_3 ratio. This approach in combination with MALDI−TOF analyses of the sol phase proves the absence of significant side reactions and a predominant influence of various cyclization reactions on the course of the polycondensation. Particularly interesting is the formation of numerous small cycles and bicycles including monofunctional compounds. These monofunctional bicycles and multicycles can act as chain terminators and explain the low molecular weights of the products before gelation. The observation of numerous low molar mass species prior to gelation was also reported by Kienle and Flory and attributed to the low conversion (≤75%).

Finally, it should be mentioned that the formation of bicyclic and multicyclic oligomers observed in this work agrees with a recent report of Colquhoun and co-workers on syntheses of cyclic oligo(ether ketone)s.[14] Those authors isolated a bicyclic dimer from the polycondensation of bisphenol A with 1,3,5-tris(4-fluorobenzoyl)-benzene under pseudo high dilution.

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References and Notes

(1) *Collected papers of W. H. Carothers on polymerization*; Mark, H., Whitby G. S., Eds.; Wiley-Interscience: New York, 1940.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca NY, 1953; Chapters VIII and IX.
(3) Jacobson, H.; Stockmayer, W. H. *J. Phys. Chem.* **1950**, *54*, 0.
(4) Jacobson, H.; Beckmann, C. O.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1607.
(5) Kricheldorf, H. R.; Rabenstein, M.; Maskos, M.; Schmidt, M.; *Macromolecules* **2001**, *34*, 713.
(6) Kricheldorf, H. R.; Böhme, S.; Schwarz, G. *Macromolecules* **2001**, *34*, 8879.
(7) Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Krüger, R.-P.; Schulz, G. *Macromolecules* **2001**, *34*, 8886.
(8) Stepto, R. F. T. In *Polymer Networks*; Stepto, R. F. T., Ed.; Blackie Academic & Professional: London, 1998; Chapter 2.
(9) Huntress, E. H.; Carter, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511.
(10) Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2967.
(11) Fritsch, D.; Vakhtangishvili, L.; Kricheldorf, H. R. *J. Macromol. Sci.—Pure Appl. Chem.* **2002**, *A39*, 1335.
(12) Kienle, R. H.; van der Meulen, F. A.; Petke, F. E. *J. Am. Chem. Soc.* **1939**, *61*, 2258 and 2268.
(13) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(14) Colquhoun, H. M.; Arico, F.; Williams, D. J. *Chem. Commun.* **2001**, 2574.

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