8886 *Macromolecules* **2001,** *34,* 8886−8893

Macrocycles. 18. The Role of Cyclization in Syntheses of Poly(ether−sulfone)s

Hans R. Kricheldorf,*,† Sigrid Böhme,† Gert Schwarz,† Ralph-Peter Krüger,‡ and Günther Schulz‡

Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany; and BAM, Haus 30, Unter den Eichen 87, D-12205 Berlin, Germany

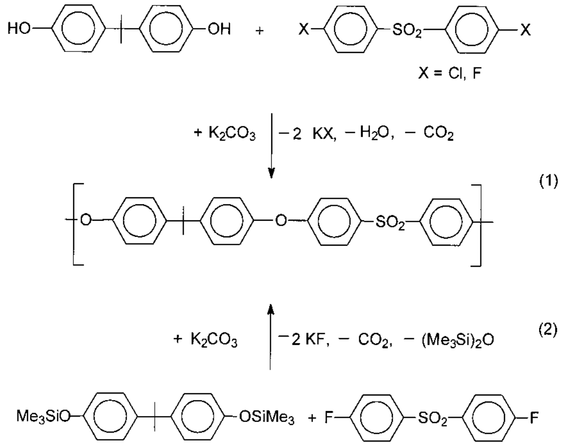
Received February 5, 2001; Revised Manuscript Received September 12, 2001

ABSTRACT: Poly(ether−sulfone)s having an identical backbone were prepared by four different methods. First, silylated bisphenol A (BSBA) was polycondensed with 4,4′-difluorodiphenyl sulfone (DFDPS) and K_2CO_3 in *N*-methylpyrrolidone with variation of the temperature. Second, analogous polycondensation were conducted using CsF as catalyst (and no K_2CO_3). Third, CsF-catalyzed polycondensations BSBA and DFDPS were conducted in bulk up to 290 °C. Fourth, free bisphenol was polycondensed with DFDPS or 4,4′-dichlorodiphenyl sulfone and K_2CO_3 in DMSO with azeotropic removal of water. MALDI−TOF mass spectroscopy revealed that the first method mainly yielded cyclic poly(ether−sulfone)s which were detected up to masses around 13 000 Da. These and other results suggest that these polycondensations take a kinetically kontrolled course at tempeatures ≤145 °C. This interpretation is also valid for the fourth method where high yields of cycles were obtained with DFDPS. With the less reactive 4,4′-dichlorodiphenyl sulfone lower conversions, lower molecular weights and lower fractions of cycles were found. In contrast to KF (resulting from K_2CO_3) CsF cleaves the poly(ether sulfone) backbone at temperatures > 145 °C. Smaller amounts of smaller cycles were found in these CsF-catalyzed polycondensations which were in this case the result of thermodynamically controlled “back-biting degradation”.

Introduction

In previous publications,[1−3] it was demonstrated for various syntheses of polyesters and polyamides that large amounts of cyclic oligomers and polymers were formed, when the reaction conditions were optimized for high conversions and high molecular weights. These results proved that in contrast to the classical theory of Carothers[4] and Flory,[5] cyclization competes with propagation at any stage of a kinetically controlled step-growth polymerization regardless of the concentration. The present work had the purpose to extend our previous studies to another class of important polycondensates, namely to aromatic poly(ether−sulfone)s (PESs). Two reasons account for this choice. First, PESs are known to be chemically and thermally so stable, that their isolation and characterization should not be affected by degradation reactions (in contrast to polyesters[2]). Second, PESs can be prepared by a variety of synthetic methods. In this work, four different methods, all based on the nucleophilic substitution reaction, should be studied and compared with regard to origin and extent of cyclization reactions.

The most widely used synthetic method for both technical and research purposes consists of polycondensations of free bisphenols with 4,4′-dichlorodiphenyl sulfone (DCDPS) or with 4,4′-difluorodiphenyl sulfone (DFDPS) in an inert polar solvent such as DMSO or NMP using K_2CO_3 as catalyst and HX acceptor (eq 1). Furthermore, silylated bisphenols may be used as nucleophilic monomers and in this work bistrimethylsilyl bisphenol A (BSBA) was used for most polycondensations (eq 2). At least for research purposes silylated bisphenols have the following advantages. First, the formation of water is avoided and, thus, the risk that the alkaline water hydrolyzed C−F bonds. Second, the lower reactivity of the silylated bisphenols allows one to study more easily the influence of reaction time and temperature on the course of the polycondensation. Third, with silylated bisphenols, polycondensations may be performed in bulk or in solution, and in solution K_2CO_3 or CsF may used as catalyst.



Finally, it should be noted that several research groups[6−14] have reported on the synthesis of cyclic oligo(ether sulfone)s, OESs. Attwood et al.[6] isolated a cyclic dimer as byproduct of polycondensations of an ortho-functional monomer prone to cyclization. All other authors prepared the cyclic OESs with the intention to use them as monomers for ring opening polymerizations. In most cases, individual (i.e. monodisperse) cycles were isolated. In the first detailed study of this working field, Mullins and co-workers[7,8] identified and isolated (by HPLC) cycles up to a degree of polymerization (DP) of 5. They observed side reactions such as hydrolysis or

---

† Universität Hamburg.
‡ BAM.

10.1021/ma010218l CCC: $20.00

Table 1. K_2CO_3-Promoted Polycondensations of BSBA and DFDPS in NMP (under Purified N_2)

polym. no.	excess of DFDPS (mol %)	T_{max} (°C)	time (h)	yield (%)	η_{inh}[a] (dL/g)
1	0	110	24	80	0.10
2	0	110	48	74	0.31[b]
3	0	110	72	87	0.38[c]
4	0	145	8	86	0.53
5	0	145	15	84	0.69[d]
6	0	145	24	81	0.73[e]
7	0	145	48	81	0.81[f]
8	1	145	24	81	0.58
9	0	180	24	76	0.44[g]
10	1	180	24	75	0.44

[a] Measured at 25 °C with c = 2g/L in CH_2Cl_2. [b] $M_n \sim 14\,000$ (GPC). [c] $M_n \sim 16\,000$ (GPC). [d] $M_n \sim 36\,000$ (GPC). [e] $M_n \sim 42\,000$ (GPC). [f] $M_n \sim 50\,000$ (GPC). [g] $M_n \sim 18\,000$ (GPC).

aminolysis (in dimethylacetamide) of C−F bonds despite low temperatures (≤140 °C) and their virgin reaction mixtures contained significant amounts of linear OESs and PESs. All these syntheses of cyclic OESs[7−14] were performed under the conditions of the Ruggli−Ziegler dilution principle, and thus, a predominant formation of cycles was not surprising.

Experimental Section

Materials. Fluorobenzene, chlorosulfonic acid, cesium fluoride, and potassium carbonate were purchased from Aldrich Co. (Milwaukee, WI) and used as received.4,4′-Dichlorodiphenyl sulfone (DFDPS) was also purchased from Aldrich Co. and recrystallized from toluene ligroin (mp 147−148 °C). 4,4′-Difluorodiphenyl sulfone (DFDPS) was prepared according to the literature.[15] After recrystallization from ethanol, the mp was 98−99 °C. Bisphenol A was a gift of Bayer AG (Leverkusen, Germany). It was silylated with hexamethyldisilazane in refluxing xylene and distilled in vacuo. The K_2CO_3 was dried over P_4O_{10} in vacuo. The *N*-methylpyrrolidone (NMP) was a gift of BASF AG (Ludwigshafen, Germany). It was twice distilled over P_4O_{10} in vacuo. The dimethyl sulfoxide (DMSO, p.a. grade) was purchased from Merck Eurolab GmbH (Darmstadt, Germany).

Polycondensations. (A) Table 1. Bistrimethylsilyl bisphenol A, BSBA, (20 mmol), DFDPS (20 mmol), and dry K_2CO_3 (21 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer and gas-inlet and gas-outlet tubes. Dry NMP (20 mL) was added, and the reaction vessel was placed into an oil bath preheated to 110 °C. The temperature was maintained or raised to 145 °C (or 180 °C). When the desired time was over, the cold reaction mixture was deluted with NMP (20 mL) and poured into water, The isolated polymer was dried in vacuo and reprecipitated from CH_2Cl_2/methanol.

(B) Table 3. Bisphenol A (20 mmol), DFDPS (20 mmol), and K_2CO_3 (21 mmol) were weighed into a 250 mL three-necked flask equipped with a mechanical stirrer, dropping funnel and distillation head. DMSO (100 mL) and toluene (25 mL) were added, and this mixture was heated in an oil bath thermostated at 140 °C. The toluene was slowly distilled off and simultaneously replaced from the dropping funnel. After 6 h, the toluene was completely removed in vacuo at a lower temperature, and the remaining DMSO solution was poured into methanol (700 mL). The precipitated polymer was, filtered off, washed with methanol, dried in vacuo and reprecipitated from CH_2Cl_2/methanol. Analogous polycondensations were conducted with DCDPS (20 mmol).

(C) Table 4. BSBA (20 mmol), DFDPS (20 mmol), and CsF (0.05 or 0.1, 0.2, and 0.5 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer and gas-inlet and gas-outlet tubes. Dry NMP (27 mL) were added and the reaction vessel was placed into an oil bath preheated to 100 °C. The temperature was rapidly raised to 180 °C, and this temperature was maintained for 24 or 48 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 and precipitated into methanol. The isolated polymer was reprecipitated from CH_2Cl_2 and ethanol.

(D) Table 5 BSBA (20 mmol), DFDPS (20 mmol), and CsF (0.1 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer and gas-inlet and gas-outlet tubes. The reaction vessel was placed into a metal bath preheated to 150 °C and the temperature was raised according to the program given in Table 5. The cold product was dissolved in CH_2Cl_2, precipitated into methanol and dried at 80 °C in vacuo.

Measurements. The inherent viscosities were measured in CH_2Cl_2 using an automated Ubbelohde viscometer thermostated at 25 °C.

The 400 MHz ^1H NMR spectra were recorded with a Bruker AM-400 FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS as solvent and shift reference.

The MALDI−TOF mass spectra of all samples derived from bisphenol A were recorded with a Kratos Kompact 3 (Shi-

Table 2. Reaction Conditions and Results of Reaction between Preferentially Cyclic Poly(ether−sulfone)s andVarious Nucleophilic Reagents

expt no	nucleophilic reactant	PES[a]/nucleophile	temp (°C)	time (h)	yield (%)	η_{inh}[c] (dL/g) reaction product	η_{inh}[c] (dL/g) starting material
1	$K_2CO_3 + H_2O$	2:1[b]	145	48	58	0.19	0.44
2	$KOC_6H_4C(CH_3)_3$	2000:1	145	48	91	0.45	0.44
3	$KOC_6H_4C(CH_3)_3$	2:1	145	48	59	0.11	0.34
4	$KOC_6H_4C(CH_3)_3$	2:1	180	48		0.08	0.34
5	CsF	2:1	145	48	69	0.22	0.34
6	CsF	2:1	180	48	43	0.11	0.34

[a] Molar ratio repeating unit/nucleophile. [b] This molar ratio concerns H_2O (K_2CO_3 was used in a 1:1 ratio). [c] Measured at 25 °C with *c* = 2g/L in CH_2Cl_2.

Table 3. Properties of Poly(ether−sulfone)s from Bisphenol A and DFDPS or DCDPS

polym no.	origin of the PES	electrophilic common.	yield[a] (%)	η_{inh}[b] (dL/g)	M_n[c] (GPC)
1	this work: 6 h in DMSO/toluene	DFDPS	94	0.71	41 000
2	this work: 6 h in sulfolane/toluene	DCDPS	62	0.08	
3	this work: 6 h in DMSO/xylene	DCCPS	85	0.18	
4	Aldrich: 42.830−2	(DCDPS)		0.38	16 000[d] (35 000)[de]
5	Aldrich: 18.244−3	(DCDPS)		0.40	22 000[d]
6	Aldrich: 37.429−6	(DCDPS)		0.47	26 000[d]

[a] After precipitation into water. [b] Measured at 25 °C with *c* = 2g/L in CH_2Cl_2. [c] GPC measurement in THF calibrated with polystyrene. [d] Information from the supplier (catalog 2000). [e] Determined by light scattering.

Table 4. CsF-Catalyzed Polycondensations of BSBPA and DFDPS in NMP

polym no.	excess of DFDPS (mol %)	CsF/BSBPA molar ratio	T_{max} (°C)	time (h)	yield (%)	η_{inh}[a] (dL/g)
1	0	1/400	145	48	71	0.17
2	+1	1/400	145	48	84	0.25
3	0	1/400	180	24	88	0.20[b]
4	0	2/400	180	24	88	0.15[c]
5	0	5/400	180	24	87	0.13
6	0	10/400	180	24	89	0.11
7	0	1/400	180	48	86	0.26
8	+1	1/400	180	48	94	0.38[d]
9	+3	1/400	180	48	72	0.28[e]

[a] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [b] $M_n \sim 8000$ (GPC). [c] $M_n \sim 6000$ (GPC). [d] $M_n \sim 16\,000$ (GPC). [e] $M_n \sim 14\,000$ (GPC).

madzu) mass spectrometer in the reflection mode using a nitrogen laser with a wavelength of 337 nm. 2,4,6-Trihydroxyacetophenone−water served as matrix and the Na ions set free from the walls of the glass ware served as dopants (in some cases a double doping by Na^+ and K^+ was observed). The range of detectable mass peaks was limited to approximately 5000 Da.

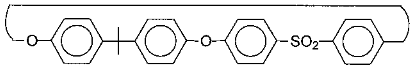
Selected samples (e.g., Figures 1−6) were also measured with a Bruker Biflex 3 in the reflection mode using again a nitrogen laser ($\lambda = 337$ nm). The irradiation targets were prepared from chloroform solutions in plastic tubes. Dithranol served as matrix and potassium trifluoroacetate as dopant. For most measurements, a cutoff limit of 10^3 Da was used, but for the detection of mass peaks above 11 000 Da a cutoff limit of 3000 Da was sometimes more helpful. Furthermore, all measurements of high molar mass PES were repeated several times with variation of the PES/matrix ratio between 1:10 and 1:300.

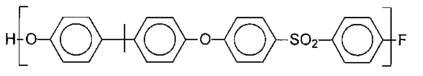
The GPC measurements were performed with an equipment consisting of a HPLC pump Rheos 4000/ERC, UV and RI detectors (Knauer GmbH) and the GPC software from PSS (Mainz, Germany). As stationary phase were used three PS−DVB columns (300 × 8 mm ID), PL−gel mix B, PL−gel mix E, and PL−gel 50A, the mobile phase was THF (Licrosolve, Roth, Germany), 50 μL of a 0.5% solution were injected. The GPC system was calibrated with polystyrene standards from PSS/Mainz.

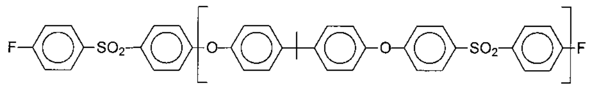
Results and Discussion

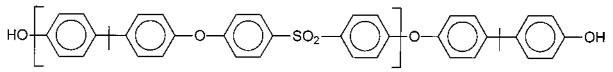
Polycondensations of BSBA with K_2CO_3. In the first part of this work, polycondensations of silylated bisphenol A and DFDPS promoted by K_2CO_3 in NMP were studied. NMP was selected as reaction medium, because it was found in previous studies[16] to be the optimum solvent for this purpose. The temperature was varied between 110 and 180 °C (in steps of 35 °C), because the polycondensation was too slow at lower temperatures and NMP not stable enough at higher temperatures. The time was varied between 24, 48, and 72 h (nos. 1−3, Table 1).

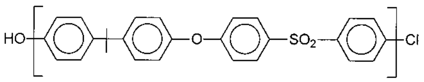
The rather low solution viscosity of the PES isolated after 24 h suggested incomplete conversion. This suggestion was confirmed by the MALDI−TOF mass spectrum (Figure 1A) which displayed intensive mass peaks of the linear species **1La**, **1Lb**, and **1Lc** whereas the peaks of cyclic oligo(ether sulfone)s (OES, **1c**) were barely detectable. After 48 h the peaks of the cyclic OESs and PESs were far more intensive than the peaks of all linear species below masses of 3000 Da, but the presence of **La**, **Lb**, and **Lc** chains indicated that the conversion was still lower than 99%. After 72 h the cycles were again the predominant reaction products up to masses around 5500 Da, but the peaks of linear chains having two OH end groups (**Lc**) were present (Figure 1B) and became more intensive above 5500 Da. The absence of **La** and **Lb** chains and the higher molecular weight (relative to no. 2, Table 1) suggest a

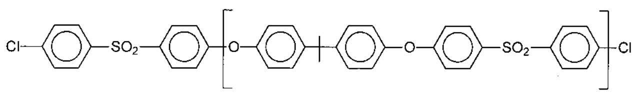

1C


1La


1Lb


1Lc


1Ld


1Le

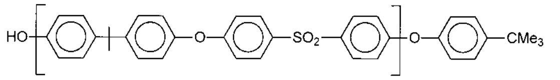

1Lx

Table 5. CsF-Catalyzed Polycondensations of BSBPA and DFDPS in Bulk

polym no	excess of DFDPS (mol %)	CsF/BSBPA molar ratio	temp (°C)	time (h)	yield (%)	η_{inh}[a] (dL/g)
1	+3	2/400	180, 210, 240, 270	1, 2, 2, 1	~10	
2	+1	2/400	180, 210, 240, 270	1, 2, 2, 1	91	0.33
3	0	2/400	180, 210, 240, 270	1, 2, 2, 1	91	0.48
4	−1	2/400	180, 210, 240, 270	1, 2, 2, 1	93	0.34
5	−3	2/400	180, 210, 240, 270	1, 2, 2, 1	~15	
6	0	1/400	180, 210, 240, 270	1, 2, 2, 1	94	0.65
7	0	2/400	180, 210, 240, 270	1, 2, 2, 1	93	0.72[b]
8	0	5/400	180, 210, 240, 270	1, 2, 2, 1	91	0.61
9	0	10/400	180, 210, 240, 270	1, 2, 2, 1	93	0.66
10	0	1/400	180, 210, 240, 270	1, 2, 2, 1	91	0.62[c]

[a] Measured at 25 °C; $c = 2$ g/L in CH_2Cl_2. [b] $M_n \sim 41\,000$ (GPC). [c] $M_n \sim 35\,000$ (GPC).

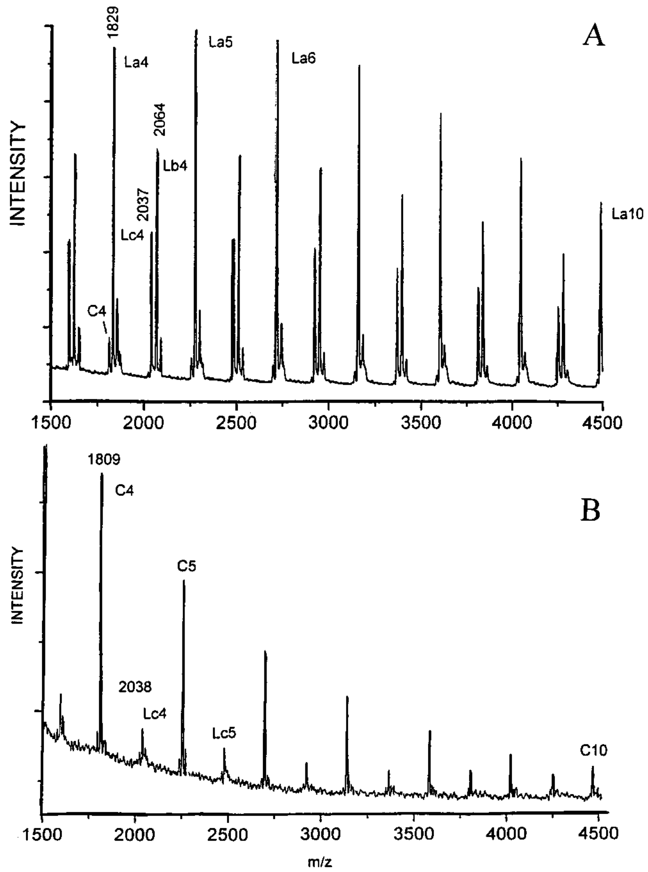


Figure 1. MALDI−TOF mass spectra: (A) PES no. 1, Table 1; (B) PES no. 3, Table 1.

high conversion. This means that in this experiment the stoichiometry (i.e. the feed ratio of both monomers) was not perfect, because BSBA was present in a slight excess. As confirmed by another experiment discussed below, the MALDI−TOF mass spectra proved to be very sensitive to slight deviations from the ideal stoichiometry.

In this connection it should be pointed out that it is not possible to calculate the conversion “p” from the average degree of polymerization ($\overline{DP}$) via the number average molecular weights (M_ns; see footnotes of Tables 1 and 3−5) using the Carothers equation $\overline{DP} = 1/(1 - p)$. The reason for this unfavorable situation is the formation of cycles which contributes to the conversion of functional groups but not to the chain growth. As long as direct quantitative determination of functional groups is not available (and such a determination for all samples was beyond the scope of this work because a reliable quantification of the MALDI−TOF mass peaks is not feasible), only a qualitative classification of the conversion is given.

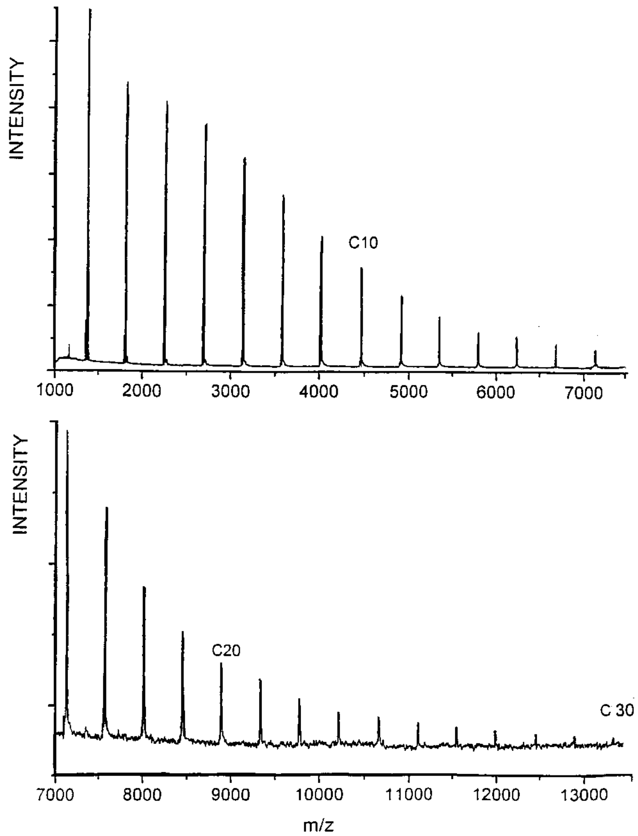


Figure 2. MALDI−TOF mass spectrum (segments) of PES no. 5, Table 1 (the spectra of nos. 6 and 7, Table 1, or no. 1, Table 3, are identical).

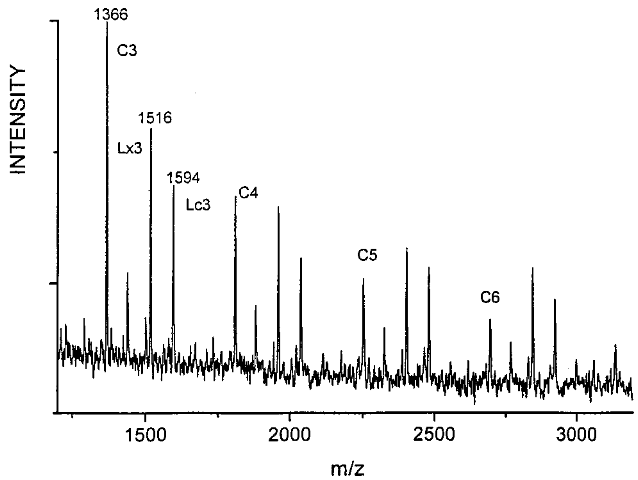


Figure 3. MALDI−TOF mass spectrum of the reaction product no. 2, Table 2.

The polycondensations performed at 145 °C (nos. 4−8, Table 1) showed the following tendencies. After 8 h, both solution viscosity and MALDI−TOF spectra suggested a conversion not higher than 99% with peaks of linear chains predominating above masses around 5000 Da. However after 15 h, high conversions with high molecular weights were obtained in combination with an almost ideal stoichiometry. The MALDI−TOF mass spectra of all three PESs (nos. 5−7, Table 1) were nearly identical and almost exclusively displayed mass peaks of cyclic PES which in the best spectrum were detectable up to 13 000 Da (Figure 2). This finding together with the high molecular weights suggest conversions above 99.9%. When 1 mol % of DFDPS was added (no. 8), the molecular weight was lower and **Lb** chains became detectable in the MALDI−TOF mass spectra. This finding confirmed the sensitivity of the MALDI−TOF mass spectra to slight variations of the stoichiometry. In summary, all results together demonstrated that any optimization of the reaction conditions toward high molecular weights also raised the fraction of cyclic OESs and PESs at the expense of all linear chains. This finding disagrees with the classical theory of step-growth polymerizations as developped by Carothers and Flory,[4,5] but it perfectly agrees with our previously

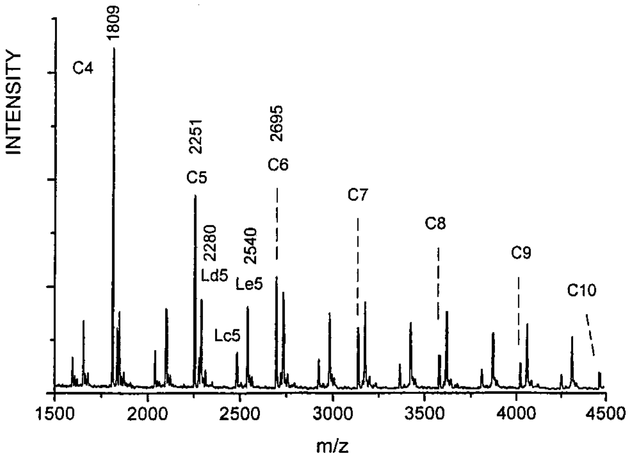


Figure 4. MALDI−TOF mass spectrum (segments) of PES no. 3, Table 3.

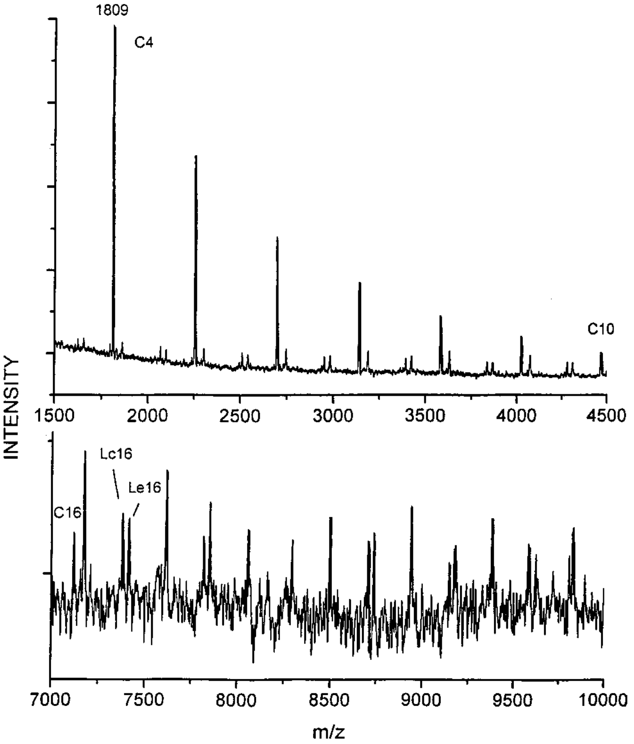
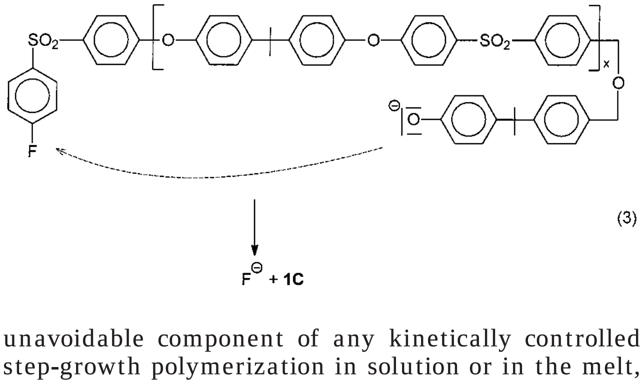


Figure 5. MALDI−TOF mass spectrum of the PES no. 6, Table 3 (Aldrich 37.429-6).

presented concept[2,3] of kinetically controlled polycondensations. In this concept cyclization (eq 3) is an unavoidable component of any kinetically controlled step-growth polymerization in solution or in the melt, and the fraction of cycles increases with the conversion and with lower concentration.



(3)

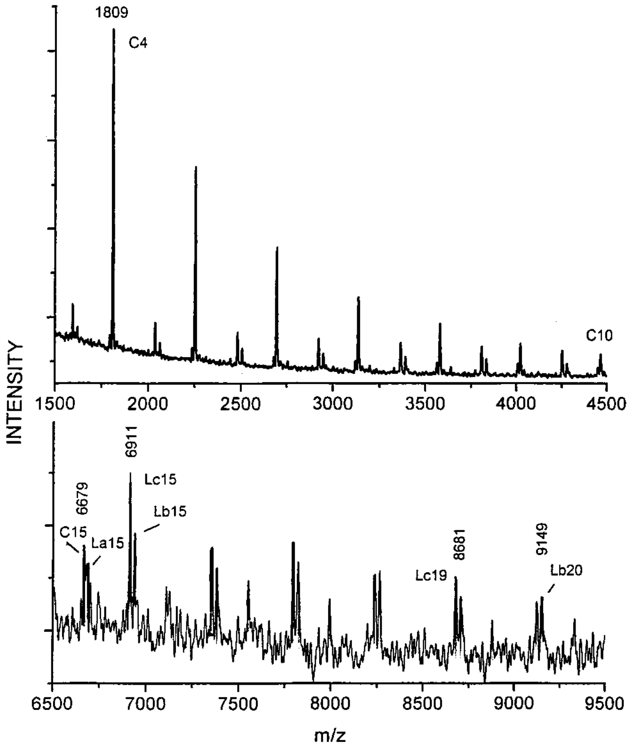
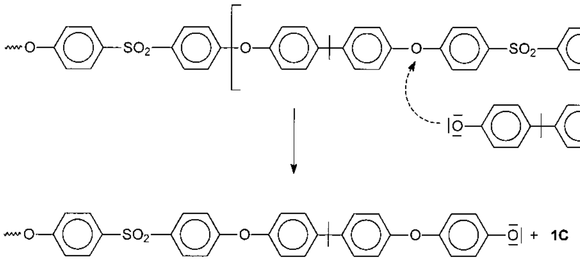


Figure 6. MALDI−TOF mass spectrum (segments) of PES no. 7, Table 5).

Two polycondensations conducted at 180 °C gave moderate molecular weights (nos. 9 and 10), but the MALDI−TOF mass spectra almost exclusively displayed peaks of cycles, detectable up to masses around 7000 and 8000 Da, respectively. For reasons discussed below "back-biting degradation" (eq 4) may have contributed to the formation of cycles in these experiments.

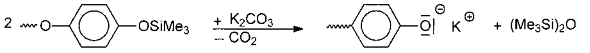


(4)

Before the polycondensations, compiled in Table 1, were performed, a first series of polycondensations was conducted at 145 °C quite analogous to those of nos. 4−7 in Table 1). However, the first series of polycondensations was conducted under a stream of a less pure ("standard") nitrogen. Surprisingly the molecular weights had a maximum after 24 h ($\eta_{inh} \sim 0.45-0.50$ dL/g) and decreased with longer reaction times. This trend proved to be reproducible and raised the suspicion that moisture carried by the nitrogen slowly hydrolyzed the initially formed PES chains. To test this hypothesis, a PES containing a large fraction of cycles (no. 9, Table 1) was heated in NMP to 145 °C in the presence of K_2CO_3, and water (50 mol % relative to the repeat unit) was added. Both yield and viscosity of the product isolated after 48 h clearly demonstrated that a partial hydrolysis had indeed occurred (no. 1, Table 2).

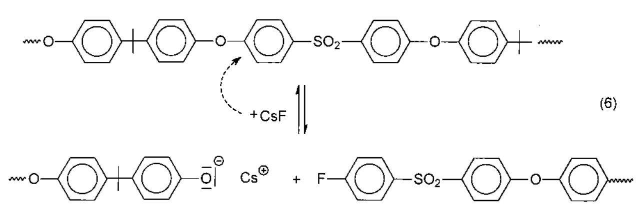
Partial hydrolysis of a PES by OH^- in DMSO above 140 °C has been reported in the literature,[7,8,17] but those authors used concentrated sodium hydroxide solutions.

The unexpected sensitivity of PES **1** toward traces of moisture in the presence of K_2CO_3 prompted us to study the impact of other nucleophiles related to the reaction conditions onto PES **1**. The K-salt of 4-*tert*-butylphenol was used in two experiments performed at 145 °C (no. 2 and Table 2) and one experiment at 180 °C (no. 4). Again a severe degradation was indicated by the low yields and viscosities when a large amount of the phenoxide was used. Furthermore MALDI−TOF mass spectra of the degradation products were recorded and the mass peaks of linear chains having one *tert*-butylphenyl ether end group were detected (**Lx** in Figure 3). There **Lx** chains are the obvious result of nucleophilic cleavage of a cyclic OESs by phenoxide ions. This finding suggest that in polycondensations at temperatures ≥145 °C the phenoxide end groups may in principle attach the PES backbone forming cycles by “back-biting” (eq 4). However the concentrations of anionic chains ends in polycondensations of a silylated bisphenol (eq 5) is certainly several orders of magnitude lower than in the degradation experiments of Table 2 as indicated by the slow progress of these polycondensations. When a small amount of potassium *tert*-butylphenoxide was added to cyclic PES (no. 2, Table 2) no catalytic degradation was observed. Therefore, it may be concluded that “back-biting” had little influence on the course of the polycondensation at temperatures ≤145 °C.



(5)

Finally, the stability of PES **1** against CsF was studied (nos. 5 and 6, Table 2) because CsF was used as catalyst in numerous polycondensations of BSBA as discussed below. Again a PES containing a large fraction of cycles in the mass range below 4000 Da was used as substrate and heated with 50 mol % of CsF (relative to moles of repeating units) either to 145 or 180 °C. The data listed in Table 2 clearly demonstrate that in both experiments a degradation took place with a stronger effect at 180 °C as expected. These results mean that CsF is capable of cleaving the PES backbone, generating a condensation/degradation equilibrium if the time suffices (eq 6). Furthermore, these results suggest that the formation of cycles in CsF-catalyzed polycondensations above 145 °C is mainly a consequence of “back-biting” and, thus, a process under thermodynamic control. Moreover, a tremendous difference in the reactivity of CsF and KF became evident. Carlier et al.[18] have reported that fluoride ions cleave PES chains only above 280 °C, but those authors only used KF and did not vary the cation. In agreement with those authors, the high molecular weights and large amounts of cycles obtained from several polycondensations of Table 1 clearly demonstrate that the KF formed in these polycondensation does not interfer with chain growth and cyclization. The largely different reactivities of KF and CsF toward PES parallels their different reactivities as catalysts in polycondensations of silylated diphenols.[19] In this case the catalytic effect consists of a cleavage of the Si−O bond by the fluoride ion (eq 7).



(6)

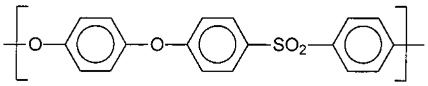
(7)

Polycondensations of Bisphenol A with K_2CO_3. As mentioned in the Introduction, the standard method most widely used for syntheses of PESs (including their technical production) is the polycondensation of free bisphenols with DCDPS and K_2CO_3 in an inert solvent. The liberated water (see eq 1) is azeotropically removed with toluene, and due to the high concentration of potassium phenoxide ions, these polycondensations are essentially complete within 3−4 h. In this work a first polycondensation was performed with DFDPS as reaction partner of bisphenol A (no. 1, Table 3) and DMSO was used as solvent, because in preliminary experiments (not described here in detail) NMP and sulfolane gave poorer results. A PES of high molecular weight was obtained and the MALDI−TOF mass spectrum revealed cycles as the predominant reaction products up to masses around 13 000 Da. The mass spectrum was quite similar to that of PES no. 6, Table 1 (Figure 2), but below 5000 Da weak signals of OH- or F-terminated chains were also detectable.

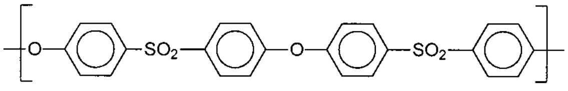
In an exactly analogous experiment, DCDPS was used as electrophilic monomer, and a lower yield and low molecular weight were obtained (no. 2, Table 3). The MALDI−TOF mass spectrum revealed the presence of linear chains having the structures **1Lc**, **1Ld**, and **1Le**, whereas cycles were almost absent. When toluene was replaced by xylene a higher reaction temperature could be achieved (160−165 °C instead of 135−140 °C) and a higher yield with a higher molecular weight was obtained (no. 3, Table 3). A considerably higher fraction of cycles was found for sample no. 3 as illustrated by Figure 4. However, even in this case the linear chains having OH and/or Cl end groups predominated at higher masses in contrast to the spectrum of the PES prepared from DFDPS (compare Figures 2 and 4). It is characteristic for a polycondensation with moderate conversion but with a good balance of the stoichiometry that the linear chains having two different end groups (**1Ld** in this case) are the most abundant species at higher masses. These results clearly demonstrate that the lower reactivity of DCDPS (relative to DFDPS) results in lower conversions and, thus, in lower molecular weights and lower fractions of cycles.

In this connection, three commercial PES samples derived from bisphenol A were characterized (nos. 4−6, Table 3). In all cases the MALDI−TOF mass spectra demonstrated the presence of linear chains having Cl end groups (**Ld** and **Le**), thus proving that these PES samples were prepared from DCPS via the standard procedure. The cycles were found to be the predominant species at masses ≤ 4000 or 5000 Da. Particularly, noteworthy is the observation that the fraction of cycles increased with increasing molecular weight of these commercial samples. Yet, even in the case of the highest molecular weight (no. 6) the content of cycles was lower than in the case of sample no. 1 as demonstrated by a comparison of Figures 2 and 5. This comparison also demonstrates that it is important to measure and evaluate the mass range above 5000 Da, because there is little difference in the lower mass range. In summary, all the results presented above suggest that the syntheses of PESs by the standard method are kinetically controlled polycondensations, which involve a tremendous increase of cyclic oligomers and polymers when stoichiometry and conversion are optimized.

Finally, two more commercial PESs were studied having structures **2** and **3**. The MALDI−TOF mass spectra proved again the presence of linear chains having Cl end groups, thereby proving that DCDPS was used as electrophilic monomer. These linear chains were the predominant species above 5000 Da (**2**) or above 4000 Da (**3**), whereas the cycles were prevailing in the lower mass range. Therefore, these mass spectra fit perfectly in with the pattern of synthesis−structure relationships elaborated for the PES samples of structure **1**. In this connection, a publication of Vitalini et al.[20] should be mentioned that displays a MALDI−TOF mass spectrum of a commercial PES (from Aldrich Co.), but unfortunately neither catalog numbers nor molecular weights were mentioned. Anyway the mass spectrum displays the peaks of cycles up to masses around 11 000 Da. Therefore, this spectrum together with the results presented here prove that the role of cyclization in kinetically controlled polycondensations is also important for commercial products and not only an academic problem.



2



3

CsF-Catalyzed Polycondensations. In contrast to polycondensations of free bisphenols which require metal oxides or carbonates as catalyst and HX-acceptor, polycondensations of silylated bisphenols may be catalyzed by small amounts of CsF. Obviously the CsF cleaves the phenoxysilane group and generates a phenoxide ion which is the active species (eq 6). The fluorosilane formed as a byproduct is highly volatile and, thus, easy to remove from the reaction mixture. This method has two advantages. First, the poly(ether−sulfone)s do not need to be purified from stoichiometric amounts of salts, and second, these polycondensations may be conducted in an inert solvent but also in bulk.[16,19] Therefore, one series of polycondensations was performed in NMP (Table 4) for comparison with the K_2CO_3-promoted experiments and a second series of polycondensations was conducted in the melt (Table 5).

Relatively low inherent viscosities were found in NMP at 140−145 °C (nos. 1 and 2, Table 4). Both, a higher yield and a higher viscosity was obtained with an 1% molar excess of DFDPS. At 180−185 °C higher viscosities were found at the same reaction time of 48 h (nos. 7 and 8), but again the best results were obtained with a slight excess (1 mol %) of DFDPS. A larger excess was contraproductive (no. 9). Obviously, a few side reactions consume C−F groups. A similar trend was previously observed for polycondensations of BSBA, DCDPS, and K_2CO_3 in NMP.[16] However, the most interesting result was found when the amount of added CsF was varied whereas all other parameters were kept constant (nos. 3−6, Table 4). The inherent viscosities showed a downward trend with larger amounts of CsF. This result perfectly agrees with the degradation of preformed PES observed in experiment no. 6, Table 2. The experiments nos. 3−6, Table 4, indicate again that CsF can easily cleave the PES backbone at temperatures above 145 °C. These results also suggest that the cyclic OESs and PESs formed during the polycondensations listed in Table 4 are mainly the result of "backbiting degradation" (eq 4) in contrast to the K_2CO_3-promoted polycondensations at temperatures ≤ 145 °C (Tables 1 and 3).

The MALDI−TOF mass spectra revealed that cyclic OESs prevailed in all samples at masses below 3000 or 4000 Da. However, linear chains having OH and F end groups (mainly **1La**) were abundant at higher masses. An important result is the observation that the fraction of cycles decreased when higher amounts of CsF were added (nos. 3−6, Table 4). In contrast, the fraction of linear chains, mainly **1La**, increased in agreement with the assumption of a reversible chain cleavage by CsF (eq 6). From the viewpoint of preparative usefulness the results compiled in Table 4 clearly demonstrate that the catalysis with CsF is inferior to the K_2CO_3-promoted polycondensations (Tables 1 and 3).

The polycondensations in bulk were started with five experiments which had the purpose to elucidate the influence of the feed ratio on the molecular weight (nos. 1−5, Table 5). The absence of a solvent and the high temperatures may have the consequence that different volatilities of the monomers may affect the stoichiometry of the reaction mixture. The data summarized in Table 5 demonstrate that an exactly equimolar stoichiometry is the optimum for polycondensations of BSBA and DFDPS in bulk. A further small series of polycondensations was conducted in such a way that purified nitrogen was used and the amount of CsF was varied (nos. 6−9, Table 5). Considerably higher molecular weights were achieved, and the best result (no. 7, Table 5) came close to the best molecular weights of the K_2CO_3-promoted polycondensations. Interestingly, the molecular weights did show not a clear downward trend with increasing amount of CsF. This finding and the turbidity of the reaction mixtures suggest that not all CsF was dissolved, and thus, had not contributed to the equilibration outlined in eq 6. A polycondensation performed at a somewhat higher temperature and slightly longer time gave the same results, proving again that the conversion was limited by the equilibrium of eq 6 and not by insufficent time and temperature.

The MALDI−TOF mass spectra proved the formation of cycles as predominant species at masses below 5000 Da for all polycondensation with equimolar stoichiometry. Figure 6 demonstrates exemplarily for the sample with the highest molecular weight (no. 7) that the linear chains, particularly the structure **1La**, predominate at masses above 5000 Da. Hence, this spectrum displays a characteristic difference when compared to the best samples of K_2CO_3-promoted polycondensations (no. 4−9, Table 1, and no. 1, Table 3, having the same molecular weights). In those cases no linear species were absent or weak even after partial removal of cyclic oligomers by reprecipitation. In other words the "K_2CO_3−polycondensates" contain a considerably higher fraction of large cycles. This difference is in good agreement with the assumption of a kinetically controlled process in the case of K_2CO_3 catalysis at temperatures ≤ 145 °C and a thermodynamical control involving "back-biting" in the case of CsF-catalyzed polycondensations in bulk.

The theory of thermodynamically controlled ring chain equilibria[21,22] predicts for flexible chains that the concentration of cycles decreases with $DP^{-5/2}$. For the kinetically controlled cyclization of the same chains a decrease with $DP^{-3/2}$ is predicted. The PESs of this work will not necessarily obey this theory in all details, but they should follow the same trend. The formation of higher fractions of larger cycles in kinetically controlled polycondensations can be rationalized from a simple consideration. Under kinetic control the cyclization of long chains can only generate large cycles having the same DP as the linear chains. Under thermodynamic control the active end groups of long chains can also attack any reactive bond (e.g., ether groups) in the chain itself, thereby generating higher amounts of relatively small cycles. Therefore, the MALDI−TOF mass spectra obtained in this work perfectly agree with the assumption that the K_2CO_3-promoted polycondensations proceed at ≤145 °C under kinetic control and the CsF-catalyzed polycondensations at ≥185 °C under thermodynamic control. In the temperature range 140−180 °C, both regimes will more or less overlap, regardless if K_2CO_3 or CsF is used as catalyst.

Conclusion

The results obtained in this work allow the following conclusions. Polycondensations of DFDPS with either BSPA or bisphenol A mainly or exclusively proceed under kinetic control, when promoted by K_2CO_3 at temperaturtes ≤145 °C. In contrast to CsF the large amounts of KF formed as byproduct do not attack the PES chains. In agreement with our concept of kinetically controlled polycondensations,[1,2] cyclic oligomers and polymers are the main reaction products in the mass range observable by MALDI−TOF mass spectroscopy, when the reaction conditions are optimized for high molecular weights. The cyclizations themselves and incomplete conversion are then the limiting factors for the chain growth. As calculated by Gordon et al.[23] and Stepto and co-workers,[24] all reaction products must be cycles under ideal conditions and 100% conversion.

Furthermore, it was confirmed that CsF may cleave PES chains more or less efficiently at temperatures ≥145 °C. This equilibration has the consequence that CsF-catalyzed polycondensations of BSBA at high temperatures proceed under thermodynamic control. This thermodynamic control automatically involves ring−chain equilibria and, thus, the formation of relatively small cycles. Regardless of how exactly the ring−chain equilibria of PES obey the Jacobsen−Stockmayer theory,[21,22] the tendency of forming large cycles is significantly lower than in the case of kinetic control and this characteristic difference is at least qualitatively reflected in the MALDI−TOF mass spectra of the PES samples obtained in this work. Further studies of cyclization reactions in syntheses of aliphatic and aromatic polyethers are in progress.

Acknowledgment. We wish to thank the Deutsche Forschungsgemeinschaft for financial support.

References and Notes

(1) Kricheldorf, H. R.; Lorenc, A.; Spickermann, J.; Maskos, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3861.
(2) Kricheldorf, H. R.; Rabenstein, M.; Maskos, M.; Schmidt, M. *Macromolecules*, in press.
(3) Macrocycles. Part 17. Kricheldorf, H. R.; Böhme, S.; Schwarz, G. *Macromolecules*, submitted for publication.
(4) *Collected Papers of W. M. Carothers on Polymerization*; Mark, H., Whitby, G. S., Eds.; Interscience: New York, 1940.
(5) Flory, J. P. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1993; Chapters IIIV and IX.
(6) Attwood, T. E.; Barr, D. A.; King, T.; Newton, A. B.; Rose, J. B. *Polymer* **1977**, *18*, 359.
(7) Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J.; Bishop, M. T.; Balon, K. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (2), 174.
(8) Mullins, M. J.; Woo, E. P.; Murray, D. J.; Bishop, M. T. *CHEMTECH* **1993**, 25.
(9) Ganauly, S.; Gibson, H. W. *Macromolecules* **1993**, *26*, 2407.
(10) Xie, D.; Gibson, H. W. *Macromol. Chem. Phys.* **1996**, *197*, 2137.
(11) Xie, D.; Gibson, H. W. *Macromolecules* **1997**, *30*, 4814.
(12) Chen, M.; Guzei, J.; Gibson, H. W. *Macromolecules* **1997**, *30*, 2516.
(13) Jiang, H.; Chen, T.; Bo, S.; Xu, J. *Polymer* **1998**, *39*, 6079.
(14) Qui, Y.; Song, N.; Chen, T.; Bo, S.; Xu, J. *Macromol. Chem. Phys.* **2000**, *201* 840.
(15) Huntress, E. M.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511.
(16) Kricheldorf, H. R.; Jahnke, P. *Makromol. Chem.* **1990**, *191*, 2027.
(17) Johnson, R. N.; Farnham, A. G. *J. Polym. Sci., Part A-1*, **1967**, *5*, 2415.
(18) Carlier, U.; Devaux, J.; Legras, R.; McGrail, P. T. *Polymer* **1993**, *34*, 167.
(19) Kricheldorf, H. R.; Bier, G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2283.
(20) Vitalini, D.; Mineo, P.; Scamporrino, E. *Macromolecules* **1997**, *30*, 5285.
(21) Jacobsen, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(22) Semlyen, J. A. In *Large Ring Molecules*; Semlyen, J. A. Ed.; J. Wiley Ltd.: New York, 1996; Chapters 1, 16, and 17.
(23) Gordon, M.; Temple, W. B. *Makromol. Chem.* **1972**, *152*, 277.
(24) Stanford, J. L.; Stepto, R. F. T.; Waywell, D. R. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1308.

MA010218L