

Macrocycles 25. Cyclic poly(ether sulfone)s derived from 4-*tert*-butylcatechol

Hans R. Kricheldorf^{a,*}, Lali Vakhtangishvili^a, Gert Schwarz^a, Günter Schulz^b, Ralf-Peter Krüger^b

^a*Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany*

^b*BAM, Haus 30, Unter den Eichen 87, D-12205 Berlin, Germany*

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Abstract

Poly(ether sulfone)s were prepared by polycondensation of silylated 4-*tert*-butylcatechol and 4,4'-difluorodiphenylsulfone in *N*-methylpyrrolidone. The feed ratio and the reaction time were varied to study the influence of stoichiometry and conversion on molecular weight and extent of cyclization. Molecular weights and molecular weight distributions (MWD)s were characterized by SEC measurements calibrated with polystyrene. Light scattering confirmed that calibration with polystyrene gives reasonable results and revealed a tendency towards a bimodal MWD for the samples rich in cycles. The MALDI-TOF mass spectrometry indicated that the extent of cyclization increased with higher conversion and with optimization of the stoichiometry. This interpretation was confirmed by ¹H NMR endgroup analyses. For the samples with the highest molar masses only mass peaks of cycles were found, which were detectable up to 20 000 Da before and up to 27 000 Da after fractionation. Via the pseudo-high dilution method low molar mass poly(ether sulfone) containing more than 95 mol% of cycles were prepared, and even these low molar mass samples had broad MWDs. DSC measurements indicated that the glass transition temperatures depend on the structure of the endgroups and increase with higher fractions of cycles.

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1. Introduction

It has been demonstrated in previous publications [1–3] that in kinetically controlled polycondensations cyclization reactions compete with propagation steps at any concentration and at any stage of the polycondensation process. The efficiency of cyclization depends on the flexibility of the polymer chain and on the concentration of active species and limits the chain growth as outlined in Eq. (1). Another aspect of this new theory of polycondensation is that the fraction of cycles rapidly increases at very high conversion together with the generation of high molecular weights.

$$\overline{DP} = \frac{1}{1 - p \left(1 - \frac{1}{x^\alpha} \right)} \quad (1)$$

\overline{DP} , is the average degree of polymerization, p , is the conversion of the functional groups, x , is the constant > 1.0 allowing for the adjustment of Eq. (1) to various

concentrations, $\alpha = V_{cg}/V_{pr}$, is the ratio of cyclization rate and rate of propagation.

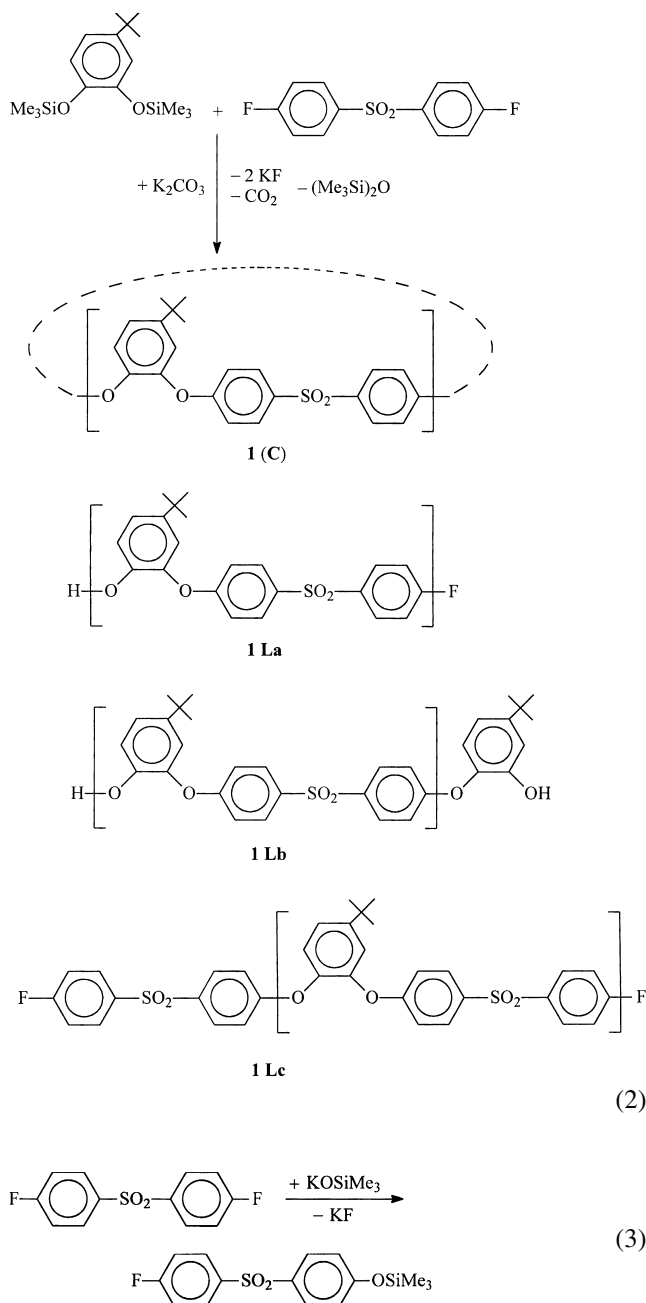
The detection of cyclic polymers by MALDI-TOF mass spectrometry was limited in most previous studies to masses around 10 000–13 000 Da [1–3]. The technical reasons responsible for the limited detection of high molar mass polymers have been discussed by several authors [4,5]. An additional problem arises from the frequency distribution of individual oligomers and polymers in polycondensates. Regardless to what extent cyclization takes place, the oligomers form the maximum of the distributions curve which decreases exponentially towards higher molar masses. The large fraction of oligomers saturates the detector before the slowly flying higher masses arrive. Therefore, fractionation of the polycondensate may be beneficial for the detection of individual reaction products with masses above 13 000 Da.

In this context the present work served the following purposes. First, poly(ether sulfone)s should be prepared from silylated 4-*tert*-butylcatechol (TBC) and 4,4'-difluorodiphenyl-sulfone (DFDPS) (Eq. (2)) with the expectation that the cyclization tendency is higher than in that of the

* Corresponding author.

E-mail address: kricheld@chemie.uni-hamburg.de (H.R. Kricheldorf).

previously studied [3] polycondensations of (silylated) bisphenol-A. Second, the new poly(ether sulfone)s should be soluble in tetrahydrofuran (THF) allowing for a characterization of the molar mass distribution and for a fractionation by SEC. Third, it should be elucidated to what extent the fractionation favors the detection of high-molar mass cycles by MALDI-TOF mass spectrometry. Fourth, it should be checked, if polycondensations of silylated diphenols with DFDPS in NMP are the clean step growth polymerizations suggested by our previous experiments with silylated bisphenol-A. Finally, all syntheses and measurements together should contribute to the confirmation of our polycondensation/cyclization theory [1–3].



2. Experimental

2.1. Materials

4-*tert*-Butylcatechol (TBC), fluorobenzene and chlorosulfonic acid were purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. 4,4'-Difluorodiphenylsulfone (DFDPS) was prepared according to the literature [6] and recrystallized (mp 98–100 °C, Aldrich gives a mp of 98–99 °C for a product of 99% purity). *N*-Methylpyrrolidone (NMP) was a gift of BASF AG (Ludwigshafen, Germany). It was twice distilled over P₄O₁₀ in vacuo prior to use. K₂CO₃ (p.a. grade, Merck KG, Darmstadt, Germany) was dried at 115 °C in vacuo.

2.2. Silylation of 4-*tert*-butylcatechol (TBC)

4-*tert*-Butylcatechol (0.4 mol) and hexamethyldisilazan (0.5 mol) were refluxed in dry toluene for 8 h. The reaction mixture was then concentrated in vacuo and the product was isolated by distillation in vacuo at a bath temperature of 115–125 °C, and 0.1 mbar. Yield 82% (the first 10 ml of the distillate were discarded).

¹H NMR (CDCl₃/TMS), δ = 0.26 (s, 9 H), 0.29 (s, 9 H), 6.78–6.89 (m, 3 H) ppm

Gas chromatography indicated a trace of hexamethyldisilazane ($\leq 0.5\%$).

2.3. Polycondensations

(A) *Variation of the stoichiometry* (Table 1). Silylated TBC (20 mmol), DFDPS (20 mmol) and dry K₂CO₃ (21 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer (flat-blade glass-stirrer), gas-inlet and gas-outlet tubes. Dry NMP (20 ml) was added and the reactor was placed into an oil bath preheated to

Table 1

Polycondensations of silylated 4-*tert*-butylcatechol (TBC) with 4,4'-difluorodiphenylsulfone (DFDPS)—variation of the stoichiometry

Exp. no.	Silyl. TBC (mmol)	DFDPS (mmol)	Yield (%)	η_{inh}^a (dl/g)	M_n^b (Da)	M_w^b
1	20.00	20.00	76	0.31	10 000	60 000
2	20.00	20.10	85	0.37	11 000	70 000
3	20.00	20.20	78	0.58	16 000	150 000
4	20.00	20.30	87	0.30	11 000	50 000
5	20.00	20.40	85	0.30	11 000	55 000
6	20.00	20.60	85	0.23	6 500	40 000
7	20.00	21.40	92	0.18	—	—
8	20.00	22.00	68	0.13	4 000	9 000
9	20.00	23.00	65	0.08	—	—
10	20.60	20.00	67	0.16	4 500	20 000
11	22.00	20.00	69	0.08	3 500	7 000

All polycondensations were performed in NMP at 140 °C/48 h.

^a Measured at 20 °C with 2 g/l in CH₂Cl₂.

^b SEC measurements in tetrahydrofuran at 23 °C calibrated with polystyrene.

140 °C. This temperature was maintained for 48 h under an atmosphere of dry nitrogen. Finally, the cold reaction mixture was poured into water, the precipitated polymer was isolated by filtration, dried and reprecipitated from tetrahydrofuran water.

All other polycondensations of this series were conducted analogously with variation of the feed ratio as indicated in Table 1.

(B) *Variation of the reaction time* (Table 2). Silylated TBC (20 mmol), DFDPS (20.2 mmol) and dry K₂CO₃ (21 mmol) were weighed into a cylindrical glass reactor and dry NMP (20 ml) was added. The reaction vessel was placed into an oil bath preheated to 120 °C. The reaction time was varied as indicated in Table 2. The reaction mixture was worked up as described for (A).

(C) *Pseudo-high dilution method* (Table 3). Silylated TBC (20 mmol) dissolved in dry NMP (50 ml) and DFDPS (20.2 mmol) dissolved in dry NMP (50 ml) were added dropwise and simultaneously to a stirred suspension of K₂CO₃ (20.1 mmol) in dry NMP (50 ml) at 140–145 °C. The complete addition of both solutions required 1 h, and the stirring at 140–145 °C was then continued for 3 more hours. The cold reaction mixture was precipitated into water, the precipitated product was filtered off and dried at 80 °C in vacuo. It was reprecipitated from a CH₂Cl₂ solution into methanol. Yield 83%, $\eta_{inh} = 0.10$ dl/g.

An analogous polycondensation was performed at 160 °C with almost identical results.

2.4. Measurements

The inherent viscosities were measured in CH₂Cl₂ with an automated Ubbelohde viscometer thermostated at 20 °C. The DSC measurement was conducted with a PERKIN–Elmer DSC-7 in aluminum pans under nitrogen.

The DSC measurements were performed on a Perkin–Elmer DSC 7 in aluminum pans under nitrogen.

The MALDI-TOF mass spectra were recorded with a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All measurements were conducted in the reflectron mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from tetrahydrofuran

Table 2
Polycondensations of silylated 4-*tert*-butylcatechol and 4,4'-difluorodiphenylsulfone—variation of the reaction time

Exp. no.	Time (h)	Yield (%)	η_{inh}^a (dl/g)	M_n^b (Da)	M_w^b (Da)
1	2	90	0.07	2 500	6 500
2	3	93	0.16	4 500	16 000
3	4	98	0.32	10 000	60 000
4	8	98	0.54	14 000	135 000
5	48	98	0.64	19 000	180 000

Molar feed ratio 15.0/15.15, in NMP at 120 °C.

^a Measured at 20 °C with $c = 2$ g/l in CH₂Cl₂.

^b SEC measurements in tetrahydrofuran calibrated with polystyrene.

Table 3

Polycondensations of silylated 4-*tert*-butylcatechol (TBC) with 4,4'-difluorodiphenylsulfone (DFDPS)—pseudo-high dilution method

Exp. no.	Excess of DFDPS (mol%)	Temp (°C)	Yield (%)	η_{inh}^a (dl/g)	M_n^b (Da)	M_w^b (Da)
1	0	140	80	0.08	1 500	9 000
2	1	140	83	0.10	1 850	12 000
3	0	160	84	0.06	1 200	5 000
4	1	160	88	0.10	1 500	13 000

Total reaction time 4 h.

^a SEC measurements in tetrahydrofuran at 23 °C calibrated with polystyrene.

^b Measured at 20 °C with 2 g/l in CH₂Cl₂.

solutions with variation of the polymer/matrix ratio. Dithranol served as matrix and K trifluoroacetate as dopant.

The SEC measurements were performed on a home-made SEC apparatus at 23 °C with THF as eluent. A combination of three PSS-SDV mix-bed columns was used along with an UV and RI-detector. Commercial PS-standards served for calibration. The fractionation and molecular weight measurements of sample No. 5, Table 2 were conducted on a Hewlett–Packard HP 1050 apparatus in CH₂Cl₂ at 30 °C. Five Lichrogel® columns having pore sizes of 4, 40, 400 (2 ×) and 4000 Å were used. The elution curves were evaluated with a triple-detector 'Viskotec TDA-301'. The molecular weights of sample No. 3, Table 1 were determined analogously.

3. Results and discussion

3.1. Syntheses

In a previous study of synthesis and cyclization of poly(ether sulfone)s based on bisphenol-A [3] the highest molecular weights combined with the highest fraction of cycles was obtained by polycondensation of the silylated bisphenol in NMP at 140–145 °C. Therefore, these reaction conditions were also used in the present work. The feed ratio of the monomers were varied from an excess of TBC to an excess of DFDPS for two reasons. First, a sample containing a maximum of cycles should be prepared and this maximum was expected for the sample with the highest molar mass. Second, a sample mainly consisting of OH-terminated chains (structure 1**b**) and a sample mainly containing C–F terminated chains (1**c**) should be prepared. The results of all these polycondensations are summarized in Table 1.

The inherent viscosities demonstrate that there is a sharp maximum of the molar mass when DFDPS is used in an excess of 1 mol%. Similar results have previously been obtained with bisphenol-A. Assuming that all components of the reaction mixture were dry, the most likely explanation for a side reaction of DFDPS is the reaction with potassium silanolate (Eq. (3)) intermediately formed from K₂CO₃ and

hexamethyldisiloxane. Experiments supporting this hypothesis have previously been published [7].

In a second series of polycondensations the reaction time, and thus, the conversion was varied whereas the optimum stoichiometry was maintained (Table 2). Furthermore, the temperature was lowered to 120 °C to slow down the reaction rates and to allow for an easier control of the conversion. The results compiled in Table 2 indicate that the conversion was almost complete after 24 h and the poly(ether sulfone) isolated after 48 h had a slightly higher molar mass than the optimum sample of Table 1 (No. 3).

A third series of polycondensations was performed using the pseudo-high dilution method (i.e. the Ruggli–Ziegler dilution principle) to obtain high fractions of cycles with low average molecular weight (Table 3). Two temperatures were compared, 140 and 160 °C, but a significant temperature effect was not found. Remarkable is the observation that at both temperatures the highest molar masses resulted from an excess (1 mol%) of DFDFS in agreement with the results obtained in concentrated solution (Table 1). The MALDI-TOF mass spectra (m.s.) discussed below confirmed an almost exclusive formation of cycles. In this connection it should be mentioned that several authors [8–16] reported on syntheses of polydisperse or monodisperse cyclic oligo(ether sulfone)s. These oligo(ether sulfone)s were different from the products studied in the present work,

different synthetic methods were used and a correlation between cyclization and MWD was not discussed.

Finally, it should be mentioned that all samples were characterized by ^1H NMR spectroscopy. As illustrated in Figs. 1 and 2, the 400 MHz ^1H NMR spectra display catechol endgroup signals when an excess of silylated TBC was used (No. 11, Table 1) or they exhibit $\text{C}_6\text{H}_4\text{F}$ endgroup signals, when an excess of DFDFS was used (No. 8, Table 1). These endgroup signals were absent, when the MALDI-TOF m.s. indicated the absence of **1La** and **1Lb** chains. Therefore, the ^1H NMR spectra clearly support the interpretation of the MALDI-TOF m.s. discussed below.

3.2. Molar masses and polydispersities

The molar masses and the polydispersities (PDs) were measured by SEC in tetrahydrofuran and calibrated with commercial polystyrene standards. In order to find out if this standard calibration gives reasonable results the samples with the highest molar masses (No. 3, Table 1 and No. 5, Table 2) were also characterized with light scattering measurements. These measurements confirmed that the weight average molar masses (M_w) obtained via calibration with polystyrene were correct.

The SEC measurements also revealed a trend towards a bimodal molar mass distribution with a first maximum (or two sharp maxima) in the mass range of the oligomers. This

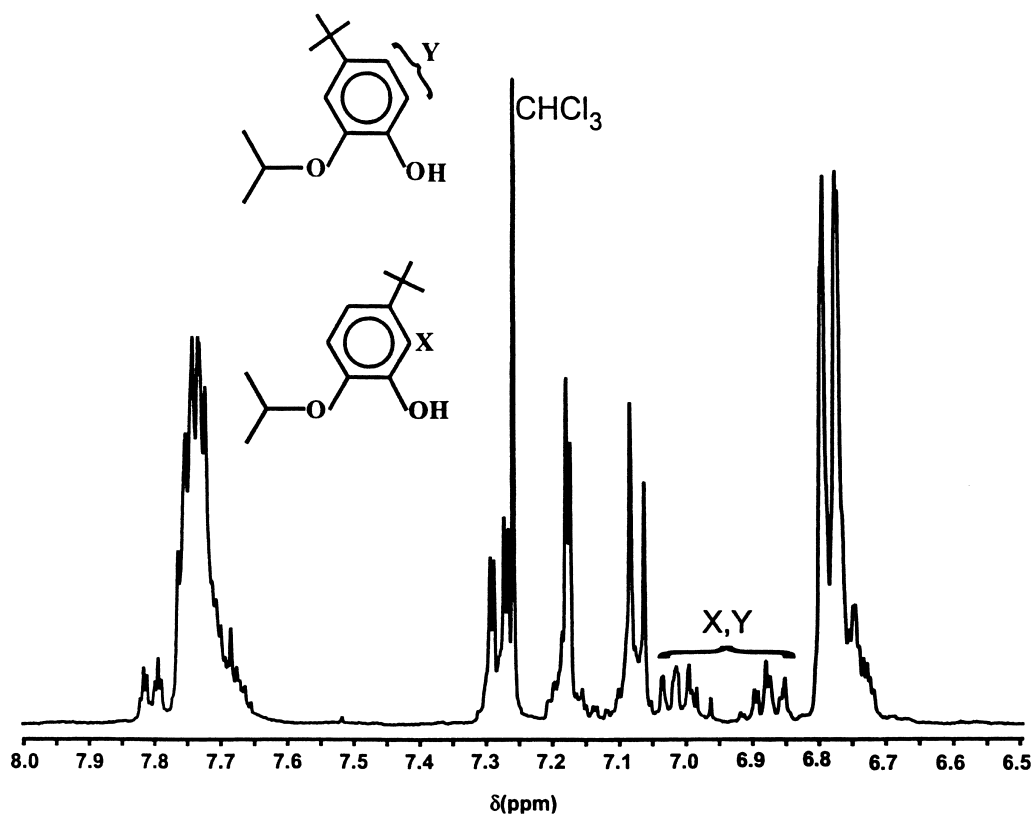


Fig. 1. 400 MHz ^1H NMR spectrum of the poly(ether sulfone) No. 11, Table 1, displaying catechol endgroup signals.

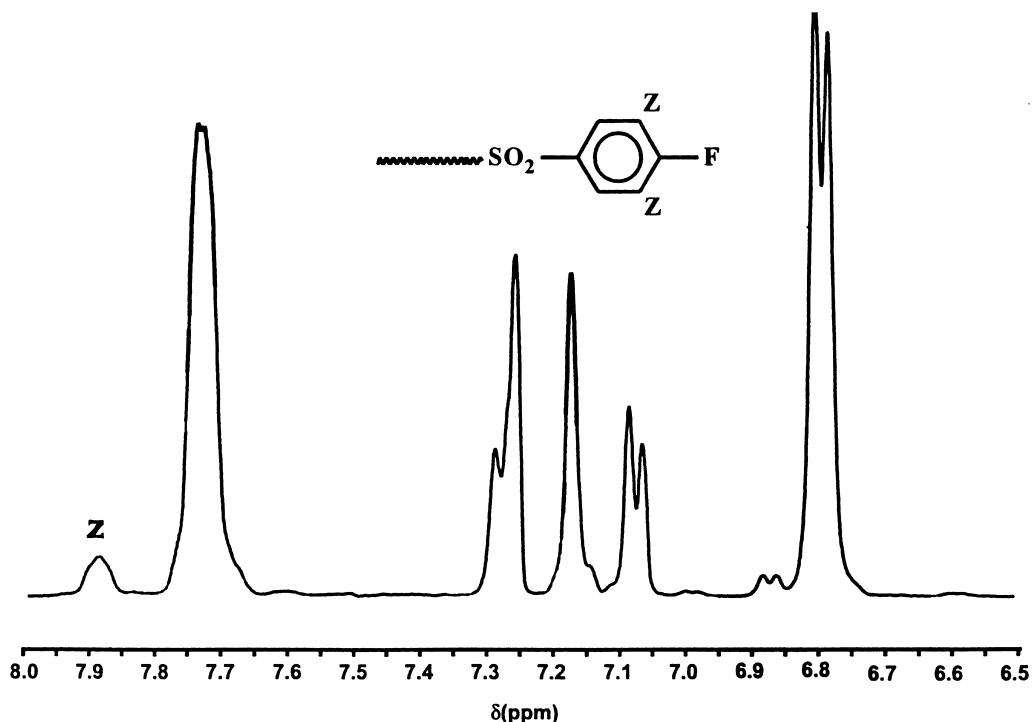


Fig. 2. 400 MHz ^1H NMR spectrum of the poly(ether sulfone) No. 8, Table 1, displaying C–F endgroup signals.

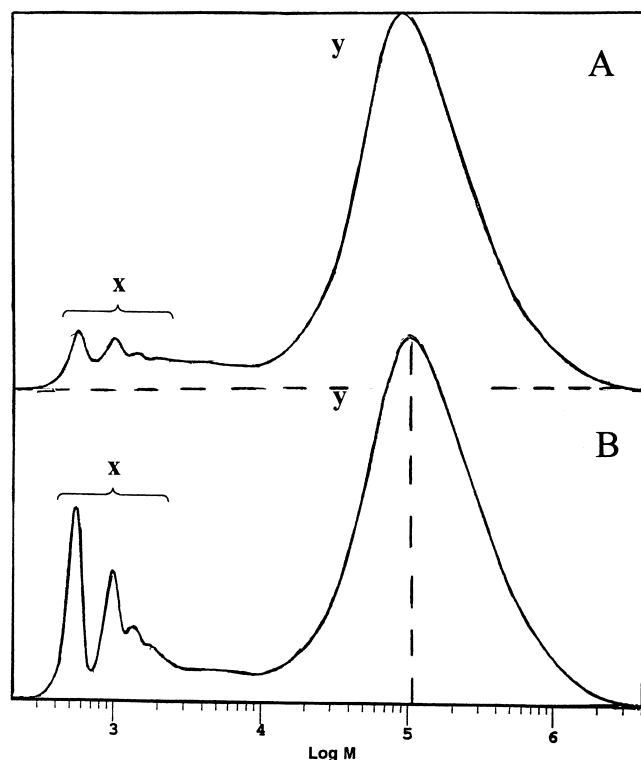


Fig. 3. SEC elution curves of the poly(ether sulfone)s No. 3, Table 1 (A) and No. 5, Table 2 (B). The broken line in spectrum B indicates the beginning of the fractionation by SEC.

trend was more pronounced for the samples prepared at the lower temperature (Table 2) as demonstrated in Fig. 3 for the samples with the highest molar masses. However, the tendency towards a bimodal mass distribution was also detectable for samples with lower molar masses as displayed in Fig. 4. Even the elution curves of the samples prepared via the pseudo high dilution method showed a tendency towards bimodal mass distributions (curve B, Fig. 4). These quasi bimodal distributions are, of course, responsible for the high PDs (values up to around 10) found for most samples. When the elution curves of the high molar mass fraction of samples No. 3, Table 1 and No. 5, Table 2, were separately characterized by SEC and light-scattering, number average molar masses (M_n s) around $80\,000 \pm 5\,000$ and $90\,000 \pm 5\,000$ Da, respectively were found. This means the polydispersities of the high molar mass fractions alone have PDs around 2 which agree with the PD expected from the classical theory of polycondensation [17,18]. In the original theory of polycondensation [17] the frequency distribution should obey Eq. (4). The oligomers like the monomers and polymers permanently contribute to the chain growth and their absolute quantity decreases with increasing conversion. However, in a kinetically controlled polycondensation involving cyclization, all cycles are stable and do not contribute anything to the further chain growth. Therefore, their absolute and relative quantity will be higher than that of linear oligomers according to Eq. (4). This aspect certainly contributes to the formation of a bimodal mass distribution with a first maximum around the cyclic tetramer or dimer (x in Figs. 3 and 4). At this point it needs to be emphasized that a trend towards a bimodal mass

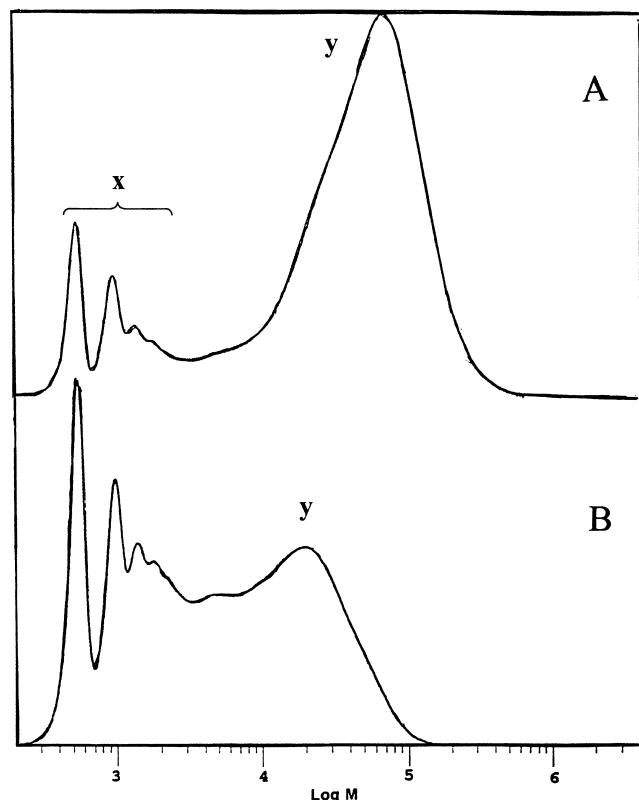


Fig. 4. SEC elution curves of: (A) poly(ether sulfone) No. 3, Table 2, (B) poly(ether sulfone) No. 2, Table 3.

distribution is not necessarily combined with a bimodal frequency distribution. In fact, the MALDI-TOF m.s. do not indicate any bimodal character in the frequency distribution. This result is obvious for the high molecular weight samples, where the MALDI-TOF m.s. do not include the masses making up the second (high molar mass) maximum (y in Figs. 3 and 4). However, in the case of samples Nos. 1–4, Table 3, the mass spectra also cover the mass range of the second maximum (y) in the SEC curve (see below). The hypothesis that the formation of stable cycles is responsible for the trend towards a bimodal mass distribution is supported by the observation that those samples rich in linear chains (Nos. 7–11, Table 1) show lower polydispersities.

$$f_{DP} = p^{DP-1}(1 - p) \quad (4)$$

f is the frequency of oligomers or polymers with individual degree of polymerization (DP)

Interestingly, Flory [17] has calculated a kind of bimodal mass distribution for polymers containing 2.5 wt% of cycles formed by equilibration in a thermodynamically controlled polycondensation. The first maximum is formed by cyclic monomers in combination with cyclic oligomers and the second maximum by linear polymers of higher molecular weight. The corresponding frequency distributions were not

calculated. Anyway, the results found in this work deviate from Flory's model in three important points:

- (I) kinetically controlled polycondensations were performed, resulting in somewhat different cyclization probabilities
- (II) the weight percentage of cycles is much higher than in Flory's model
- (III) in the case of polymers listed in Table 3, even the second maximum of the mass distribution (y in Figs. 2 and 3) mainly or exclusively consists of cycles.

To the best of our knowledge, a mathematical treatment of the MWD of kinetically controlled polycondensations involving permanent cyclization (Eq. (1)) is still lacking, and thus, a quantitative interpretation of the present results cannot be given at this time.

3.3. MALDI-TOF mass spectra (m.s.)

The MALDI-TOF m.s. of the poly(ether sulfone)s prepared with variation of the feed ratio (Table 1) displayed the expected variation of the composition of the reaction products. A pattern of four peaks was found originating from cycles (1C) and from the three endgroup combinations 1La, 1Lb and 1Lc. With an excess of TBC the mass peaks of the OH-terminated chains 1Lb were predominant (Fig. 5(A)), whereas with an excess of DFDPS the mass peaks of the F-terminated chains were prevailing (Fig. 5(B)). The sample with the highest molar mass in Table 1 (No. 3) gave a m.s. exclusively exhibiting mass peaks of cycles which were detectable up to 20 000 Da (Fig. 6). This m.s. proves that the synthesis of sample No. 3, Table 1 is indeed based on a nearly ideal stoichiometry of both monomers despite the slight excess of DFDPS in the feed. All these m.s. together indicate a clean course of the polycondensation process without detectable side reactions. Furthermore, these m.s. suggest that neither the cycles nor one of the linear chains 'fly' extremely better than the other species under the MALDI-TOF conditions of this work (see discussion below).

The influence of the conversion (Table 2) is documented in the m.s. of Fig. 7. Again the pattern of the characteristic four mass peaks is present and the fraction of cycles strongly increases with higher conversions. The m.s. of the polymer isolated after 48 h (No. 5, Table 2) was identical with that of sample No. 3, Table 1 (Fig. 6). Sample No. 5, Table 2, was then fractionated by SEC so that 14 narrow fractions were obtained beginning with the top of the elution curve (see Fig. 3) and continuing along the low molar mass wing of the elution curve. The MALDI-TOF measurements of the first six fractions containing the higher molar masses were unsuccessful, whereas mass spectra were obtained from fractions 7 through 14. Fig. 8 displays the m.s. of the fractions 8 and 7 and demonstrates that the measurement

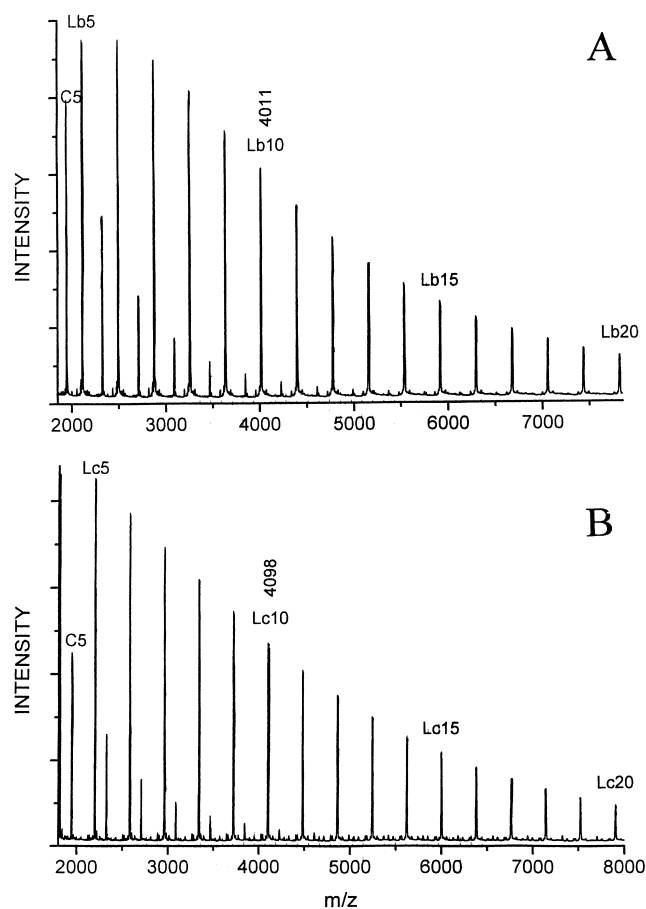


Fig. 5. MALDI-TOF mass spectrum of a poly(ether sulfone) prepared with (A) an excess of TBC (No. 11, Table 1), (B) an excess of DFDPS (No. 8, Table 1).

of fraction 7 represents the feasibility limit of the MALDI-TOF technique we had in hand. Despite this limit cycles were detected up to masses around 27 000 Da which proved that even relatively long chains cyclized in these kinetically controlled polycondensations.

The MALDI-TOF m.s. of the poly(ether sulfone)s prepared via the pseudo-high dilution method gave the following results. No significant difference between samples prepared at 140 or 160 °C was found. When an exact 1:1 feed ratio was used (Nos. 1 and 3, Table 3) the mass peaks of the cycles were predominant up to 11 000 or 12 000 Da. At higher masses the peaks of **Lb** chains terminated by two catechols prevailed. With a 1 mol% excess of DFDPS (Nos. 2 and 4) the peaks of the **Lb** chain disappeared and the mass peaks of cycles dominated the m.s. up to the technical limit around 19 000 Da, quite analogous to the mass spectrum presented in Fig. 7. However, at high masses (> 10 000 Da) very weak peaks of **Lc** chains (terminated by C–F groups) became detectable, indicating that the excess of DFDPS was a little above the optimum stoichiometry. Considering the low M_n s of these samples their MALDI-TOF m.s. suggest that samples Nos. 2 and 4 contain more than 95 mol% of cycles. This result is not only interesting from the

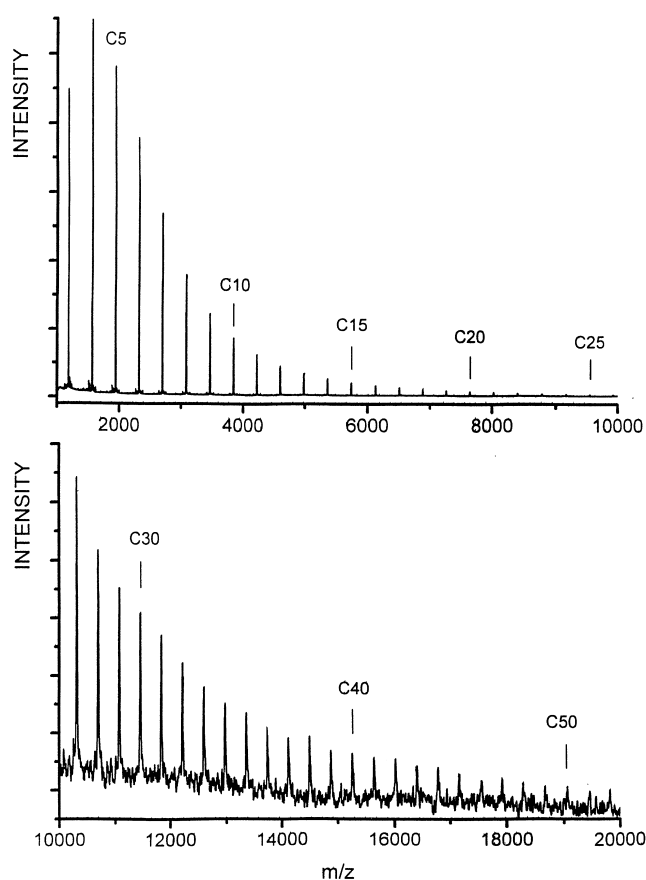


Fig. 6. MALDI-TOF mass spectrum of the poly(ether sulfone) prepared with nearly perfect stoichiometry (No. 3, Table 1). The upper segment was recorded with a cut-off range of 1 000 Da, the lower segment with 4 000 Da.

preparative point of view. Another interesting aspect is the observation of rather high polydispersities (Table 3 and Fig. 4(B)). Here the trend towards a bimodal mass distribution cannot be explained by a low molar mass fraction consisting of cycles and high molar mass fraction consisting of linear chains. Here, the cycles cover nearly the full mass range.

After the characterization of the individual samples, equimolar mixtures of samples having different structures but nearly identical solution viscosities were studied. When sample No. 9, Table 1 (rich in **Lc** chains) was mixed with No. 1, Table 1 or No. 2, Table 1, nearly identical m.s. were obtained. These spectra displayed a predominance of the cycles below 3 500 Da (Fig. 9(A)) because sample No. 9, Table 1 contained a small amount of low molar mass cycles, whereas the samples Nos. 1 and 2 of Table 3 were free of **Lc** chains. However, above 3 700 Da, the mass peaks of the linear chains became more intensive. A similar pattern was found for the mixture of No. 11, Table 1 (rich in **Lb** chains) and No. 2, Table 3 (Fig. 9(B)), because No. 11, Table 1 contained low molar mass cycles. Finally, the samples Nos. 9 and 11 of Table 1 were mixed, and the **Lb** chains displayed the more intensive mass peaks (Fig. 10). In other

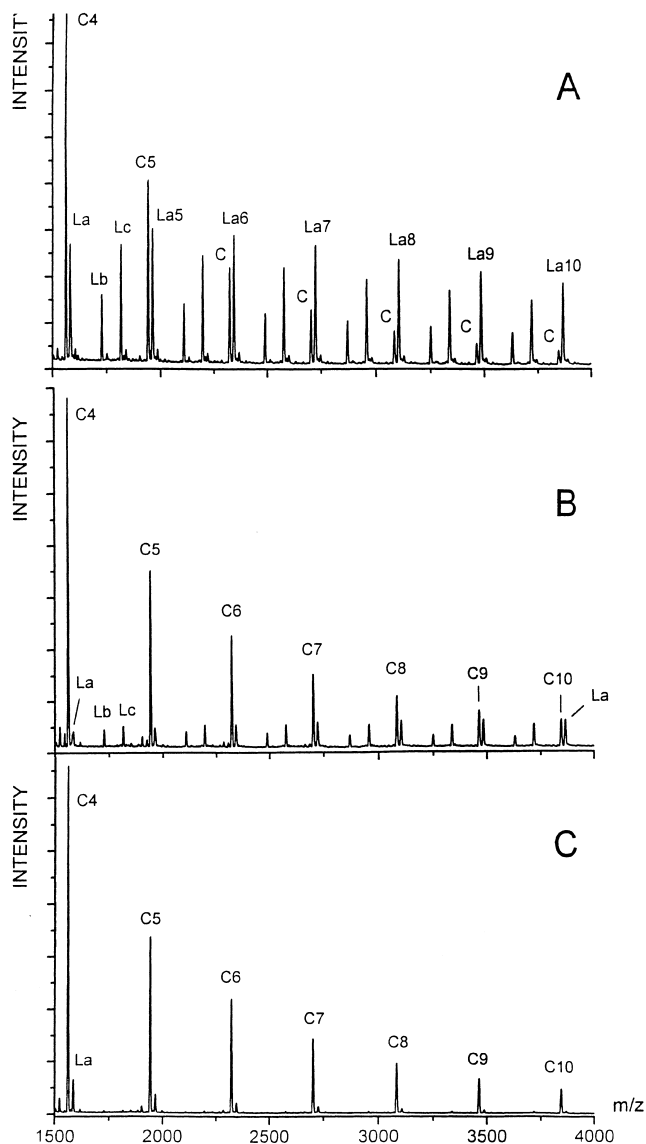


Fig. 7. MALDI-TOF mass spectra illustrating the influence of the reaction time (conversion): (A) No. 1, Table 2, (B) No. 2, Table 2, (C) No. 3, Table 2.

words, the ‘volatility’ or ‘detectability’ decreased in the order $Lb > Lc > C$. This result agrees well with the spectra recorded for the individual samples, because the best signal-to-noise ratios were obtained for the mass peaks of **Lb** chains. Furthermore, the same trend was observed in a previous study dealing with poly(ether sulfone)s of bisphenol-A [3]. Therefore, it may be concluded that our MALDI-TOF measurements rather underestimate the content of cyclic poly(ether sulfone)s and certainly do not overestimate it.

Although the MALDI-TOF mass spectra do not allow an exact quantification of individual products, a crude estimation of the content of cycles is feasible when the frequency distribution is taken into account. Assuming that the frequency distribution follows Eq. (4), 65 mol% of the cycles have masses below M_n . Considering that the

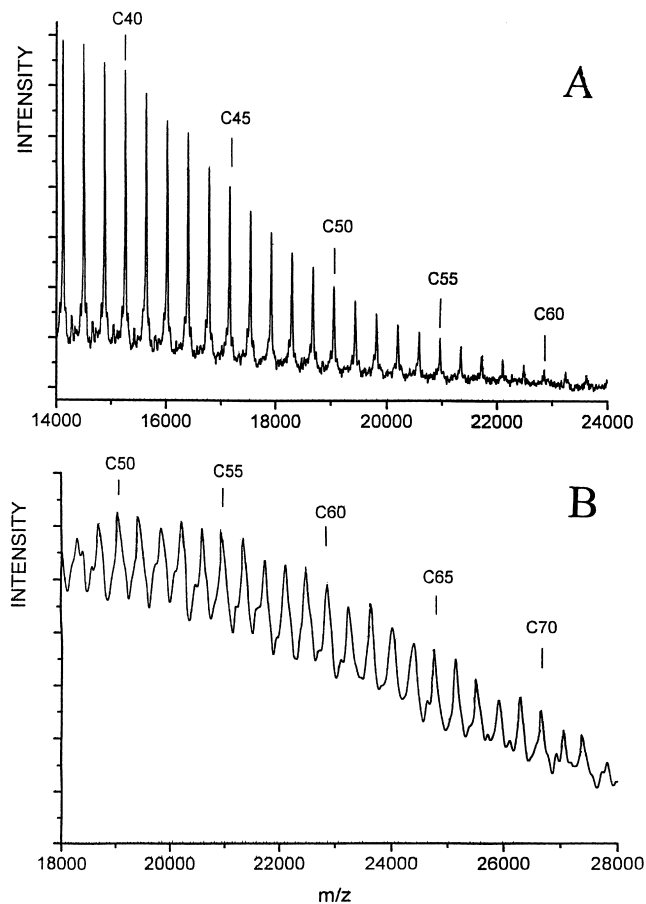


Fig. 8. MALDI-TOF mass spectra of two fractions of the poly(ether sulfone) No. 5, Table 2: (A) fraction 8, (B) fraction 7.

frequency distributions of cycles is steeper (as discussed by Flory [17] for thermodynamically controlled polycondensations), the percentage of cycles below M_n should even be higher than 65%. Since the M_n of sample No. 5, Table 2, is around 19 000 Da, the exclusive detection of cycles up to 27 000 Da suggests that at least 80 mol% of this sample consists of cycles. Furthermore, it should be taken into account that the MALDI-TOF spectra of this work rather underestimate the content of cycles. Therefore, this estimation and the absence of detectable side reactions indicate that the cyclization reactions have limited the chain growth of the samples No. 3, Table 1, and No. 5, Table 2, in agreement with our theory of kinetically controlled polycondensations [1–3].

3.4. DSC measurements

The results discussed above demonstrate that samples almost completely consisting of cyclic poly(ether sulfone)s with low or high average molecular weights were obtained. Furthermore, samples mainly containing OH-terminated or CF-terminated linear chains were prepared (Table 1). This situation suggested study of how the glass-transition temperature (T_g) responds to these variations of the primary structure.

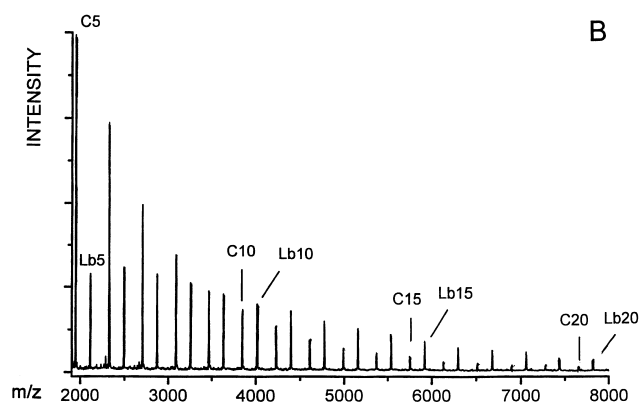
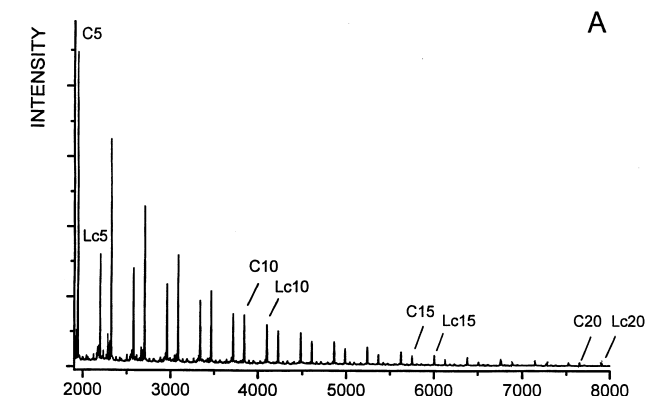


Fig. 9. MALDI-TOF mass spectra of binary, equimolar mixtures: (A) No. 9, Table 1 + No. 2, Table 3, (B) No. 11, Table 1 + No. 2, Table 3.

The DSC curves of selected samples were recorded with a heating rate of 20 °C/min, and the T_g values thus obtained were compiled in Table 4. These data revealed that the CF-terminated chains (Lc) possess the lowest T_g s, whereas cycles and OH-terminated (Lb) chains showed similar T_g values. This result can be rationalized by the following consideration. The loose ends of linear chains have a higher mobility than the main part of the chains, and thus, cycles should have higher T_g s than linear chains. However, the mobility of OH-terminated chains may be reduced by H-bonds. Analogous studies of

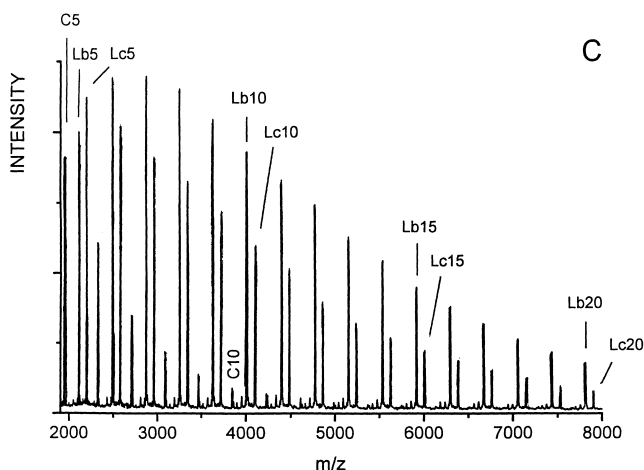


Fig. 10. MALDI-TOF mass spectrum of an equimolar mixture of No. 9, Table 1 + No. 11, Table 1.

Table 4

DSC measurements of selected poly(ether sulfone)s

Sample	Properties	T_g (°C) ^a	
		1st Heat	2nd Heat
No. 2, Table 3	Cycles, $\eta_{inh} = 0.10$	175	175
No. 3, Table 1	Cycles, $\eta_{inh} = 0.58$	186	186
No. 11, Table 1	OH-Endgr., $\eta_{inh} = 0.08$	172	171
No. 10, Table 1	OH-Endgr., $\eta_{inh} = 0.16$	176	177
No. 1, Table 1	OH-Endgr., $\eta_{inh} = 0.31$	184	184
No. 8, Table 1	F-Endgr., $\eta_{inh} = 0.13$	166	164
No. 5, Table 1	F-Endgr., $\eta_{inh} = 0.30$	182	182

^a Recorded with a heating rate of 20 °C/min.

other polymers should reveal, if the above structure-property pattern has broader validity.

4. Conclusion

The results of this work allow the following conclusions. The polycondensation of silylated TBC with DFDPS in NMP/ K_2CO_3 is in agreement with previous studies [3] a rather clean kinetically controlled step growth polymerization. However, the MWDs of samples prepared with nearly ideal stoichiometry show a tendency towards a bimodal mass distribution with high polydispersities which differ from the classical theory of step growth polymerizations. However, the MALDI-TOF m.s. do not show any bimodal character in the frequency distribution. Another, but expected, difference from the classical theory of polycondensation [17,18] is the high extent of cyclization. The fraction of cycles increases with increasing conversion and increasing perfection of the stoichiometry, so that the MALDI-TOF m.s. of the best samples only display mass peaks of cycles. The identification of cycles up to 27 000 Da doubles the mass range previously limiting the detection of cyclic poly(ether sulfone)s [3,19] and proves that cyclization is not limited to oligomers. This pattern is in perfect agreement with our recent theory [1–3] of kinetically controlled step growth polymerization and indicates that the chain growth under ideal reaction conditions is limited by the extent of cyclization (Eq. (1)).

Finally, it should be mentioned that the poly(ether sulfone) derived from *t*-butylcatechol possesses several useful properties. It is soluble in more organic solvents than commercial poly(ether sulfone)s, for instance, in tetrahydrofuran. It shows excellent film-forming properties and the glass-transition temperature is nearly as high as that of Udel[®] which is based on bisphenol-A.

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