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# Syntheses of Polyethers from Pentafluorobenzonitrile or Pentafluorobenzophenone and Flexible Diphenols

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Cyanopentafluorobenzene (CPFB, pentafluorobenzonitrile) or pentafluoro-benzophenone (PFBP) were polycondensed with long flexible diphenols at a 1:1 feed ratio in the presence of  $K_2CO_3$ . A rather selective substitution of two C-F groups was achieved with the formation of cyclic polyethers as the main products. Polycondensations of CPFB with flexible diphenols at 3:2 feed ratio ( $a_2/b_3$ ) yielded soluble multicyclic polyethers by highly selective substitution of three C-F groups. Yet, polycondensation at a feed ratio of 5:2 gave a complex reaction mixture and substitution of all five C-F groups was not observed. In all experiments, cyclization played a key role for the avoidance of gelation.

**Keywords:** aromatic polyethers; polycondensation; macrocycles; MALDI-TOF

## 1 Introduction

The present work is part of a broader study of polycondensations involving trifunctional, tetrafunctional or higher functional monomers (“ $a_2 + b_n$ ” polycondensations). Polycondensations based on trifunctional (“ $b_3$ ”) monomers have a long history beginning with the work of Kienle (1, 2) and Flory (3, 4). Those authors used feed ratios of 3:2 and obtained gels at high conversions. Meanwhile, numerous research groups have demonstrated that variation of stoichiometry and concentration allow for syntheses of soluble hyperbranched polymers, bicyclic oligomers or multicyclic polymers. Relatively little is known about “ $a_2 + b_4$ ” polycondensations, but a few syntheses of multicyclic polyesters and polyethers were reported (3, 5–12) beginning with the work of Flory (3, 5). To the best of our knowledge, polycondensations of pentafunctional ( $b_5$ ) monomers have thus never been studied. In previous studies, cyclic and multicyclic polyethers were prepared by polycondensations of activated difluoro- (13–16), trifluoro- (17, 18) or tetrafluoroaromatics (10, 11). In this context, the present work had the purpose to study polycondensations of cyanopentafluorobenzene (CPFB, pentafluorobenzonitrile) or pentafluorobenzophenone (PFBP) with three long flexible diphenols (**1a,b** and **2**). Since the cyano- or keto-groups activate the C-F bonds in ortho- and para-

position more than in meta-position, two questions should be answered. First, is a clean substitution of all five C-F groups by phenoxide ions feasible, so that soluble multicyclic polyethers corresponding to formula **3** can be isolated? Second, is a selective substitution of two or three C-F bonds feasible, so that either soluble hyperbranched or multicyclic polyethers (e.g. structure **4** and Scheme 1) can be obtained?

## 2 Experimental

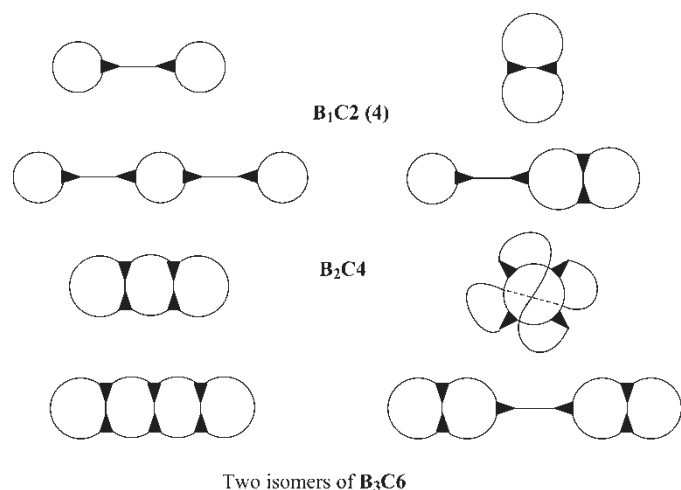
### 2.1 Materials

Cyanopentafluorobenzene (CPFB, pentafluorobenzonitrile), pentafluoro-benzophenone (PFBP), resorcinol and 1,6-dibromohexanes were purchased from ACROS Organics (Geel, Belgium) and used as received. The 4,4'-(1,4-phenylene diisopropylidene)bisphenol (**1**) was purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. The bisphenol **2** was prepared from resorcinol and 1,6-dibromohexane as described previously (12, 13). Dimethylformamide was distilled over  $P_4O_{10}$  *in vacuo*.

### 2.2 Polycondensations

A) With feed ratio 5:2 in DMF (No. 1, Table 1). CPFB (10 mmol) and diphenol **1a** (25 mmol) were dissolved in dry DMF (180 mL) and  $K_2CO_3$  (26 mmol) was added. This suspension was stirred in a closed Erlenmeyer flask at 80°C for 72 h and then precipitated into water. The isolated polyether was dried at 65°C *in vacuo*. In an analogous experiment

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**Sch. 1.** Simplified isomeric multi-cycles of the general formula  $B_{1/2N}CN$  resulting from polycondensations with a feed ratio of 3:2.

(No. 2, Table 1), the temperature was raised to 120°C after 48 h.

Analogous polycondensations were conducted with PFBP (Nos. 1 + 2, Table 2).

B) With feed ratio 3:2 in DMF (No. 4, Table 1). CPFB (10 mmol) and a diphenol (15 mmol) were dissolved in dry DMF (180 mL) and  $K_2CO_3$  (16 mmol) was added. This suspension was stirred in a closed Erlenmeyer flask at 80°C for 72 h and precipitated into water.

Analogous polycondensations were performed with PFBP (Nos. 3,4, Table 2).

C) With feed ratio 1:1 in DMF (No. 8, Table 1). CPFB (15 mmol) and diphenol **2** (15 mmol) were dissolved in dry DMF (180 mL) and  $K_2CO_3$  (16 mmol) was added. This suspension was stirred in a closed Erlenmeyer flask at 80°C for 72 h and precipitated into water. Elemental analyses calcd. for cycles of Scheme 3:  $C_{31}H_{24}F_3NO_2$  (499.5).

C 74.54, H 4.84, N 2.80, found C 73.98, H 4.75, N 2.71%.

An analogous polycondensation was performed with PFBP (No. 5, Table 2).

D) With feed ratio 1:1 in DMSO (No. 6, Table 2). PFBP (15 mmol), diphenol **2** (15 mmol) and  $K_2CO_3$  (16 mmol) were weighed in a three-neck flask equipped with mechanical stirrer and distillation head and dropping funnel. DMSO (80 mL) and toluene (20 mL) were added. The reaction mixture was stirred for 6 h at 130–135°C, so that a slow azeotropic distillation of toluene occurred. The loss of toluene was replaced from the dropping funnel. Finally, the reaction mixture was concentrated in vacuo to approximately 50 mL and poured into water.

Elemental analyses calcd. for cycles in Scheme 4:  $C_{37}H_{29}F_3O_3$  (578.6).

C 76.80, H 5.05, found C 76.31, H 5.11%.

### 2.3 Measurements

The inherent viscosities were measured in  $CHCl_3/TFA$  (volume ratio 3/1) using an automated Ubbelohde viscometer thermostated at 20°C. The MALDI-TOF mass spectra were recorded with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ( $\lambda = 337$  nm). The irradiation targets were prepared from  $CHCl_3/TFA$  solutions (volume ratio 9:1) with dithranol as matrix and potassium trifluoroacetate as dopant. The SEC measurements were performed with an apparatus of Polymer Laboratories containing a RT detector Shodex “RT 101”. A combination of three PL mixed bed columns was used with chloroform as eluent (flow rate 1.0 mL/min). Commercial polystyrene standards served for calibration.

## 3 Results and Discussion

### 3.1 Polycondensations of Cyanopentafluorobenzene (CPFB)

Prior to the discussion of experimental results, the simplified formulas used in this work for the determination of multi-cycles should be explained. This terminology was also used in previous publications dealing with “ $a_2 + b_3$ ” or “ $a_2 + b_4$ ”

**Table 1.** Polycondensation of cyanopentafluorobenzene with various diphenols in DMF

Exp. no.	Diphenol	Base	Feed ratio	Temp. (°C)	Time (h)	Yield (%)	$\eta_{inh}^a$ (dL/g)
1	<b>1a</b>	$K_2CO_3$	5:2	80	72	~100	—
2	<b>1a</b>	$K_2CO_3$	5:2	80 + 120	48 + 24	~100	—
3	<b>1a</b>	$K_2CO_3$	3:2	80	72	95	0.05
4	<b>2</b>	$K_2CO_3$	3:2	80	72	94	0.06
5	<b>2</b>	EDPA	3:2	80	72	94	0.03
6	<b>2</b>	TMP	3:2	80	72	98	0.06
7	<b>1b</b>	$K_2CO_3$	1:1	80	72	97	0.07
8	<b>2</b>	$K_2CO_3$	1:1	80	72	98	0.09
9	<b>2</b>	EDPA	1:1	80	72	95	0.03
10	<b>2</b>	TMP	1:1	80	72	97	0.08

<sup>a</sup>Measured at 20°C with  $c = 2$  g/L in  $CHCl_3/TFA$  (volume ratio 2:1).

**Table 2.** Polycondensation of pentafluorobenzophenone with various diphenols

Exp. no.	Diphenol	Base	Feed ratio	Temp. (°C)	Time (h)	Yield (%)	$\eta_{inh}^a$ (dL/g)
1	<b>1a</b>	K <sub>2</sub> CO <sub>3</sub>	5:2	80	72	~100	—
2	<b>1a</b>	K <sub>2</sub> CO <sub>3</sub>	5:2	80 + 120	48 + 24	~100	—
3	<b>1a</b>	K <sub>2</sub> CO <sub>3</sub>	3:2	80	72	93	0.03
4	<b>1a</b>	EDPA	3:2	80	72	94	0.04
5	<b>2</b>	K <sub>2</sub> CO <sub>3</sub>	1:1	80	72	91	0.05
6	<b>2</b>	K <sub>2</sub> CO <sub>3</sub>	1:1	130	6	94	0.12

<sup>a</sup>Measured at 20°C with  $c = 2$  g/L in CHCl<sub>3</sub>/TFA (volume ratio 3:1).

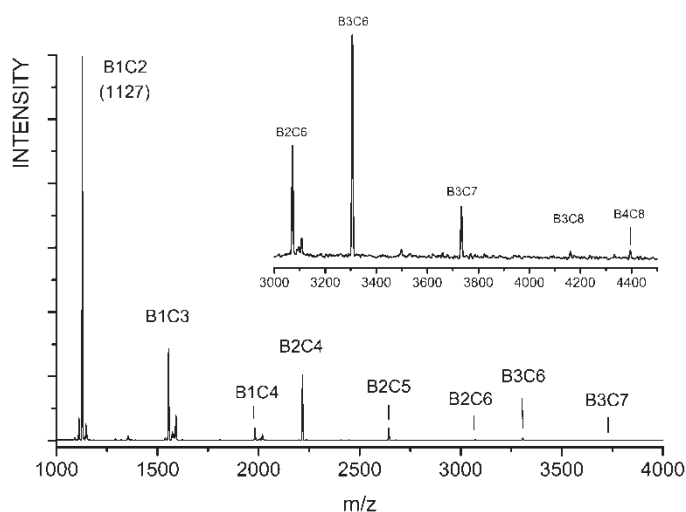
polycondensations and it proved to be useful for assignments of peaks in MALDI-TOF mass spectra as illustrated in Figures 1–4. In “ $a_2 + b_3$ ” polycondensations (which are relevant for this work), feed ratios of 3:2 and nearly quantitative conversions yield multi-cycles free of functional (end)-groups which obey the general formula  $B_{1/2N}CN$ . In this formula, C stands for cyclic structure, N for the degree of polymerization, and B means bridge unit (based on  $a_2$  monomers) connecting or bridging cycles. Scheme 1 illustrates this formula on the basis of simplified structures, where the triangles represent  $b_3$  units (the non-activated F-atoms in meta-position of CPFB or PCBP are ignored).

When a stoichiometry <3:2 is used or when the incorporation of “ $a_2$ ” monomers is incomplete, multi-cycles having functional groups of the “ $b_3$ ” monomers are formed as exemplarily illustrated in Scheme 2. Scheme 1 has the additional purpose to demonstrate that even the smallest multicycles may consist of isomers, which are not distinguishable by mass spectroscopy.

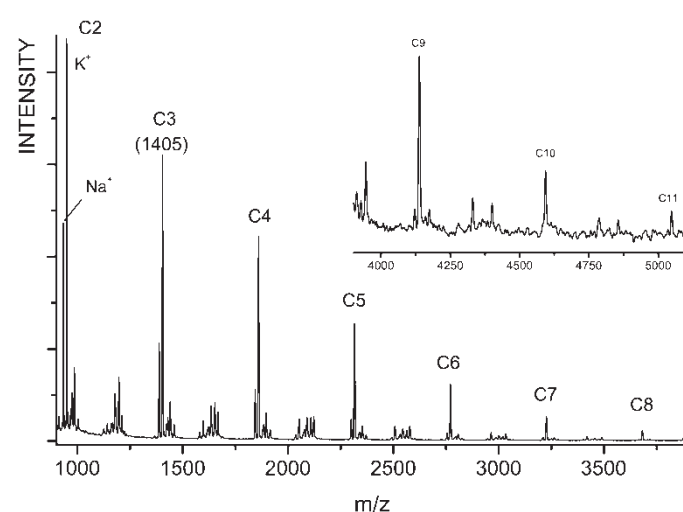
The first polycondensations of CPFB (Nos. 1 and 2, Table 1) or PFBP (No. 1, Table 2) were conducted with diphenol **1a** and a feed ratio of 5:2 to find out if substitution of all five F-atoms in CPFB is feasible. DMF was selected as reaction medium and the temperature was fixed at 80°C because it was found in

previous experiments with activated tetrafluoroaromatics that these conditions are optimum for clean polycondensations with high conversions. The products obtained under these conditions showed complex MALDI-TOF mass spectra. Weak peaks of  $B_{1/2N}CN$  multicycles (see Scheme 1) were present, but multicycles resulting from substitution of all five F-atoms were not detectable. Therefore, two more experiments with harder reaction conditions were performed (No. 2, Tables 1 and 2). Yet, the results were, in principle, the same. Compounds based on a “pentasubstitution” were not detectable.

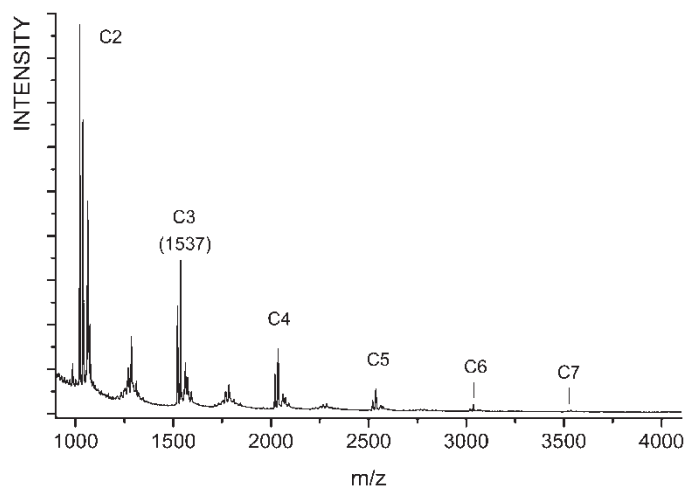
These findings indicate that the F-atoms in meta-position to the activating groups are not reactive enough to undergo clean substitution reactions with phenoxide ions. Therefore, further polycondensations were conducted with feed ratios of 3:2 considering that the F-atoms in ortho- and para-position of the nitrile or ketogroup are more activated than those in meta-position. The polycondensations of CPFB gave rather negative results, when the diphenol **2** was used as comonomer (Nos. 4–6, Table 1). The mass spectra indicated incomplete conversions and the peaks of the  $B_{1/2N}CN$  multi-cycles expected from a perfect “ $a_2 + b_3$ ” polycondensation were barely detectable. However, when the diphenol **1a** was used (No. 3, Table 1) a predominant formation of the  $B_{1/2N}CN$  multicycles was indeed found as illustrated in Figure 1.



**Fig. 1.** MALDI-TOF mass spectrum of the multicyclic polyethers obtained from CPFB and diphenol **1a** at a feed ratio of 2:3 with K<sub>2</sub>CO<sub>3</sub> as catalyst (No. 3, Table 1).



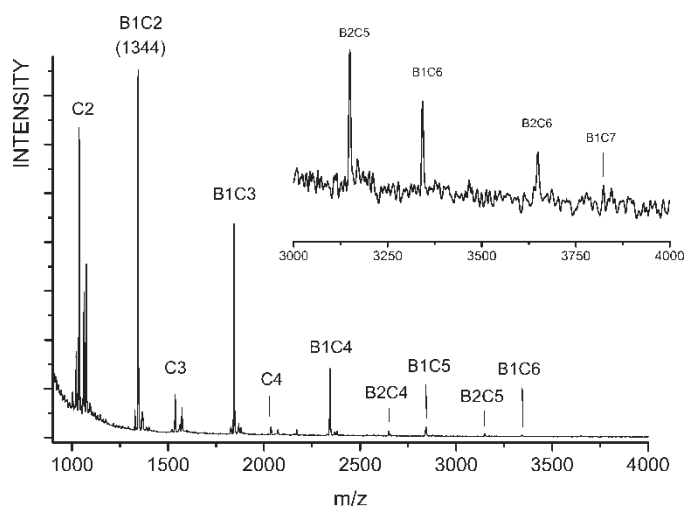
**Fig. 2.** MALDI-TOF mass spectrum of the cyclic polyethers obtained from CPFB and diphenol **1b** at a feed ratio of 1:1 with K<sub>2</sub>CO<sub>3</sub> as catalyst (No. 7, Table 1).



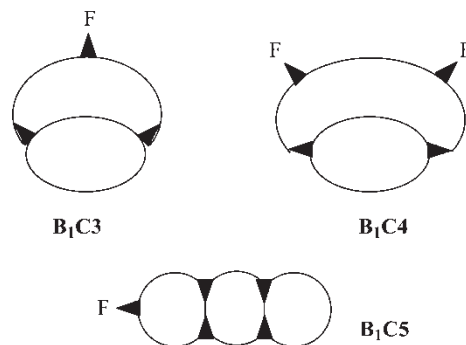
**Fig. 3.** MALDI-TOF mass spectrum of the cyclic polyethers obtained from CPFEB and diphenol **2** at a feed ratio of 1:1 with  $K_2CO_3$  as catalyst (No. 8, Table 1).

Weak peaks of incomplete multicycles lacking diphenol units (e.g.,  $B_1C_3$ ,  $B_1C_4$  or  $B_2C_5$ , see Schemes 1 and 2) were also present. Hence, this spectrum demonstrates that CPFEB can indeed react as “ $b_3$ ” monomer.

A third series of polycondensations was then performed with a feed ratio of 1:1. When  $K_2CO_3$  was used as a base as usual, CPFEB yielded reaction products mainly consisting of plain cycles as illustrated in Figures 2 and 3 for both diphenols **1b** and **2**. However, a variation of the base in connection with diphenol **2** had an unexpected effect. With TMP a product was obtained containing more bi- and tricyclic species than simple cyclic oligomers (Figure 4). This effect was not observed for EDPA, but it proved reproducible for TMP. Finally, it should be mentioned that the above mentioned term “simple cycles” means in reality a complex mixture of isomers as exemplarily illustrated for the cyclic



**Fig. 4.** MALDI-TOF mass spectrum of the multicyclic polyethers obtained from CPFEB and diphenol **2** at a feed ratio of 1:1 with TMP as base (No. 6, Table 1).

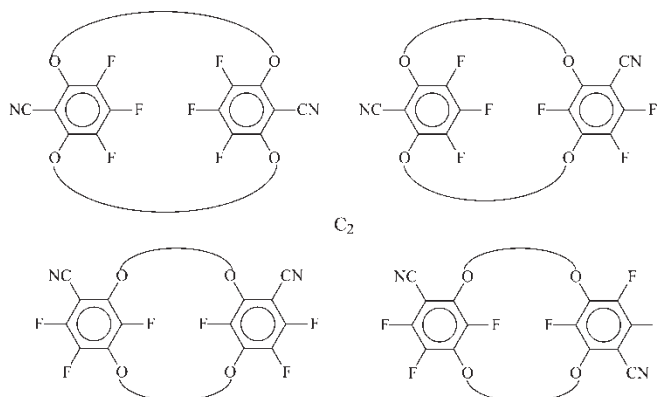


**Sch. 2.** Simplified structures of multi-cycles resulting from incomplete incorporation of  $a_2$  units in “ $a_2 + b_3$ ” polycondensations conducted with a feed ratio of 3:2.

dimers in Scheme 3. It is obvious that the number of isomers experimentally increases with the degree of polymerization, but at the current state no analytical method exists allowing for the identification of individual isomers in a complex reaction mixture.

### 3.2 Polycondensations of Pentafluorobenzophenone (PFBP)

PFBP was polycondensed with the flexible diphenol **1a** at a feed ratio of 2:5 under the same conditions as CPFEB (Nos. 1 in Tables 1 and 2). A yield around 100% (an exact determination is not feasible because of the complex reaction product) indicated that PFBP was reactive enough to enable a polycondensation under the mild conditions of experiment No. 1. However, the mass spectrum presented a complex reaction mixture with numerous C-F and C-OH groups indicating incomplete conversions. The mass peaks of multi-cycles resulting from a perfect substitution of all five C-F bonds were not detectable. A higher reaction temperature (No. 2, Table 2) did not significantly change the situation quite analogous to the results obtained with CPFEB. Two polycondensations with a feed ratio of 2:3 (**1a**: PFBP) were also performed under the standard reaction conditions (Nos. 3



**Sch. 3.** The four isomeric dimers, which may result from polycondensation of CPFEB with a feed ratio of 1:1.

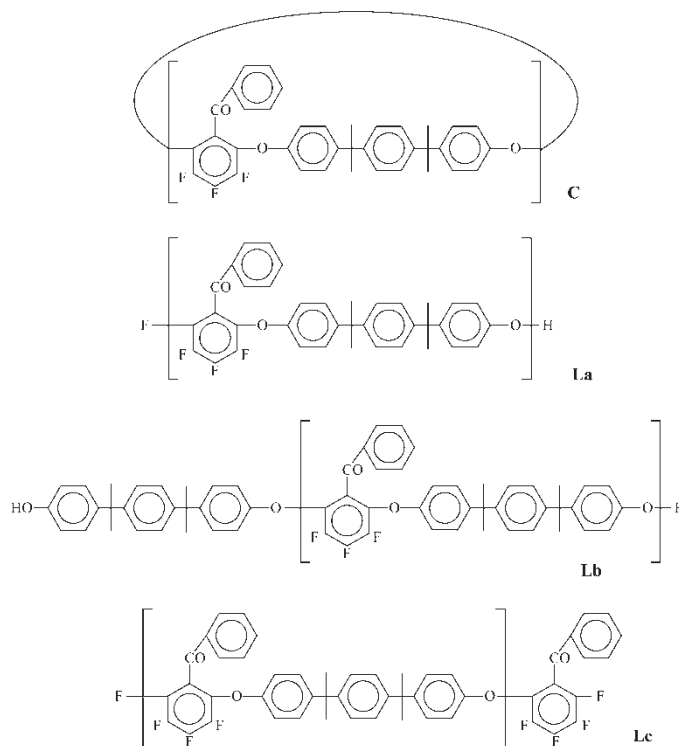


and 4, Table 2). Again complex reaction products were obtained resulting from incomplete conversions and the peaks of  $B_{n/2N}CN$  multi-cycles were weak, regardless which base was used. Therefore, these results differ from those obtained with CPFB (see Figure 1) and prove that the reactivity of PFBP is lower.

A polycondensation with a feed ratio of 1:1 under mild conditions (No. 5, Table 2) yielded a low molar mass product, which according to the mass spectrum (Figure 5) consisted of the four series of oligomers outlined in Scheme 4. This means that the conversion was again low, but it also means that this polycondensation took a rather clean course. To achieve a higher conversion an additional experiment was performed (No. 6, Table 2) with a procedure typically used for the preparation of polyethers from activated difluoroaromatics. DMSO served as reaction medium in combination with toluene which had the duty to remove the liberated water by azeotropic distillation. As demonstrated in Figure 6, the MALDI-TOF mass spectrum was now completely different and exclusively displayed peaks of cyclic polyethers (structure C in Scheme 4). This finding indicates an almost complete conversion and suggest that the chain growth was mainly limited by cyclization.

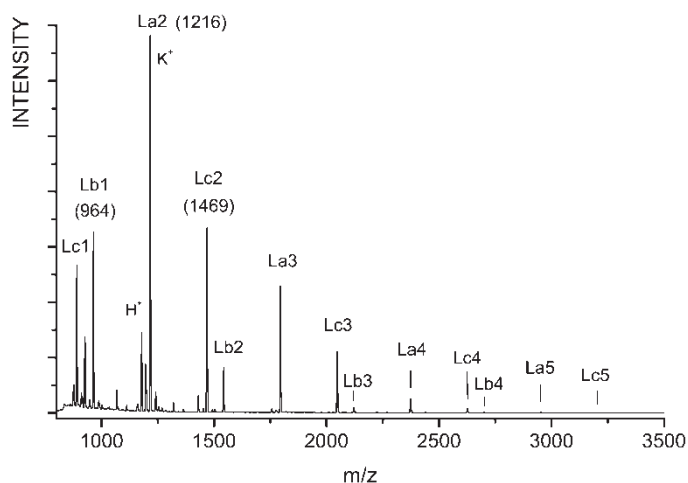
### 3.3 SEC Measurements

Three polyethers were exemplarily characterized by SEC measurements to illustrate the correlations between solution viscosity, chemical structure and SEC elution curves. For the multi-cycle of sample No. 3, Table 1 an inherent viscosity of 0.05 dL/g was found which in the case of linear oligomers corresponds to a number average molecular weight of 500–700 Da only. However, multi-cycles possess a rather compact globular architecture, so that low viscosity values correspond to higher molecular weights. In agreement with this rule a  $M_n$  of 2000 Da was found for sample No. 3,

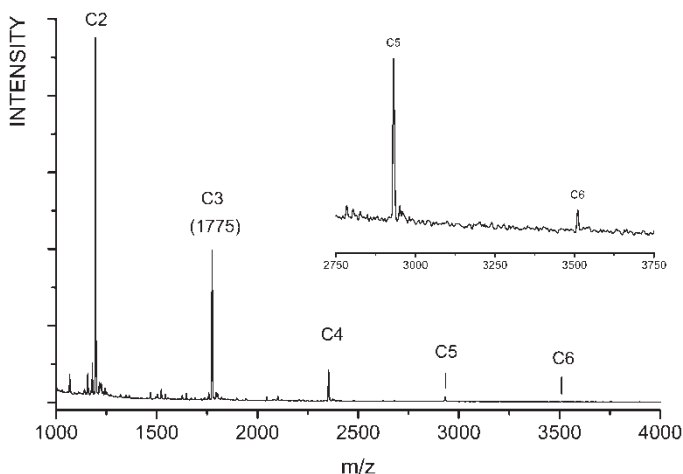


**Sch. 4.** Reaction products of the polycondensation of PFBP with diphenol **2** at a feed ratio of 1:1 (No. 5, Table 2).

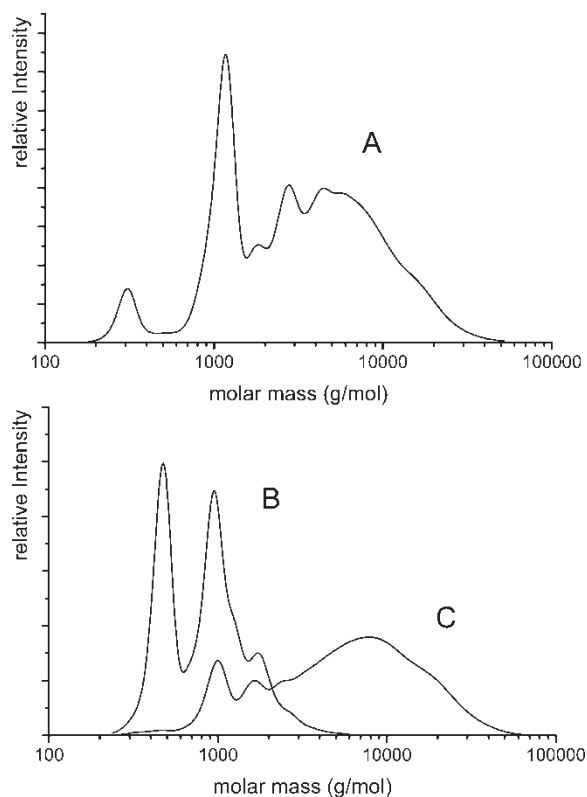
Table 1, together with a weight average ( $M_w$ ) of 5500 Da (see curve A, Figure 7). The mainly linear oligoethers No. 5, Table 2 possesses again an inherent viscosity of 0.05 dL/g, but due to its less compact structure the molecular weight  $M_n$  is lower than that of the multicycles No. 3, Table 1, namely around 800 Da (curve B, Figure 7). The higher conversion and viscosity achieved in experiment No. 6, Table 2 for the same monomer combination is reflected in curve C of Figure 7 with a  $M_n$  around 3500 Da and a  $M_w$  around



**Fig. 5.** MALDI-TOF mass spectrum of the polyether obtained from PFBP and diphenol **2** at a feed ratio of 1:1 in DMF (No. 5, Table 2).



**Fig. 6.** MALDI-TOF mass spectrum of the polyether obtained from PFBP and diphenol **2** at a feed ratio of 1:1 in DMSO (No. 6, Table 2).



**Fig. 7.** SEC elution curves of: A) multi-cyclic polyether No. 3, Table 1; B) linear oligoethers No. 5, Table 2; C) cyclic polyethers No. 6, Table 2.

9000 Da. In other words, viscosity data, SEC measurements and architecture showed the expected correlation.

#### 4 Conclusions

The results of this work suggest the following conclusions. First, gelation was avoided in all experiments partially due to incomplete conversions, partially due to cyclization reactions. Second, substitution of all five fluoroatoms did never occur. Third, CPF B was considerably more reactive than PF B. Fourth, relatively clear polycondensations of CPF B

with diphenols were feasible, when feed ratios of 3:2 ( $a_2/b_5$ ) or 1:1 were used, so that multicyclic or cyclic polyethers were obtained as main reaction products. Fifth, PF B may also yield rather clean reaction products when 1:1 polycondensations are conducted at temperatures  $>100^\circ\text{C}$ . All 1:1 polycondensations indicate an unexpectedly high cyclization tendency. In summary, neither CPF B nor PF B may be used as “ $b_5$ ” monomers in combination with diphenols, but in combination with bithiophenols or dimercaptanes a substitution of all C-F groups might be possible.

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