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Oligo(Ether-Sulfones). 1. Functionalized Oligo(Ether-Sulfones) from 4,4-*Bis*(4-Hydroxyphenyl)-Pentanoic Acid And *Bis*(4-Chlorophenyl)Sulfone: Synthesis, Properties, and Substitution of the Chlorophenyl-Endgroups

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OLIGO(ETHER-SULFONES). 1. FUNCTIONALIZED OLIGO(ETHER-SULFONES) FROM 4,4-*BIS*(4-HYDROXYPHENYL)-PENTANOIC ACID AND *BIS*(4-CHLOROPHENYL)SULFONE: SYNTHESIS, PROPERTIES, AND SUBSTITUTION OF THE CHLOROPHENYL-ENDGROUPS

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SUMMARY

Several oligo(ether-sulfones) with carboxylic groups in the side chains and chlorophenyl--endgroups were synthesized by polycondensation of different relative amounts of bis(4-chlorophenyl)sulfone (**1**) and 4,4-bis(4-hydroxyphenyl)pentanoic acid (**2**). The molecular weight distributions of the oligo(ether-sulfone)-fractions were estimated by GPC and MALDI-TOF (**3a-c**). The glass transition temperatures of the oligo(ether-sulfones) increase with the molecular weight of the oligomers. Additionally, the chlorophenyl-endgroups of **3b** were substituted with different 4-alkoxyphenols via nucleophile aromatic displacement. The resulting oligo(ether-sulfones) **4b**, **5b** and **6b** with alkyloxy-endgroups show slightly lower Tg-values compared with the corresponding oligomer with chlorophenyl-endgroups.

INTRODUCTION

In the last decades several materials based on aromatic poly(ether-sulfones) have been developed and commercialized [1]. In this connection, we recently described the synthesis and chemical modification of new poly(ether-sulfones)

[2]. However, up to now, only few informations are available dealing with synthesis of corresponding oligomers [3]. Such oligomeric systems containing two reactive endgroups are typical telechelics, which may be useful as building blocks for networks or block-copolymers.

Thus, the present paper deals with the synthesis and thermal properties of new oligosulfones prepared from 4,4-bis(4-hydroxyphenyl)pentanoic acid as the bisphenol component and an excess of bis(4-chlorophenyl)sulfone as a second monomer. The substitution of the chlorophenyl-endgroups of the oligomers with different substituted alkoxyphenols is also described.

EXPERIMENTAL

Materials

Bis(4-chlorophenyl)sulfone **1** and 4,4-bis(4-hydroxyphenyl)pentanoic acid **2** were obtained from Fluka GmbH, Neu Ulm, FRG. Bis(4-chlorophenyl)sulfone **1** was purified by recrystallization from toluene and 4,4-bis(4-hydroxyphenyl)pentanoic acid **2** from water. Dimethyl sulfoxide (DMSO) was dried with CaH_2 and distilled. Toluene was dried by azeotrop distillation.

Synthesis of the oligo(ether-sulfones) with chlorine-endgroups **3a** - **3h**

4,4-Bis(4-hydroxyphenyl)pentanoic acid **2** was dissolved in a mixture of dry DMSO and toluene. Then, K_2CO_3 was added to the solution (Tab. 1). The mixture was stirred and heated at 170°C for removing water and toluene by azeotrop distillation for about 4 h. Then, bis(4-chlorophenyl)sulfone **1** was added to the dispersion. After about 15 h at 170°C, the resulting mixtrure was diluted with 150 mL of THF and 80 mL of conc. HCl. The aqueous phase was extracted with THF and the organic phase was evaporated yielding a viscous solution. Then, the crude condensate was obtained by pouring this viscous solution into about 2500 mL of water. After stirring for about 20 h, the oligo(ether-sulfon) was filtered off, washed with water, dissolved in 80 mL of THF and precipitated again in 2000 mL of EtOH. The product was finally dried for 3 days at 80°C under reduced pressure. The analytical data are summarized in Tab. 2.

IR (KBr) of **3a**: ν = 3080-3040m (ν C-$H_{aromat.}$), 2980-2940 (ν C-$H_{aliphat.}$), 1900w, 1720s (ν C=$O_{carbonic\ acid}$), 1585s (ν C=$C_{aromat.}$), 1485s (ν C=$C_{aromat.}$), 1400m (br, δ_s CH_3), 1320m (ν SO_2), 1300m, 1250s (ν Ph-O-Ph), 1160 (sh), 1150s (ν SO_2), 1100m, 1090 (sh), 1070w (sh), 1010m, 950m, 875m + 860w + 840m (δ C-H; 1,4-disubst. arom. ring), 800w, 760m, 710w (ρ CH_2), 680w, 640w, 610w, 560m, 520w, 475w [cm^{-1}]. The same IR signals were obtained for **3b** - **3h**.

Tab. 1. Weight instructions for the synthesis of the oligo(sulfon-ethers) 3a, 3b and 3c

3...	Amount of **1**		Amount of **2**		Wt. of K_2CO_3	DMSO/ toulene
	in g	in mmol	in g	in mmol	in g	in mL/mL
a	34.4604	120	22.9064	80	22.1	200/90
b	17.9475	62.5	14.3165	50	15.2	100/50
c	22.9728	80	20.0431	70	19.3	200/90

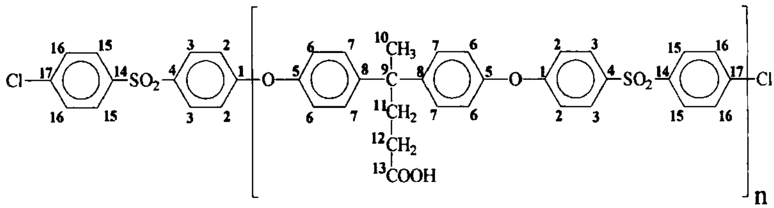
Tab. 2. Analytical data of the oligomeric condensates 3a, 3b and 3c

OES	Elemental analysis						Yield in g	
	% C		% H		% Cl			
	calc.*	found	calc.*	found	calc.*	found	calc.	found (%)
3a	65.71	62.28	4.43	4.80	4.88	4.88	51.9	50.3 (97)
3b	68.12	66.47	4.68	4.66	1.87	1.87	28.5	21.1 (74)
3c	68.70	67.18	4.74	4.73	1.13	1.13	36.5	31.0 (85)

* calculated for the results from ^{1}H-NMR; **3a**: n = 2.3, **3b**: n = 7, **3c**: n = 12

^{1}H-NMR (400 MHz, d_6-DMSO; for assignment of protons see Fig. 1) of **3a** - **3h**:

δ**Error! Bookmark not defined.** = 1.61 {s, 3n H, $C\underline{H}_3$(5)}, 2.02 {t, ^3J = 7.8 Hz, 2n H, $C\underline{H}_2$(6)}, 2.37 {t, ^3J = 7.5 Hz, 2n H, $C\underline{H}_2$(7)}, 7.05-7.08 {m, 4n H, H(3)}, 7.10-7.14 {m, 4n H, H(1)}, 7.26-7.28 {m, 4n H, H(4)}, 7.67-7.72 {m, 4H, H(9)}, 7.87-8.00 {m, 4n+4 H, H(2)} [ppm]



^{13}C{^{1}H}-NMR (100.6 MHz, d_6-DMSO) of **3a** - **3h**:

δ = 175.2 {C(13)}, 162.4 {C(1)}, 153.3{C(5)}, 146.1 {C(8)}, 141.3

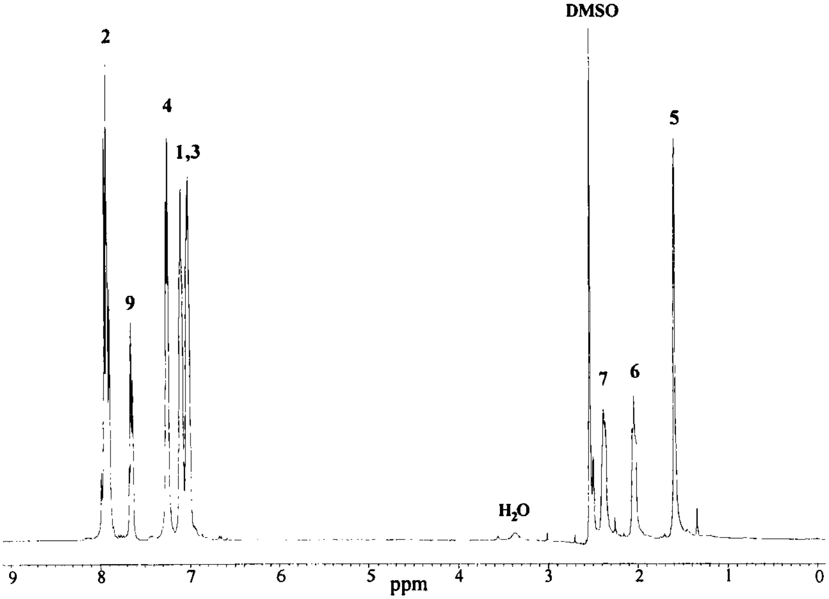


Fig. 1. ^{1}H-NMR spectrum of **3a** (solvent: d_6-DMSO)

{C(14)}, 139.5 {C(17)}, 136.1 {C(4)}, 131.0 {C(16)}, 130.7 {C(3)}, 130.3 {C(15)}, 129.8 {C(7)}, 120.6 {C(2)}, 118.8 {C(6)}, 45.7 {C(9)}, 37.0 {C(11)}, 30.7 {C(12)}, 27.9 {C(10)} [ppm]

Oligo(ether-sulfones) **4b, 5b, 6b**

4.5 Equivalents of 4-alkoxyphenol were dissolved in a mixture of dry DMSO and toluene. Then, 4.5 equivalents of K_2CO_3 were added to the solution (Tab. 3). The mixture was stirred and heated at 170°C for removing water and toluene by azeotrop distillation for about 4 h. Then, 1 equivalent of oligo(ether-sulfone) **3b** was added to the dispersion. After about 15 h at 170°C, the resulting mixtrure was diluted with 150 mL of THF and 30 mL of conc. HCl. The aqueous phase was extracted with THF and the organic phase was evaporated yielding a viscous solution. Then, the condensate was obtained by pouring this viscous solution into a suitable precipitant (Tab.3). After intensive stirring the oligo(ether-sulfon) was filtered off, washed and dried for 3 days at 80°C under reduced pressure.

Tab. 3. Weight instructions for the synthesis of the oligo(sulfon-ethers) 4b, 5b and 6b

	4b	**5b**	**6b**
starting materials			
4-alkoxyphenol:	ethyl-	butyl-	hexyl-
alkylrest, amount	3.6 mmol (0.50 g)	3.6 mmol (0.60 g)	0.6 mmol (0.11 g)
K_2CO_3	3.6 mmol (0.50 g)	3.6 mmol (0.50 g)	0.6 mmol (0.08 g)
DMSO / Toluol	20 ml / 25 ml	20 ml / 25 ml	30 ml / 20 ml
oligo(ether-sulfone) **3b**	0.80 mmol (1.83 g)	0.80 mmol (1.83 g)	0.13 mmol (0.50 g)
precipitant	600 ml ethanol	700 ml i-propanol	400 ml ethanol
*degree of conversion**	100 %	100 %	80 %

* from ^{1}H-NMR

IR (KBr) of **4b**, **5b** and **6b**:

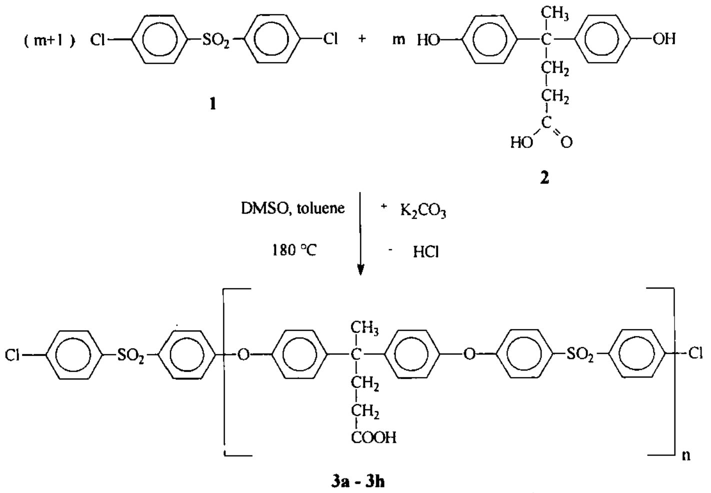
ν = 3080-3040m (ν C-$H_{aromat.}$), 2980-2940 (ν C-$H_{aliphat.}$), 1900w, 1720s (ν C=$O_{carbonic\ acid}$), 1585s (ν C=$C_{aromat.}$), 1485s (ν C=$C_{aromat.}$), 1400m (br, δ_s CH_3), 1320m (ν SO_2), 1300m, 1250s (ν Ph-O-Ph), 1160 (sh), 1150s (ν SO_2), 1100m, 1070w (sh), 1010m, 875m + 860w + 840m (δ C-H; 1,4-disubst. arom. ring), 800w, 760m, 710w (ρ CH_2), 680w, 640w,560m, 520w, 475w [cm^{-1}]

RESULTS AND DISCUSSION

The oligomeric sulfones **3a-3h** were prepared from different amounts of bis(4-chlorophenyl)sulfone (**1**) and the bisphenol 4,4-bis(4-hydroxyphenyl)pentanoic acid (**2**) via nucleophile aromatic displacement. Due to the excess of bis(4-chlorophenyl)sulfone, the resulting oligo(ether-sulfones) (OESs) contain two chlorophenyl-endgroups.

The degrees of polymerisation have been determinated by analysis of the proton-NMR-spectra and, in the case of **3a-3c**, from the chlorine-content. It was found that the experimentally determinated degrees of polymerisation were, in general, significantly higher than the calculated ones (Tab.4). This effect may be explained by fractionation during reprecipitations.

Scheme 1:



3...	a	b	c	d	e	f	g	h
n	2,3	7	12	7,2	2,8	9,3	2,5	2,8

Tab. 4. Comparison of the calculated (m) and the observed degrees of polymerisation (n)

	weight instructions		results from analytical data
3...	m / (m+1)	m	n
a	0,666	2	2,3 *1
b	0,800	4	7 *1
c	0,875	7	12 *1
d	0,800	4	7,2 *2
e	0,666	2	2,8 *2
f	0,857	6	9,3 *2
g	0,666	2	2,5 *2
h	0,500	1	2,8 *2

*1 ^{1}H-NMR end group determination; chlorine content from elemental analysis

*2 only ^{1}H-NMR end group determination

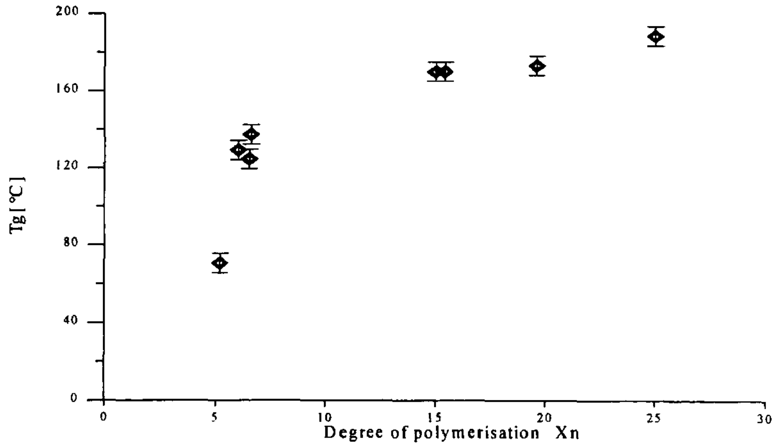
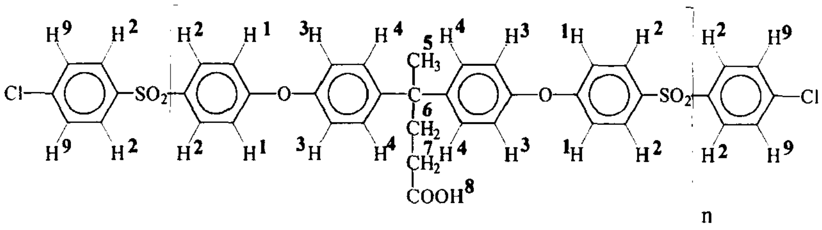


Fig. 2. Influence of degree of polymerisation X_n on the glass transition temperatures T_g of the oligo(ether-sulfones) **3a** - **3h**

As illustrated in Fig. 1, the calculation of the degree of polymerisation by ^{1}H-NMR-spectroscopy can be easily performed e.g. by comparing the integrals of the signal at 7.7 ppm, which is caused of the ortho-protons of the chlorine-endgroups, with the signals of the residual aromatical protons at 7.0-7.3 and 7.9 ppm. In the series of products, the shortest oligomer (**3a**, see Fig.1) has a degree of polymerisation of about 5.6.



The influence of the chain length on the glass transition temperature of the products is shown in Fig. 2. As expected, the glass transition temperatur (T_g) increases with molecular weight of the oligomers. The longer oligo(ether-sulfones) with n more than 7 has approximatly the same T_g-value as the corresponding high molecular weight poly(ether-sulfon) [4b].

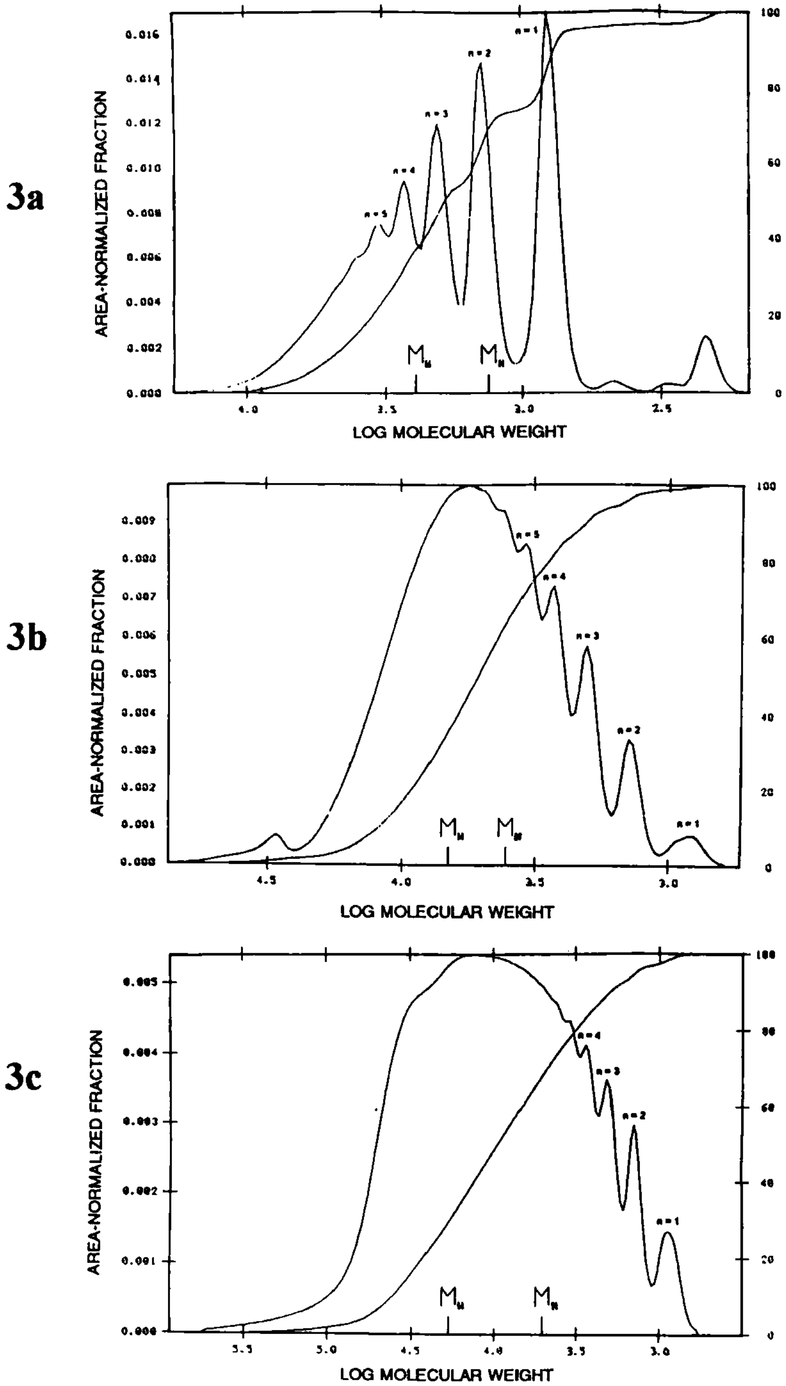


Fig. 3. GPC-diagrams of the oligo(ether-sulfones) **3a**, **3b** and **3c**

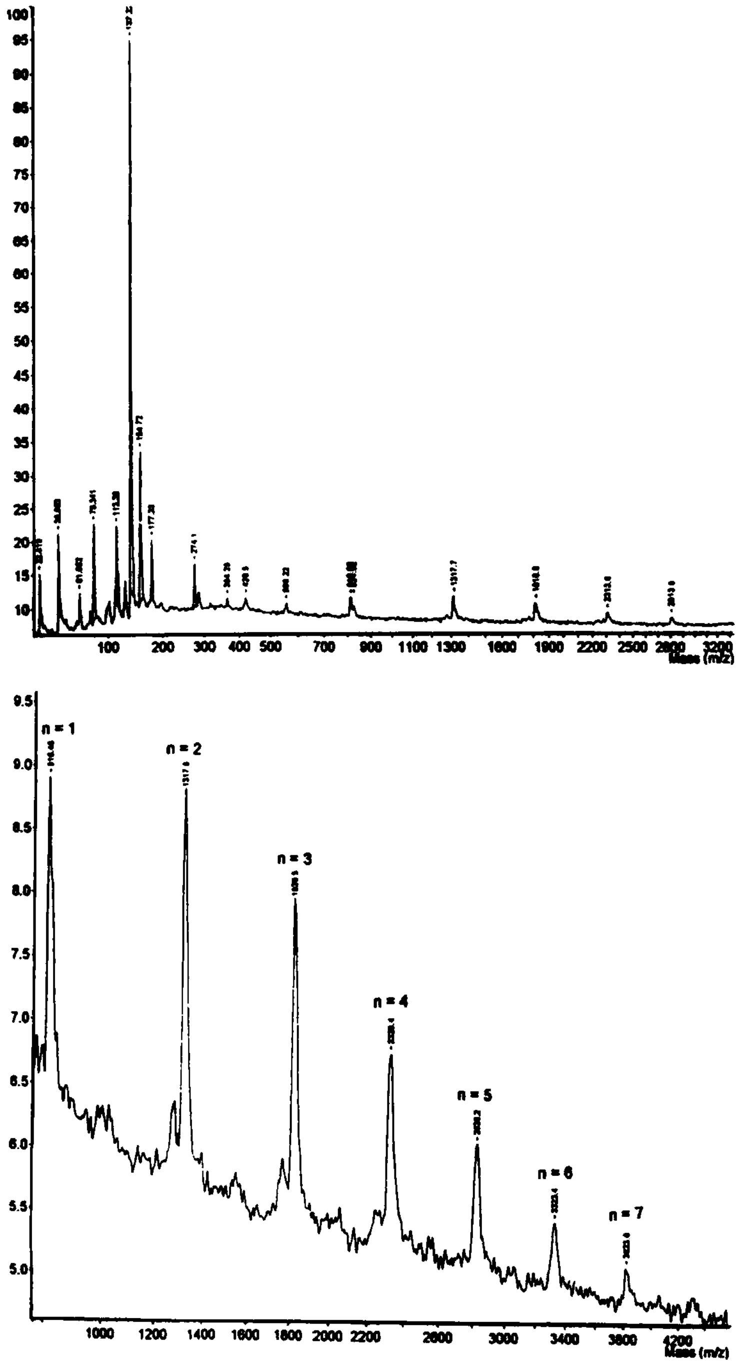
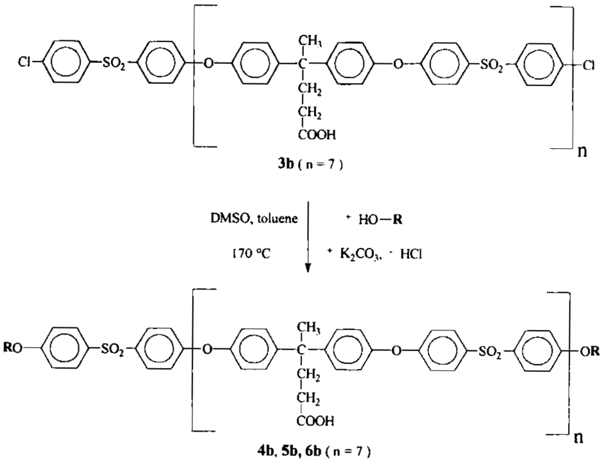


Fig. 4. MALDI-TOF-spectra of **3a**

(top: overview with 40 eV; bottom: oligomeric area with 50 eV)

Scheme 2:

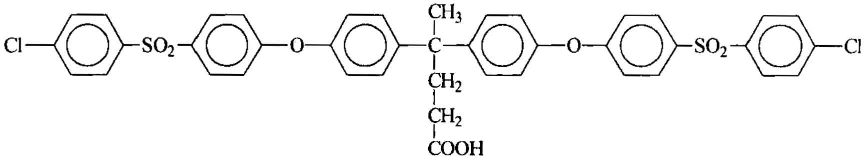


OES	4b	5b	6b
R	$-C_2H_5$	$-C_4H_9$	$-C_6H_{13}$

Tab. 5. Reduced viscosities η_{red} [ml/g] of the oligomeric condensates 3a, 3b and 3c

c [g/l]	1	2	3	4	5
3a	6.5	7.6	6.5	5.4	6.5
3b	10.8	10.8	9.4	9.8	13.9
3c	17.2	17.3	18.7	19.4	19.8

The GPC-diagrams show the distribution of the oligo(ether-sulfone)-fractions. It is interesting to note that the components with shorter chain lengths appear as separated peaks (Fig. 3). For example, in the case of the oligo(ether-sulfon)



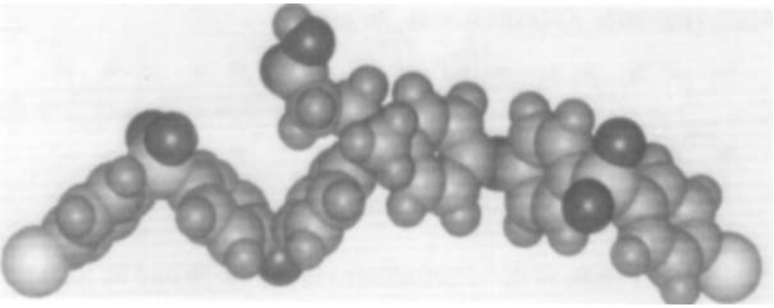


Fig. 5. Molecular model of a trimeric oligo(ether-sulfone) with chlorophenyl-endgroups

Tab. 6. Results from DSC-measurements of the oligo(ether-sulfones) 3a-h, 4b, 5b and 6b

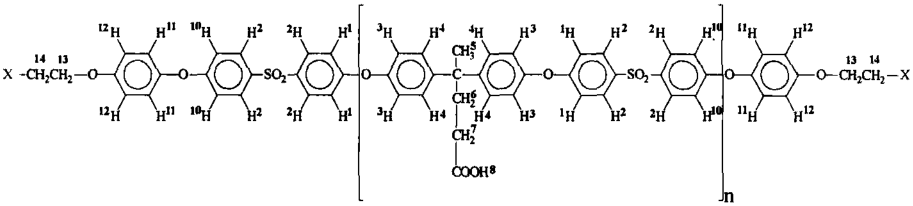
OES	T_g [°C]	OES	T_g [°C]
3a	71 *1	**4b**	153 *1 / 131 *2
3b	171 *1	**5b**	155 *1 / 150 *2
3c	189 *1	**6b**	161 *1 / 145 *2
3d	171 *1		
3e	125 *1		
3f	174 *1		
3g	129 *1		
3h	138 *1		

*1 second heating; *2 first heating

3a, the fractions with n equal to 1 up to 5 can be detected. With MALDI-TOF-spectroscopy, the exact mass-values of the lower fractions appear as molpeaks. A complete mass-spectrum of the oligo(ether-sulfon) **3a** is shown in Fig. 4. Additionally, Fig. 4 also represents the peaks for definite n-values from 1 up to 7. All molpeaks are obviously sodium-clusters.

The reduced viscosities of the oligo(ether-sulfones) have values of about 5 up to 20 ml/g (Tab.5). There is a linear relationship between the concentration of the oligomer-solution and the reduced viscosity.

^{1}H-NMR (400 MHz, d_6-DMSO) of **4b**, **5b** and **6b**:



Tab. 7. ^{1}H-NMR-shifts of the oligo(sulfone-ethers) 4b, 5b and 6b [ppm]

Nr. of H-atoms	**4b** (X = H)	**5b** (X = C_2H_5)	**6b** (X = C_4H_9)
1, 3, 10 - 12	6.98 - 7.11	6.96 - 7.10	6.95 - 7.10
2	7.90 - 7.91	7.88 - 7.90	7.86 - 7.94
4	7.25 - 7.27	7.24 - 7.26	7.24 - 7.26
5	1.60	1.59	1.59
6	2.02	2.01	2.01 - 2.03
7	2.37	2.35	2.34 - 2.35
8	12.04	12.04	12.06
13	4.00 - 4.02	3.93 - 3.96	3.92 - 3.95
14 - end	1.32	1.39 - 1.74	1.28 - 1.84

A spatial structure of the trimeric ether-sulfone containing chlorophenyl-endgroups has been computer generated (Fig.5). The end to end distance of the stretched molecule is about 300 nm.

As mentioned above, the new oligomers containing two chlorophenyl endgroups are potential building blocks for the synthesis of block-copolymers or networks. As a model reaction, the oligo(sulfon-ether) **3b** was condensed with different para-substituted alkoxy-phenols via nucleophilic aromatic displacement (Scheme 2). Additionally, the change of T_g-values due to the endgroup modification was determinated (Tab. 6). It was found that the mean T_g-values of the substituted oligomers **4b**, **5b** and **6b** are about 20 degrees lower than the T_g-value of the oligomer **3b** with chlorophenyl-endgroups.

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