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Oligo(ether sulfones). 3.† Block Copolymers via Condensation Reactions of Telechelic Oligo(ether sulfones) Bearing Phenolic Endgroups and Oligomeric α,ω-Diols

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Introduction

Block copolymers combine chemical and physical properties of the segments in one linear polymer chain. Normally a phase separation of the segments occurs, leading to the formation of domains.[3]

For example, poly(ethylene glycol)s are widely used as soft segments in various block copolymers because of their water solubility and the fact, that they are easy to purchase. In combination with, e.g., poly(styrene), the resulting block copolymers may form micelles in solution.[4,5] Poly(ethylene glycol)s can also be condensed with polyesters which have LC properties to build microphase-separated blocks.[6] As macroinitiators they were connected with PMMA via radical polymerization.[7] Other papers describe the thermodynamics of block cooligomers containing ethylene glycol.[8] The anionic polymerization of ϵ-caprolactone initiated with alkali metal alkoxide salts of poly(ethylene glycol) results in the formation of triblock copolymers.[9] Another interesting research area is the biodegradable drug carriers based on poly(ethylene glycol) block copolymers.[10]

Segmented oligomers consisting of frequently uesd poly(oxybutylene) soft segments and polyoctylene hard segments have been described recently.[11] These copolymers have been prepared via acyclic diene metathesis (ADMET) polymerization.

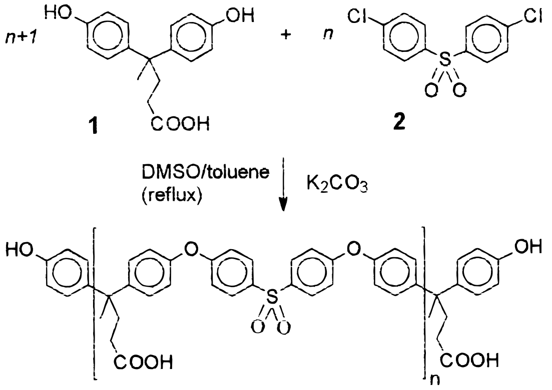
Recently some blockpolymers containing polysulfone segments were described in combination with LC polymers[12] or as a middle segment in triblock copolymers.[13,14] Up to now, these polysulfone segments were only synthesized from Bisphenol A and bis(4-chlorophenyl)sulfone (**2**). The synthesis of step−growth block copolymers with poly(aryl ether) segments, which have been combined with glassy polystyrene or polycarbonate blocks, has been reported by McGrath et al.[15] However, no block copolymers bearing functionalized polysulfones as block components are known from the literature.

In this paper we describe the synthesis of block copolymers containing polyether components as soft and hydrophilic segments and functionalized poly(ether sulfone)s bearing ester and carboxylic groups as hard segments.

Results and Discussion

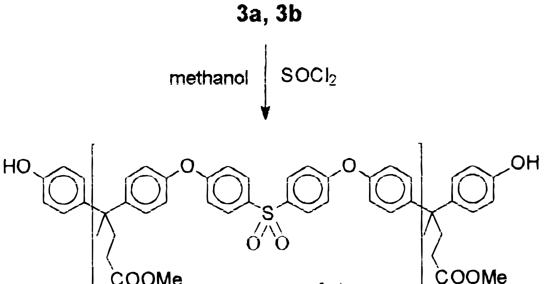
Bis(4-chlorophenyl)sulfone (**2**) and 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**) have been condensed via nucleophilic aromatic displacement according to Scheme 1. Because of a definite excess of the bisphenol, the resulting oligo(ether sulfone)s (OES) contain phenolic endgroups and the degree of polymerization can be controlled. The OES **3a** and **3b** were characterized by use of IR and NMR spectroscopy and thermal measurements. NMR and IR spectra are identical for both chain lengths of OES **3**. In the (FT)IR spectra of **3a** and **3b**, the formation of dimerized carboxylic functions is indicated. Both spectra show typical signals at 1708 and 1728 cm^{-1} which can be assigned to acid dimers.[16] However, DSC measurements showed different glass transition temperatures at 160 (**3a**) and 175 °C (**3b**), respectively. In comparison, the corresponding high molecular weight poly(ether sulfone) has a T_g value at 185 °C.[17]

Scheme 1



3	*n*
a	3
b	9

Scheme 2



4	*n*
a	3
b	9

To prevent side reactions of the carboxylic acid groups during the coupling reaction of the phenolic endgroups, in the next step they have been protected as methyl esters via activation with thionyl chloride in absolute methanol (Scheme 2).

The methyl esters **4a** and **4b** of the oligo(ether sulfones) have been characterized by IR and NMR spectroscopy, proving the high conversion in the ester formation. From DSC-measurements it was demonstrated that in analogy to the OES **3a** and **3b** a dependency of T_g with molecular weight can be confirmed (T_g of **4a** at 135 °C and of **4b** at 150 °C, respectively). This means that the formation of methyl esters lowers the T_g by approximate 25 °C in comparison with T_g values of OES containing the free carboxylic acid groups (**3a**, **3b**). As mentioned above, this effect may result from dimerization of carboxylic groups of **3a** and

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† Part 1: Reference 1. Part 2: Reference 2.

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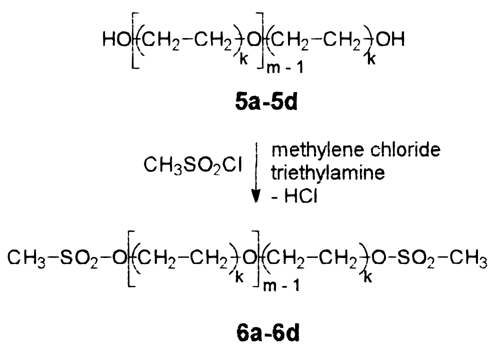
Scheme 3

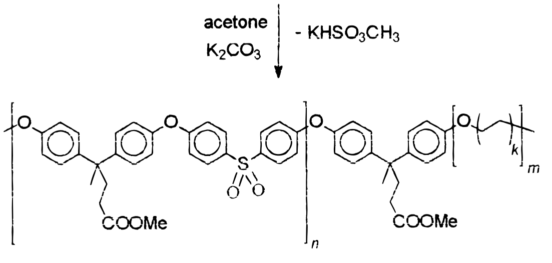


5	k	m	trivial name
a	1	4	TEG
b	1	6.4	PEG 300
c	1	8.7	PEG 400
d	2	19	PBG 1400

6	k	m
a	1	4
b	1	6.4
c	1	8.7
d	2	19

Scheme 4

4 + 6



7a-7h

3b via hydrogen bonds that lowers the mobility of the segments.

The OH end groups of oligoethers **5a**−**5d** have been mesylated to incorporate leaving groups (Scheme 3). NMR and IR spectroscopy have been used to confirm the high yield of the mesylations.

The oligo(ether sulfone methyl esters) (**4**) and the mesylated polyethers (**6**) have been condensed via a nucleophilic aliphatic substitution (Scheme 4) yielding the block copolymers **7a**−**7h**.

block copolymer	*n*	*k*	*m*	applied OES	applied bis(mesylate)s
7a	3	1	4	**4a**	**6a**
7b	3	1	6.4	**4a**	**6b**
7c	3	1	8.7	**4a**	**6c**
7d	3	2	19	**4a**	**6d**
7e	9	1	4	**4b**	**6a**
7f	9	1	6.4	**4b**	**6b**
7g	9	1	8.7	**4b**	**6c**
7h	9	2	19	**4b**	**6d**

In the NMR spectra of the block copolymers **7a**−**7h** almost no signals due to the endgroups of both prepolymers appeared. From GPC measurements (with polystyrene standard) it was shown that the molecular weights (M_n) of the block copolymers are in the region 11 000−30 000 (see Table 4). A general relation between the molecular weights (M_w or M_n) or the dispersity (M_w/M_n) determined by the GPC measurements and the chemical structures of the block copolymers **7a**−**7h** could not be determined.

As an example the block copolymer **7h** was fractionated by use of GPC. A series of these fractions were measured with FTIR spectroscopy yielding exactly the same spectra in all cases. This strongly indicates a high chemical homogeneity of block **7h** that is independent of the molecular weight.

DSC diagrams did not show glass transitions of the segments in the case of the blockpolymers **7a**−**7h**.

It can be concluded that the new type of block copolymers presented in this paper containing polyethers and functionalized polysulfone segments can easily be prepared. These block copolymers may be useful in the medical area, e.g., as material in contact with living tissue or as material for semipermeable membranes which may be modified chemically to optimize the permselectivity and mechanical stability.

Experimental Section

Materials and Methods. Bis(4-chlorophenyl)sulfone (**2**) and 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**) were obtained from Fluka GmbH, Neu Ulm, Germany. Bis(4-chlorophenyl)sulfone (**2**) was purified by recrystallization from toluene and 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**) by recrystallization from water. Dimethyl sulfoxide (DMSO) was dried over CaH_2 and distilled. Toluene was dried by azeotropic distillation. Tetraethylene glycol (TEG) was purchased from Janssen, poly(ethylene glycol) (PEG) with an average molecular weight of $M_w = 300$ was purchased from Merck GmbH and with a $M_w = 400$ from Fluka. Polybutylene glycol with an average molecular weight of 1400 (PBG 1400) was obtained from Aldrich (Terathane 1400). Triethylamine was refluxed over potassium hydroxide for 3 h and distilled. All other chemicals were obtained commercially and used without further purification.

OES with Phenol Endgroups (3a, 3b). The synthesis was conducted similar to the preparation of oligo(ether sulfone)s bearing chlorophenyl endgroups described in earlier papers.[1,2] Bis(4-chlorophenyl)sulfone (**2**) was dissolved in a mixture of dry DMSO and toluene. K_2CO_3 was added to the solution (Table 1). The mixture was stirred and heated at 170 °C for about 3 h to remove water and toluene by azeotropic distillation. Then, 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**), dissolved in 20 mL of DMSO, was added to the dispersion. After 15 h at 170 °C, the resulting mixture was diluted with 150 mL of THF and 80 mL of concentrated HCl. The aqueous phase was extracted with THF, and the organic phase was evaporated, yielding a viscous solution. The crude condensate was obtained by pouring this viscous solution into 2500 mL of water. Again the product was dissolved in 40 mL of THF and precipitated in 200 mL of petroleum ether. The product was finally dried for 3 days at 80 °C under reduced pressure yielding a colorless amorphous solid.

The weight instructions and the yields are summarized in Table 1.

DSC: **3a** $T_g = 160$ °C (2. heating); **3b** $T_g = 175$ °C (2. heating). TG: **3a** $\Delta m = -0.4$ (100), −0.6 (150), −0.8 (200) [% of lost mass (°C)]; **3b** $\Delta m = -1.5$ (100), −1.7 (150), −2.1 (200), −2.4 (250) [% of lost mass (°C)].

Methyl Esters of the Oligo(ether sulfones) (4a, 4b). Thionyl chloride (1.631 g; 14 mmol) was dropped slowly at 0−5 °C into 50 mL of absolute methanol. Then 2 g (4 mmol of COOH) of the oligo(ether sulfone) **3a** {**3b**} were added in five to six portions to the cooled and stirred solution. After 2 h at 0 °C, the mixture was stirred additional for 2 days at room temperature. The precipitated solid powder was filtered off, dissolved in THF, and precipitated again in 800 mL of water. The product was finally dried at reduced pressure. Yield: 1.72 g (85%) of **4a** {1.52 g (69%) of **4b**} as a colorless amorphous solid.

DSC: **4a** $T_g = 135$ °C; **4b** $T_g = 150$ °C. TG: **4a** $\Delta m = -1.2$ (100), −1.7 (150), −3.5 (200), −4.5 (250) [% of lost mass (°C)]; **4b** $\Delta m = -1.0$ (100), −1.2 (150), −1.4 (200), −1.46 (250) [% of lost mass (°C)].

Mesylation of TEG, PEG, and PBG (6a−6d). Poly(ethylene glycol)s **5a**−**5c** and poly(butylene glycol) **5d** respectively were dissolved in THF or dichloromethane and trieth-

Table 1. Weight Instructions for the Synthesis of the Oligo(ether sulfones) 3a and 3b

OES	amount of **1**, g (mmol)	amount of **2**, g (mmol)	amount of K_2CO_3, g	DMSO/toluene, mL/mL	yield, g
3a	8.0172 (28)	6.0304 (21)	8.3	70/70	9.5 (76%)
3b	20.6160 (72)	18.6099 (65)	22	200/70	27.3 (80%)

Table 2. Weight Instructions for the Mesylations 6a−6d

	amount of 5a−5d, g (mol)	solvent; amount, (mL)	amount of triethylamine, mL (mol)	amount of mesyl chloride, mL (mol)
6a	15.5 (0.08), TEG	CH_2Cl_2; 250	14 (0.18)	28 (0.2)
6b	30.0 (0.1), PEG 300	THF; 100	39 (0.5)	98 (0.7)
6c	16.0 (0.04), PEG 400	CH_2Cl_2; 250	7 (0.09)	17 (0.12)
6d	30.0 (0.021), TT 1400	THF; 200	7 (0.09)	20 (0.14)

Table 3. Weight Instructions for the Block Polymers 7a−7h

	amount of **4**, mg (mmol)	amount of **6**, mg (mmol)	amount of K_2CO_3, g (mmol)
7a	**4a**: 116.4 (0.145)	**6a**: 50.9 (0.145)	0.4 (2.9)
7b	**4a**: 198.3 (0.248)	**6b**: 112.9 (0.248)	0.5 (3.6)
7c	**4a**: 122.8 (0.153)	**6c**: 85.3 (0.153)	0.4 (2.9)
7d	**4a**: 200.0 (0.250)	**6d**: 390.0 (0.250)	0.5 (3.6)
7e	**4b**: 456.0 (0.093)	**6a**: 32.5 (0.093)	0.2 (1.45)
7f	**4b**: 226.4 (0.046)	**6b**: 21.0 (0.046)	0.1 (0.72)
7g	**4b**: 406.7 (0.083)	**6c**: 46.0 (0.083)	0.2 (1.45)
7h	**4b**: 325.5 (0.066)	**6d**: 103 (0.066)	0.2 (1.45)

Table 4. Results from GPC Measurements (Polystyrol Standard)

	n	k	m	M_w	M_n	M_w/M_n
7a	3	1	4	26 000	11 000	2.4
7b	3	1	6.4	54 000	12 000	4.5
7c	3	1	8.7	90 000	26 000	3.5
7d	3	2	19	43 000	22 000	2.0
7e	9	1	4	115 000	18 000	6.4
7f	9	1	6.4	130 000	30 000	4.3
7g	9	1	8.7	35 000	12 000	2.9
7h	9	2	19	132 000	12 000	6.3

Table 5. Results from Thermal Investigations (TG)

				weight lost, %			
	n	k	m	100 °C	150 °C	200 °C	250 °C
7a	3	1	4	0,5	1,1	1,5	2,5
7b	3	1	6.4	0,3	1,0	1,4	1,8
7c	3	1	8.7	1,7	6,1	9,1	9,7
7d	3	2	19	5,3	10,9	14,3	*a*
7e	9	1	4	1,1	3,7	4,2	*a*
7f	9	1	6.4	0,8	1,5	1,8	2,1
7g	9	1	8.7	2,1	6,2	13,4	13,8
7h	9	2	19	1,3	1,7	2,1	4,2

[a] Not measured.

ylamine was added to the solution (Table 2). After the reaction was cooled to −10 °C, the mesyl chloride was added drop by drop over a period of 2 h. The mixture was allowed to warm to room temperature and stirred for 2 days. Then 100 mL of ice water and 100 mL of dichloromethane were added. The organic phase was washed three times with 100 mL of ice water and then with 10% hydrochloric acid solution, three times with saturated sodium hydrogen carbonate solution, and finally with saturated sodium chloride solution. The organic phase was dried over $MgSO_4$. The solvent was removed yielding viscous, slightly yellow, liquid products.

Coupling of the Prepolymers To Block Copolymers (7a−7h). The mesylated poly(ethylene glycols) **6a**−**6d** were dissolved in 30 mL of acetone. Then an equivalent amount of the methyl ester of an oligo(ether sulfone) **4** and potassium carbonate were added (Table 3). The mixture was heated at 60 °C for 20 h. The precipitated polymer was removed from the solvent, dissolved in 15 mL of THF and precipitated again in 250 mL of petroleum ether. The product was finally dried for 3 d at 50 °C under reduced pressure. The experimental data of this procedure are listed in Table 3.

GPC−FTIR of **7h**: solvent THF; GPC, 1000 A column combined with 100000 A column; SDV 5 μm; LC interface, model 410; scanning with Nicolet Impact 400, DTGS detector; the observed IR signals were the same in each scan (see spectral data in Results and Discussion).

Spectral Measurements. IR spectra were recorded on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer and the FTIR spectra on a Nicolet 5DXC FTIR spectrometer. The NMR spectra were determined on a Bruker ARX 400 (400 MHz) with DMSO-d_6 as internal standard. The thermogravimetric properties were investigated with a Mettler TA 3000. The GPC measurements were carried out with Ultrastyragel columns (Waters) with pore widths of 10^5, 10^4, 10^3, and 500 Å; several standards of polystyrene were used with average molecular weights in a range of 600−2950000; the blockpolymers were dissolved in NMP; a differential refractometer (ARC) was used at 33 °C to detect the signals.

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