

New polymer syntheses

55. Aromatic poly(ether-sulfide)s of pyridine and pyridazine

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SUMMARY:

Various poly(ether sulfide)s were prepared by polycondensation of 4-mercaptophenol or silylated 4-mercaptophenol with 2,6-dichloropyridine or 3,6-dichloropyridazine. A "two step" and an "one-pot" procedure were compared. The poly(ether-sulfide)s were characterized by elemental analyses, inherent viscosities, ^{13}C -NMR spectroscopy, gel-permeation chromatography and DSC-measurements.

INTRODUCTION

Aromatic polyethers possess a combination of useful properties, and have found great interest as membranes for reverse osmosis or gas separation. Variation of permeability and selectivity requires chemical modification of the simple homopolymers. One approach to reach this goal is the incorporation of nitrogen-heterocycles, because these heterocycles enhance the polarity and hydrophilicity and allow a further modification by alkylation. In previous parts of this series¹⁻⁴) we have reported on the synthesis of polyethers or polysulfides containing pyridin rings. The present work was aimed at synthesizing pyridin and pyridazin containing poly(ether-sulfide)s by polycondensation of silylated 4-mercaptophenol.

EXPERIMENTAL

Materials:

2,6-Difluoropyridine, 2,6-dichloropyridine and 4-mercaptophenol were purchased from Aldrich Co. (Milwaukee, Wisc. USA) and distilled prior to use. 2,6-Dichloropyridazine, 4,4'-dichlorodiphenylsulfone and 4,4'-difluorodiphenylsulfone were purchased from Aldrich Co. and purified by recrystallization from toluene. N-Methylpyrrolidone (NMP) was once distilled over dry K_2CO_3 and twice over P_4O_{10} (in vacuo). Dimethylformamide (DMF) was distilled over P_4O_{10} in vacuo.

O,S-Bistrimethylsilyl-4-mercaptophenol

4-Mercaptophenol (0,3 mol) and hexamethyldisilazane (0,2 mol) were refluxed in toluene (150 ml) until the evolution of NH_3 had ceased. The reaction mixture was then concentrated in vacuo and the product isolated by distillation. Yield 91 %;

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b.p. 114-116°C/ 15 mbar. Analyses calcd. for $C_{12}H_{22}OSSi_2$ (254.5): C 56.59, H 8.73, S 12.59, found: C 56.83, H 8.67, S 12.51%.

Synthesis of the diphenols 4a and 5a (s. Tab. 1)

4-Mercaptophenol (0.55 mol) and potassium tert.-butoxide (0.55 mol) were dissolved in dry DMF (500 ml) purged with nitrogen. A concentrated solution of 2,6-dichloropyridine (0,25 mol) in DMF was then added dropwise with stirring and cooling with ice. Finally the reaction mixture was heated to 120°C for 2 h and after cooling poured into cold water. The product was extracted with two 600 ml portions of ethylacetate. The combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was recrystallized from dioxane/ligroin. The same procedure was applied to 3,6-dichloropyridazine.

Silylation of diphenols 4a and 5a (s. Table 1)

A diphenol (4a or 5a) (0,1 mol) and hexamethyldisilazane (0,12 mol) were refluxed in toluene until the evolution of NH_3 had ceased. The reaction mixture was concentrated in vacuo and the crude products (4b or 5b) recrystallized from ligroin.

Table 1: Yields and properties of the diphenols 4a, 5a and their bistrimethylsilyl derivatives 4b, 5b

Formula No	Yield (%)	m.p. (°C)	Elem. Formula (Form.weight)	Elem. Analyses			
				C	H	N	
<u>4a</u>	61	172-174	$C_{17}H_{13}NO_2S_2$ (327.3)	Calcd.	62.33	4.01	4.28
				Found	61.74	3.97	4.29
<u>5a</u>	73	212-214	$C_{16}H_{12}N_2O_2S_2$ (328.3)	Calcd.	58.49	3.69	8.53
				Found	58.72	3.75	8.63
<u>4b</u>	91	63-64	$C_{23}H_{29}NO_2S_2Si_2$ (471.6)	Calcd.	58.52	6.21	2.97
				Found	58.67	6.22	3.11
<u>5b</u>	89	88-90	$C_{22}H_{28}N_2O_2S_2Si_2$ (472.6)	Calcd.	55.86	5.98	5.93
				Found	55.62	6.04	5.88

Polycondensation

A) in solution

A silylated diphenol (4b or 5b, 30 mmol), a dichloroaromatic (1 or 2, 30 mmol) and dry K_2CO_3 (16 mmol) were heated under stirring in NMP (50 ml, purged with nitrogen) to 180°C. This temperature was maintained for 24 h. The progress of the polycondensation is indicated by the evolution of nitrogen. After cooling the reaction mixture was poured into cold water. The dry poly(ether sulfide) was dissolved in CH_2Cl_2 and precipitated into methanol.

B) in bulk

O,S-Bistrimethylsilyl-4-mercaptophenol (30 mmol) a difluoroaromatic (30 mmol) and CsF were weighed into a cylindrical glass-reactor equipped with stirrer gas-inlet and -outlet tubes. The reaction mixture was heated to 140 - 160°C were the condensation started. The temperature was gradually

Table 2: Yieldsole(ester-anhydride)s prepared from silylated phenylhydroquinone and 4-hydroxybenzoic acid

Polymer Formula	Synth. Method	Halogen ^a	Yield (%)	$\eta_{inh}^{b,c}$ (dl/g)	Tgd ^d (°C)	Elem. Formula (Form. weight)	Elem. Analyses			
							C	H	N	S
<u>6</u>	A	F	80	0.12b)	-	C ₂₂ H ₁₄ N ₂ O ₂ S ₂ (402.3)	Calcd. 65.62 Found 64.01	3.75 3.47	6.96 7.14	15.93 16.17
<u>6</u>	A	Cl	71	oligom.	-	-	Calcd. Found			
<u>7</u>	A	Cl	75	0.20b)	116	C ₂₁ H ₁₃ N ₃ O ₂ S (403.3)	Calcd. 63.48 Found 61.45	3.25 3.23	10.42 10.14	15.89 14.93
<u>7</u>	B	F	86	0.15c)	118	C ₂₁ H ₁₃ N ₃ O ₂ S (403.3)	Calcd. 62.48 Found 60.15	3.25 3.29	10.42 9.78	15.89 15.82
<u>8</u>	A	Cl	93	0.18b)		C ₂₀ H ₁₂ N ₄ O ₂ S ₂ (404.3)	Calcd. 59.36 Found 57.07	2.99 2.98	13.86 13.38	15.86 16.33
<u>9</u>	A	Cl	83	0.18b)	107	C ₂₉ H ₁₉ NO ₄ S ₃ (541.4)	Calcd. 65.28 Found 64.31	3.54 3.61	2.59 2.67	17.76 17.58
<u>9</u>	B	F	90	0.13c)	104	C ₂₉ H ₁₉ NO ₄ S ₃ (541.4)	Calcd. 64.28 Found 62.83	3.54 3.60	2.59 2.60	17.76 16.97
<u>10</u>	B	F	94	0.32c)	129	C ₂₈ H ₁₈ N ₂ O ₄ S ₃ (542.4)	Calcd. 61.95 Found 61.40	3.35 3.24	5.16 5.27	17.73 17.42

a) Halogen of the activated dihaloaromatic

b) measured at 25°C with c = 2 g/l in CH₂Cl₂

c) measured at 25°C with c = 2 g/l in CH₂Cl₂/trifluoroacetic acid (volume ratio 4:1)

d) DSC measurements with a heating rate of 20°C/min

raised to 290°C over a period of 2 h. Finally vacuum was applied for 0,5 h. The cold poly(ether-sulfide) was dissolved in CH₂Cl₂ and precipitated into methanol.

Measurements

Inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C. Gel permeation chromatography was conducted in dichloromethane at 25°C with a Kontron HPLC equipped with a Waters Md 410 differential refractometer and a combination of four Ultrastyrigel[®] columns (Waters Co.).

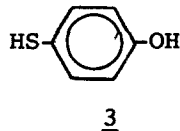
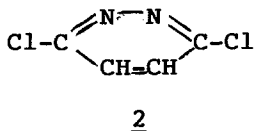
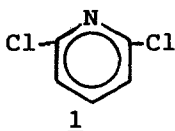
A commercial set of polystyrene standards was used for calibration, and the weight average molecular weights were calculated by the universal calibration method from the maxima of the elution curves. DSC measurements were conducted with a Perkin-Elmer DSC-4 at a heating rate of 20°C/min in aluminium pans under nitrogen.

RESULTS and DISCUSSION

The synthetic approach of this work is mainly based on the following three monomers: 2,6-dichloropyridine (1) or 3,6-dichloropyridazine (2) as electrophilic reactants and 4-mercaptophenol (3) as nucleophilic reaction partner. For the polycondensation of these monomers two different strategies (I and II) were studied.

Strategy I is a two step procedure starting with synthesis and isolation of the two new diphenols 4 and 5. These diphenols were easily obtained by condensation of monomers 1 or 2 with the double molar amount of 3 in the presence of potassium tert-butoxide. Since the mercapto group is more acidic than the hydroxy group and the sulfide anion more nucleophilic than the oxide ion, this condensation shows a high selectivity for the formation of the diphenols 4 and 5, even without intermediate protection of the OH-groups of monomer 3. The diphenols 4 and 5 were silylated with hexamethyl disilazane and the resulting crude bistrimethylsilyl derivatives were used for the polycondensation with 1 or 2 without additional purification.

The polycondensations were conducted in N-methylpyrrolidone (NMP) in the presence of K₂CO₃ according to a procedure recently described³) for the synthesis of high molecules weight poly(ether-sulfone)s (method A, Eq. 1). Furthermore, two polycondensations were conducted in such a way that the crude silylated diphenols were condensed with 2,6-difluoropyridine in bulk (method B). Finally, the silylated diphenols were condensed with 4,4'-dichlorodiphenyl sulfone in NMP. Yields and properties of the five different poly(ether-sulfide)s 6-10 prepared in this way are summarized in Table 2.



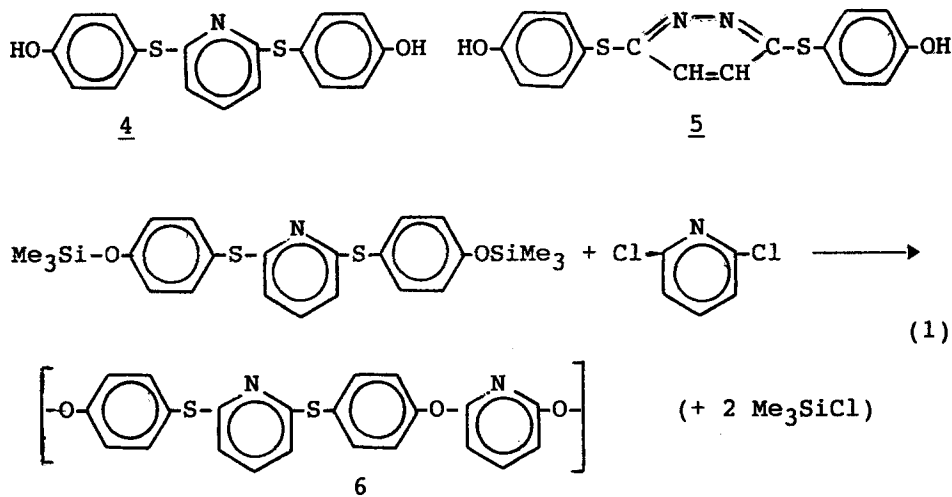


Table 3: Yields and properties of poly(ester-sulfide)s prepared by polycondensation of O,S-bis(trimethylsilyl)-4-mercaptophenol

Poly. Form.	Yield (%)	$\eta_{inh}^c)$ (dl/g)	Elem. Formula (Form. weight)	Elem. Analyses			
				C	H	N	S
<u>11a)</u>	45	0.13	C ₁₁ H ₇ NOS (201.1)	Calcd. 65.62 Found 64.07	3.51 3.51	6.96 6.45	15.93 17.30
<u>11b)</u>	90	0.15 ^{d)}	C ₁₁ H ₇ NOS (201.1)	Calcd. 65.62 Found 63.75	3.51 3.43	6.96 6.58	15.93 16.33
<u>12b)</u>	85	0.17	C ₁₆ H ₆ NOS (202.1)	Calcd. 59.36 Found 58.65	2.99 3.21	13.86 12.91	15.88 17.58

a) Polycondensation in bulk (Method B)

b) Polycondensation in solution (Method A)

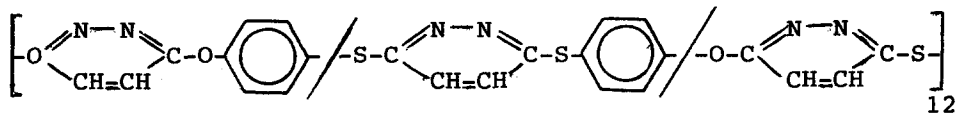
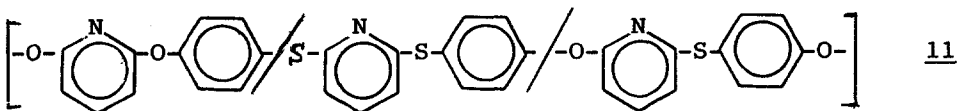
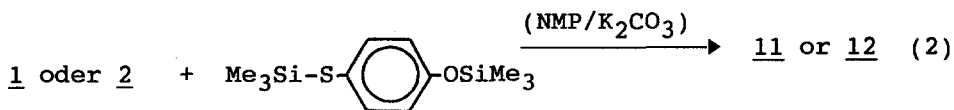
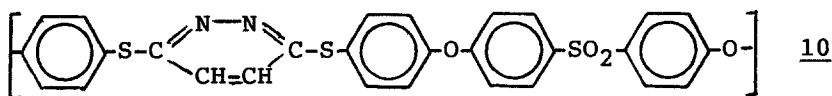
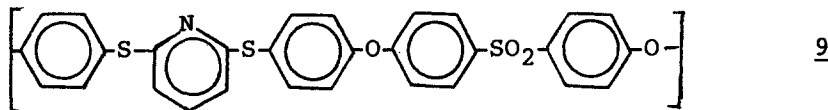
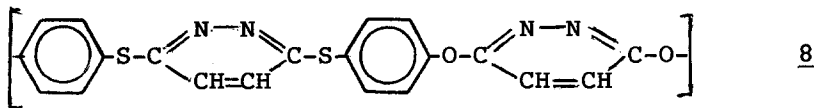
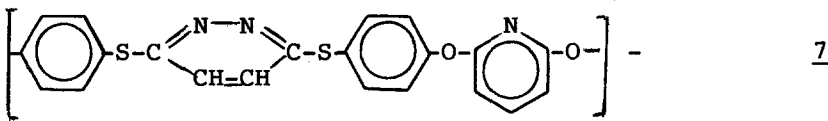
c) measured at 25°C with $c = 2$ g/l in CH₂Cl₂

d) $M_w = 12$ 000 from GPC measurements

Strategy II consist in an one-pot procedure based on the polycondensation of silylated 4-mercaptophenol with either monomer 1 or 2. These polycondensations were again conducted in NMP in the presence of K₂CO₃. Furthermore, one polycondensation of silylated 4-mercaptophenol with 2,6-difluoropyridine was conducted in bulk. For the resulting poly(ether-sulfide)s 11 and 12 a more or less random sequence of three different repeating units was expected in contrast to the primary structure of poly(ether-sulfide)s prepared according to strategy I. Yields and properties of these poly(ether-sul-

fide)s are listed in Table 3.

When methods A and B are compared for polymers 6 and 7 (Tab. 2) or 11 (Tab. 3) the higher viscosities were found for method A. Polycondensations in bulk at temperatures above 200°C have the short coming that evaporation of a volatile monomer affects the stoichiometry of the reaction mixture. This effect is particularly pronounced in small-scale experiments. However, it is conspicuous that all polycondensation yielded relatively low inherent viscosities. when compared with syntheses of polyethers conducted under similar reaction conditions²). Similarly low or moderate molecular weights were found for syntheses of aromatic polysulfides from silylated dimercapto aromatics^{4,5}). Obviously, the sulfur causes side reactions. This conclusion is supported by the broad and sometimes bimodal molecular weight distributions (Fig. 1) and by relatively high S-elemental analyses of polymers derived from silylated mercaptophenol (Eq. 2, and Tab. 3).



GPC measurements gave weight average molecular weights (M_w) around 40 000 for polymer 10 and M_w values \leq 20 000 for polymers 7 and 11.

The ^{13}C -NMR spectra confirm a rather regular structure for poly(ether sulfide)s 6 and 9, whereas in the case of 7, 8 and 10 more signals (of low intensity) were detectable than expected. Also this observation supports the occurrence of side reactions, in particular with monomer 5. In contrast, a relatively regular structure was seemingly formed, when polymer 11 was synthesized in NMP (method A in Tab. 3), because the DSC measurements revealed a reproducible melting endotherm (Fig. 2, A-C) which was not detectable in the DSC-traces of other poly(ether-sulfide)s (eg. 12, Fig. 2D).

The results of the present work and those of a previous study⁴) suggest that polycondensations of silylated thiophenols involve side reactions that have presumably a radical character. These side reactions also seem to be responsible for the relatively low molecular weights ($M_w \leq$ 40 000) obtained in all cases. Anyway polycondensations in NMP yield better results than polycondensations in bulk.

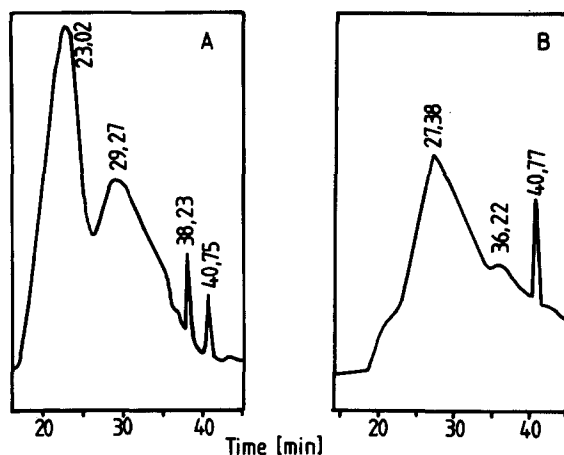


Fig. 1: GPC measurements conducted at 25°C in CH_2Cl_2 with Ultra-styragel^R columns: A) poly(ether sulfide) 10, B) poly(ether-sulfide) 11

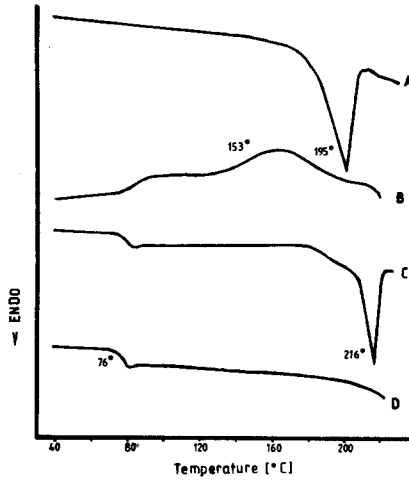


Fig. 2: DSC measurements of poly(ether-sulfide)s conducted at a heating and cooling rate of 20°C/min, A) first heating of 11, B) first cooling of 11, C) second heating of 11, D) first heating of 12

References

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