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New polymer syntheses

53. Aromatic polysulfides by polycondensation of silylated 1,3-bismercaptobenzene

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SUMMARY

1,3-Bis(trimethylsilylmercapto)benzene was condensed with 4,4'-difluorodiphenylsulfone, 2,6-difluorobenzonitrile or 2,6-difluoropyridine in bulk. A second series of polycondensations was conducted with activated dichloroaromatics in N-methylpyrrolidone. The latter method gave the higher molecular weights (weight-average molecular weights up to approx. 35000). All polysulfides are amorphous materials with glass-transition temperatures in the range of 105-155°C.

INTRODUCTION

Aromatic polysulfides, in particular polyphenylene sulfide (PPS), have found great technical interest as thermostable engineering plastics. Most procedures described for the synthesis of PPS only yield low molecular weight linear polymers and the thermostabile high molecular weight material is formed in second step (heat treatment) involving radical and/or cationic crosslinking[1,2]. It is also known that PPS prepared by standard methods contains disulfide groups. Therefore new synthetic methods allowing the preparation of linear polysulfides free of disulfide groups are of general interest.

The present work had the purpose to study polycondensation of 1,3-bis(trimethylsilylmercapto)benzene (1,3-BTMSM-benzene) with various activated dihalogenoaromatics. The silyltion of thiophenols and mercaptanes has two advantages. It enables efficient purification by distillation and it prevents deprotonation followed by oxydation of the resulting sulfide anion to disulfides. Polycondensation of several silylated bisthiophenols with 4,4'-difluorodiphenylsulfone have already been mentioned in literature[3], but only low viscosities were reported despite the high reactivity of 4,4'-difluorodiphenylsulfone. Recently we could show[4] that high molecules weight polyethers can be prepared from silylated diphenols and various dichloroaromatics when the polycondensation is conducted in N-methylpyrrolidone (NMP) with potassium carbonate. Therefore, this method should be preferentially studied in the present work.

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EXPERIMENTAL

Materials:

4,4'-Difluorodiphenylsulfone, 4,4'-dichlorodiphenylsulfone, 2,6-difluorobenzonitrile, 2,6-difluoropyridine, 2,6-dichloropyridine and sodium benzene-1,3-disulfonate were purchased from Aldrich Co. (St. Louis, MO USA) and purified by recrystallization or distillation. The synthesis of 1,3-dimercaptobenzene was conducted according to literature[5]. N-Methylpyrro-lidone (NMP) was once distilled over dry K_2CO_3 and twice over P_4O_{10} in a vacuum of 10^{-1} mbar.

Bristrimethylsilyl-1,3-dimercaptobenzene

1,3-Dimercaptobenzene (0,5 mol) and hexamethyldisilanzane (0,3 mol) were refluxed in 150 ml of dry toluene until the evolution of NH_3 had ceased. The product was then isolated by dis-tillation over a short column. Yield: 81 %, b.p. 117 - 119°C/15 mbar; n^{25}_D 1.5670.
Analyses calcd for $C_{12}H_{22}S_2Si$ (286.51): C 50.26, H 7.75, S 22.37; found: C 50.30, H 7.71, S 22.30 %.

Polycondensations

A) in bulk

1,3-Bis(trimethylsilylmercapto)benzene (25 mmol), a difluoroaromatic (25 mmol) and 10 mg CsF were weight into a cyclindrical glass reactor equipped with stirrer, gas-inlet and outlet tubes. The reaction mixture was heated to 130 - 150°C where the reaction started. The temperature was gradually raised to 290°C over a period of 2 h. Finally vaccum was applied for 20 min. The cold product was dissolved in CH_2Cl_2 and precipitated into methanol.

B) in solution

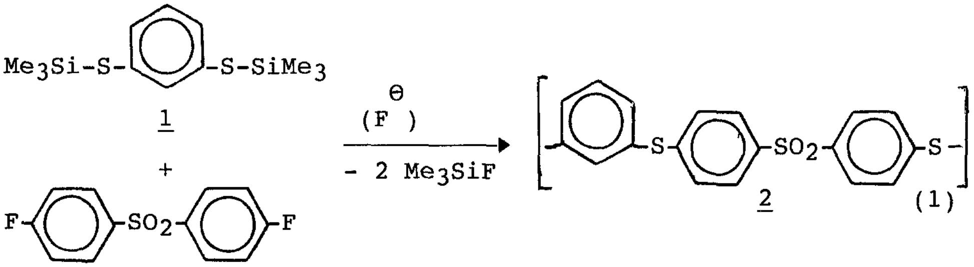
Bistrimethylsilyl-1,3-dimercaptobenzene (30 mmol), a dihalogenoaromatics (30,5 mmol) and dry potassium carbonate (16 mmol) were stirred and heated in 50 ml of NMP purged with nitrogen. The progress of the polycondensation is indicated by the evolution of nitrogen. After stirring for 24 h at 180 - 185°C the reaction mixture into water. The polysulfide was isolated by filtration, dried in vacuo and reprecipitated (e.g. from dichlorometane/methanol). The NMP used for polycondensations was first distilled over dry K_2CO_3 in vacuo and then twice over P_4O_{10}.

Measurements

Inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C. Gelpermeation chromatography was conducted in dichloromethane at 25°C with Kontron GPC HPLC chromatograph equipped with a Waters Md 410 differential refractometer. A combination of four Ultrastyragel ^{R} columns (waters) was used with molecular weight ranges of 50-1,5 · 10^3, 10^2-10^4, 2 · 10^2 - 3 · 10^4 and 5 · 10^3 - 6 · 10^5. A commercial set of polystyrene standards were usedfor 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

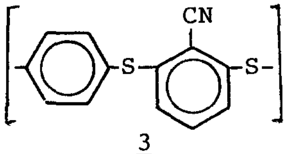
In a first series of experiments three polycondensations of 1,3-BTMSM-benzene were conducted in bulk (Eq. 1). In analogy to similar condensations of silylated diphenols$^{6-9)}$ no reaction took place in the absence of a catalyst, when the pure reactants were heated up to 250°C, whereas addition of cesium fluoride gave a satisfactory catalytic effect. Since the Si-F bond is nearly twice as stable as the Si-S bond, it is likely that the catalytic effect consists in the intermediate formation of thiolate ions (Eq. 1). However, it was found that it may be difficult in small scale experiments to achieve a smooth continuous course of the polycondensation. In two cases the initially sluggish reaction became violent upon further heating. Distillation or sublimation of the most volatile reaction partner affects the stoichiometry, and thus reduces the molecular weight. It seems that the relatively low inherent viscosities of the three bulk polymerizations (Nos. 1-3, Tab. 1) result from problems with the stoichiometry.



(1)

$$\text{Ar-S-SiMe}_3 + \text{F}^{\ominus} \rightleftarrows \text{Ar-S}^{\ominus} + \text{F-SiMe}_3 \qquad (2)$$

In a second series of polycondensations monomer 2 was reacted with several dichloroaromatics or 4,4'-difluorodiphenylsulfone in NMP in the presence of K$_2$CO$_3$. From both series of polycondensations four homopolymers$^{(2-5)}$ and one copolymer (6) were isolated. Their yields and properties are sumarized in Tab. 1. Two aspects of the results listed in Tab. 1 are worth to be emphasized. First, yields and viscosities were as good or better than those obtained with difluoroaromatics from polycondensations in bulk. Second, the molecular weights of the two best samples of 2 (Nos. 4 and 5) were higher than expected from the low inherent viscosities. GPC-measurements evaluated by means of the universal calibrations method on the basis of commercial polystyrenestandards gave weight average molecular weights of 38 000 for No. 4 (Tab. 1) and 32 000 for No. 5.



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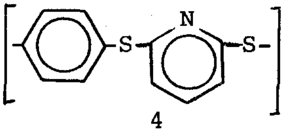

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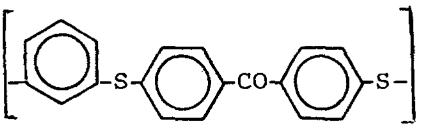
Table 1: Polycondensations of bistrimethylsilyl-1,3-dimercaptobenzene with various difluoro- and dichloroaromatics

No	Polymer Formula	Reaction partner (Reaction condition)	Yield in %	η_{inh} a) dl/g	Elem. Formula (Formula weight)	Elemental Analyses	C	H	N	S	T_g b) °C
1	2	4,4'-Difluorodiphenylsulfone (in bulk)	95	0.20	$C_{18}H_{12}O_2S_3$ (356.30)	Calcd.	60.62	3.40	-	26.98	140
						Found	60.88	3.30	-	27.65	
2	3	2,6-Difluorobenzonitrile (in bulk)	88	0.17	$C_{13}H_7NS_2$ (241.2)	Calcd.	64.67	2.93	5.80	26.58	130
						Found	61.55	2.73	5.70	25.93	
3	4	2,6-Difluoropyridine (in bulk)	84	0.17	$C_{11}H_7NS_2$ (217.20)	Calcd.	60.77	3.25	6.45	29.52	105
						Found	60.03	3.27	6.00	30.13	
4	2	4,4'-Difluorodiphenylsulfone (in NMP)	86	0.35	$C_{18}H_{12}O_2S_3$ (356.30)	Calcd.	60.62	3.50	-	26.98	153
						Found	-	-	-	-	
5	2	4,4'-Dichlorodiphenylsulfone (in NMP)	95	0.30	$C_{18}H_{12}O_2S_3$ (356.30)	Calcd.	60.62	3.40	-	26.98	147
						Found	59.31	3.32	-	26.31	
6	5	4,4'-Dichlorobenzophenone (in NMP)	92	0.17	$C_{19}H_{12}OS_2$ (320.24)	Calcd.	70.38	3.77	-	20.20	107
						Found	71.19	3.78	-	20.05	
7	4	2,6-Dichloropyridine (in NMP)	75	0.18	$C_{11}H_7NS_2$ (217.20)	Calcd.	60.77	3.25	6.45	29.52	89
						Found	61.80	3.10	6.32	30.40	
8	6	2,6-Dichloropyridine + 4,4'-Dichlorodiphenylsulfone (in NMP)	65	0.20	$C_{29}H_{19}NO_2S_3$ (573.50)	Calcd.	60.68	3.34	2.44	27.95	107
						Found	60.76	3.26	2.36	28.28	

a) Inherent viscosities measured at 25°C with c = 2 g/l in CH_2Cl_2

b) Glass-transition temperatures from differential scanning calorimetry with a heating rate of 20°C/min



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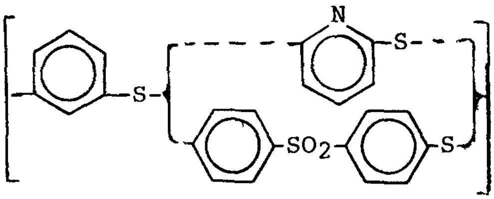

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It has been reported for poly(ether-sulfone)s4) that M_w-values determined in this way overestimate the M_w-values obtained by light-scattering by ca. 20%. Even if this difference is taken into account the best samples of this work still posses M_w-values in the range of 25000 - 30000. The low inherents viscosities found in CH_2Cl_2 obviously result from a high coil density (so called ϑ-condition) as reported for aromatic polyethers4).

In this connection it is of interest that the molecular weights of linear polyphenylenesulfide (PPS) prepared from Na_2S and 1,4-dichlorobenzene in NMP are rather low (< 5000). Furthermore, a radical reaction mechanism is assumed for the synthesis of PPS, whereas an ionic nucleophilic substitution is assumed for the polycondensations of this work (Eqs. 1,2). This difference is underlined by the observation that 1,4-dichlorobenzene did not react with 2 (and K_2CO_3) when heated in NMP for 36 h to 190°C.

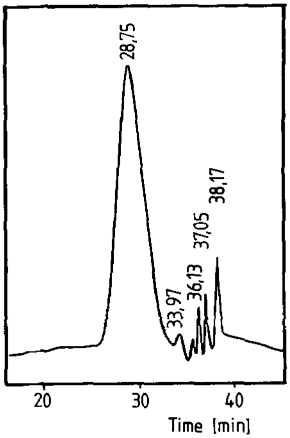

Fig. 1: GPC measurement of the polysulfide in CH_2Cl_2 at 25°C

Finally it should be mentioned that the GPC-measurements of polymers 2, 4, 5 and 6 prepared in NMP reveald the presence of oligomers (Fig. 1). Obviously the dependence of their concentration on the molecular weight does not obey the Jacobsen. Stockmeier relationship suggesting that some thermodynamically favoured cyclic oligomers were formed. The same observation has been recently reported for aromatic polyethers synthesized in NMP$^{4)}$.

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