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Polymerization of 3-Vinylbenzenethiol

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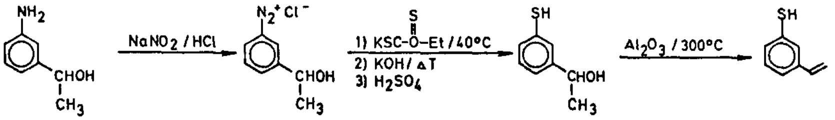
Summary

3-Vinylbenzenethiol (4) was synthesized and its polymerization yielded poly-(thio-1,3-phenylenethylene), which could be oxidized giving poly-(sulfonyl-1,3-phenylenethylene).

1. Introduction

The non-Markovnikov addition of benzenethiol to the vinyl group of styrene is a well known reaction (POSNER 1905; ASHWORTH et al. 1928) for which a radical mechanism is generally accepted (KHARASCH et al. 1938; PRYOR 1962; KELLOGG 1969; GIESE et al. 1979). This reaction offers a possibility for the synthesis of a new polysulfide and after oxidation, of a new polysulfone.

2. Synthesis of 3-vinylbenzenethiol (4)



1 2 3 4

1 was diazotized (2) and allowed to react with potassium ethyl xanthate, hydrolyzed with alkali and then acidified forming 3. By distillation over a Al_2O_3-catalyst (300°C) 3 was dehydrated to 4.

3. Polymerization of 4

"Spontaneously" without any additional initiator, 4 polymerized, even at -30°C. (The resulting polymer was dissolved in DMF and precipitated by isopropanol). For this polymer, one has to consider at least 3

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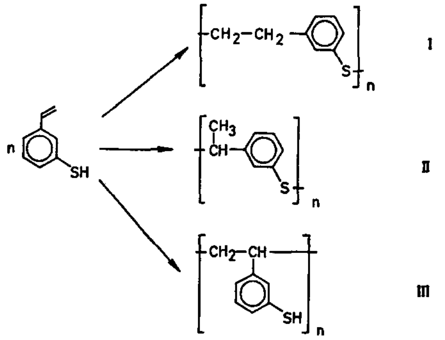
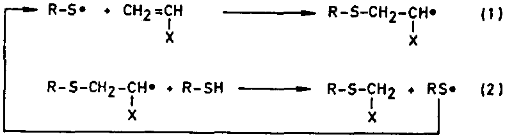
different structures and their combinations:



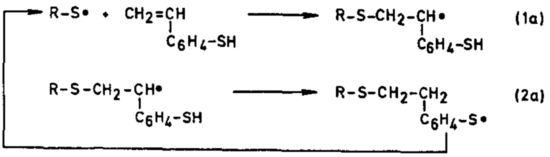
Structure I is more favourable as compared to II and III (ASHWORTH 1928; PRYOR 1962). Polymerization of 4, initiated by AIBN or photochemically, leads to a product of structure I. ^{1}H NMR and ^{13}C NMR of the polysulfide (I) and the polysulfone (IV) show no evidence of Markovnikov addition. Structure III is certainly of minor importance because of the very small IR - absorption in the region of the SH - group (2400 cm^{-1}) which can also be explained by polymer endgroups. Most probably polymerization proceeds via a radical mechanism, because benzenethiol which is not handled under entirely oxygen free conditions, normally generates enough radicals to start a radical chain reaction (KHARASCH 1961). The addition of a thiol to a double bond by the KHARASCH mechanism



$$R\text{-}S\bullet + \underset{X}{CH_2{=}CH} \longrightarrow R\text{-}S\text{-}CH_2\text{-}\underset{X}{CH}\bullet \qquad (1)$$

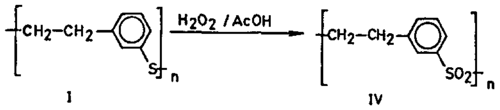
$$R\text{-}S\text{-}CH_2\text{-}\underset{X}{CH}\bullet + R\text{-}SH \longrightarrow R\text{-}S\text{-}\underset{X}{CH_2} + RS\bullet \qquad (2)$$

usually leads to low molecular compounds, as the H-transfer (reaction 2) occurs intermolecularly. In our case this mechanism predominantly represents a step polymerization with the consequence that polymers of high molecular weight are formed at high conversion only. The observed higher molecular weights, however, can eventually be explained by an intramolecular H shift reaction (reaction 2a):



4. Oxidation of the polysulfide I

The polysulfide was oxidized to the corresponding polysulfone with H_2O_2/acetic acid at boiling temperature (IVIN et al. 1968).



The polymer was reprecipitated from DMF/isopropanol. Polysulfones of the structure IV are not reported in the literature.

5. Experimental

3-(1-hydroxyethyl)-benzenethiol (3):
The diazonium salt was prepared as already described (KERBER et al. 1973). For the introduction of the SH-group the xanthogenate method was used (BOURGEOIS 1899).

Yield: 60%; b.p.: 76°C/0,05 Torr

^{1}H NMR (CDCl$_3$) δ (ppm): 1,40 (d, -CH$_3$); 1,95 (s, -OH);
3,47 (s, -SH); 4,80 (q, -CH); 7,20 (d, -C$_6$H$_4$-);

IR (CHCl$_3$) $\tilde{\nu}$ (cm^{-1}): 3660 sh (O-H); 3600 ms (O-H);
3100 s (aromatic C-H); 2950 (aliphatic C-H);
2400 ssh (S-H); 1220 s (O-H); 1055 ssh (C-O).

3-vinylbenzenethiol (4):
Analogous to descriptions in the literature for the purpose of dehydration (MANECKE et al. 1964; KERBER et al. 1978), 3 was distilled over Al_2O_3/300°C and purified by fractional distillation.

Yield: 60%; b.p.: 46°C/0,45 Torr

^{1}H NMR (CDCl$_3$) δ (ppm): 3,40 (s, -SH); 5,25 (d, =CH$_2$);
5,70 (d, =CH$_2$); 6,65 (dd, =CH); 7,25 (m, -C$_6$H$_4$)

IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}): 3010-3060 (aromat. and aliphat. C-H); 2570 m (S-H); 2400 w (S-H); 1630 ssh (C=C).

Poly-(thio-1,3-phenylenethylene):
Sulfur-analysis: calc.: 23,54%; det.: 23,46%
M (GPC): 10 000; 200 000 (eluation with DMF, RI-detection, calibrated with polystyrenestandards)
^1H NMR ($CDCl_3$): δ (ppm): 3,00 (m, CH_2); 7,20 (m,$-C_6H_4$)
IR ($CHCl_3$) $\tilde{\nu}$ (cm^{-1}): 2400 (S-H), very small.

Poly-(sulfonyl-1,3-phenylenethylene):
Sulfur-analysis: calc.: 19,06%; det.: 18,32%
M (GPC): 10 000, 200 000 (eluation with DMF)
^1H NMR ($CDCl_3$) δ (ppm): 3,05 (m, CH_2); 7,25 (m,$-C_6H_4$)
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 1300, 1135 (SO_2)

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