New Sulfur Containing Polymers, 2*

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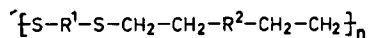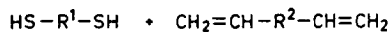*Dedicated to Professor Georg Manecke on his 65th birthday*

Summary

It was shown that 3-vinylbenzenethiol ($\underline{1}$) and 4-vinyl-benzenethiol ($\underline{2}$) polymerize, slowly, in the dark. However, the polymerizations can be accelerated by U.V.-light. The progress of the polymerization were followed by ^{1}H NMR spectroscopy.

1.) Introduction

Polysulfides of the general structure

$$\left[(CH_2)_x - S \right]_n \quad , \quad \left[Ar - S \right]_n \quad , \quad \left[Ar - S - (CH_2)_x - S \right]_n$$
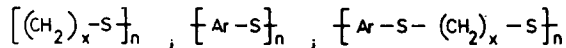
have been synthesized either by step growth or ring opening polymerizations (R.H.GOBRAN, 1969; H.A. SMITH, 1969; R.N.Johnson 1969; F.O.DAVIS et al. 1962). An alternative route to such polymers is via the reaction of di-thiols with di-olefins (J.v.BRAUN et al. 1926; A.L.AYERS et al. 1956; A.A.OSWALD, 1970; W.COOPER et al. 1969; D.A.MACKILLOP, 1969)

$$HS - R^1 - SH \;\; + \;\; CH_2 = CH - R^2 - CH = CH_2$$

$$\downarrow$$

$$\left[S - R^1 - S - CH_2 - CH_2 - R^2 - CH_2 - CH_2 \right]_n$$

New types of polysulfides (NUYKEN et al. 1980), with highly ordered structures can be expected from monomers such as $\underline{1}$ and $\underline{2}$ which contain both functional groups in the same molecule:
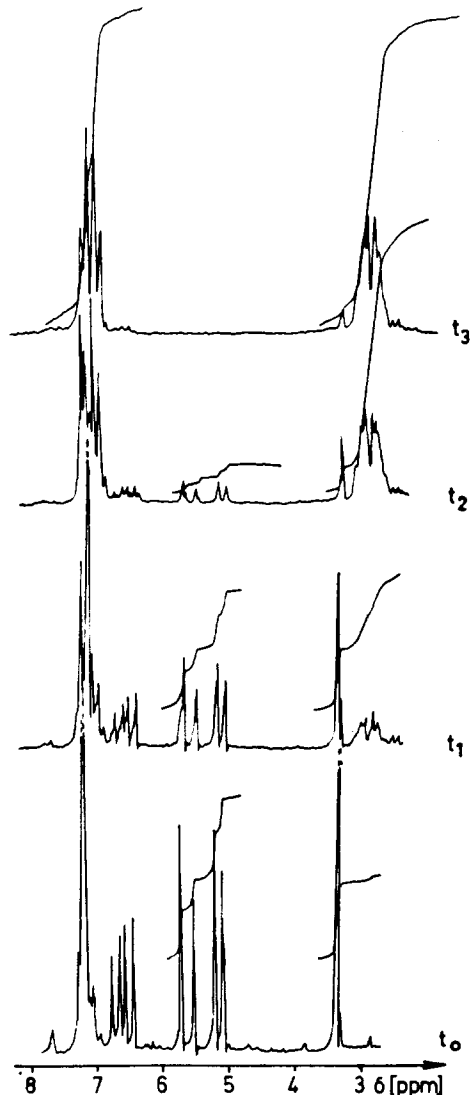
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* part 1: reference 5
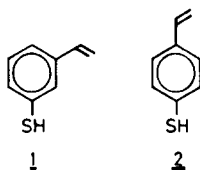
This paper describes the syntheses of the monomers 1
and 2 and their polymerisations under U.V.-light and
in the dark without any additional initiator.

2. Polymerisation
2.1. ^{1}H NMR measurements

The ^{1}H NMR spectra of 1 and
2 show the typical signals
of CH_2=CH- , -SH and aro-
matic protons. During the
polymerization of 1 (2) the
CH_2=CH- and SH- peaks de-
crease while the concentra-
tion of -CH_2-CH_2-S-unites
increases. The disappearence
of the peaks due to the SH-
and -CH=CH_2-groups and the
increasing intensity of the
CH_2-CH_2-S- signals with
time could be conveniently
followed ^{1}H-NMR-spectros-
copically (Fig. 1).

Fig. 1:
Sequential ^{1}H NMR spectra
of 4-Vinylbenzenethiol (2)
at different times (t_o, t_1,
t_2, t_3)

The monomer conversion U was calculated using the fol-
lowing equations:

$$U \, [\%] = \frac{(\int_{CH_2-CH_2-S-})_t}{(\int_{CH_2-CH_2-S-})_t + 2 \cdot (\int_{CH_2=C})_t} \cdot 100 \quad (1)$$

$$U \, [\%] = \frac{(\int_{CH_2-CH_2-S-})_t}{(\int_{CH_2-CH_2-S-})_t + 4 \cdot (\int_{SH})_t} \cdot 100 \quad (2)$$

$(\int_{CH_2-CH_2-S-})_t$ = integral of the peak arising from the four methylene protons of the polymer at time t

$(\int_{CH_2=C})_t$ = integral of the peak arising from the two methylene protons of the monomer at time t

$(\int_{SH})_t$ = integral of the SH-protons of the monomer at time t

The conversion, determined from equations (1) and (2),
is independent of the (unknown) volume contraction of
these polymerization processes because only integrals
taken at the same time are compared.

2.2. Polymerization under U.V. light
Solutions of 1 and 2 in NMR-tubes, were exposed to light
from a high pressure mercury lamp. The exposure time
was varied between one and ten minutes and the ^{1}H NMR
spectra were taken immediately after the irradiation
was stopped. The polymerization of both 1 and 2 follow
first-order kinetics. (Fig. 2, 3) However, before we
can offer a detailed kinetic scheme further investiga-
tions (effect of light density, distance between U.V.

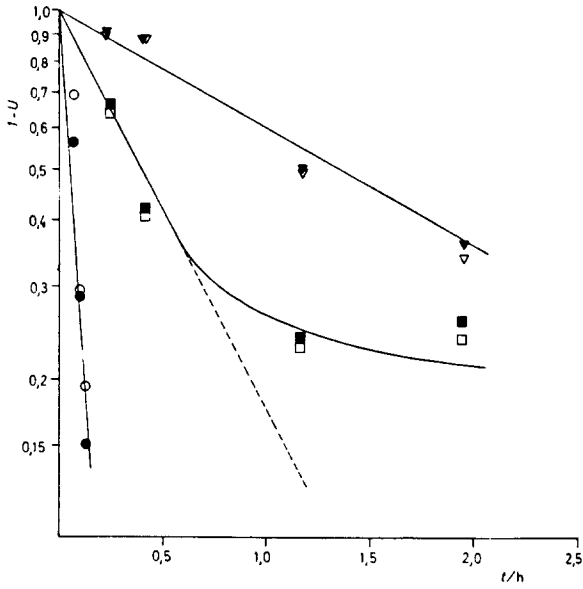source and solution,...) are necessary.

Fig. 2: Polymerization of 3-Vinylbenzenethiol (1)

●o U.V.;　　　▼ ▽　　dark, 22°C;　■ □　　dark, 50°C

(●　▼　■　　　conversion (equation 1))
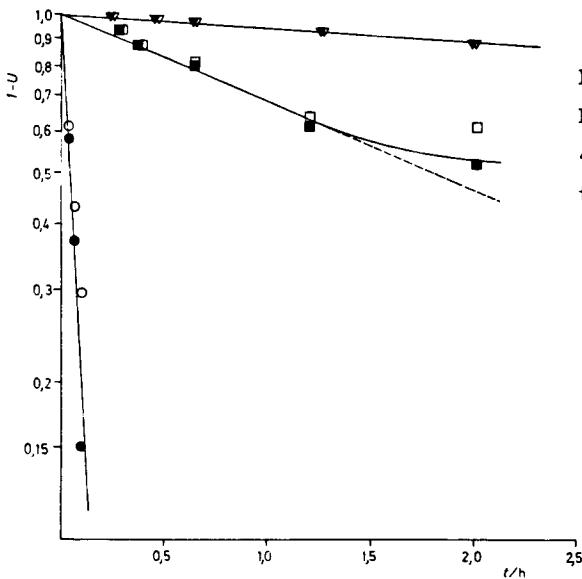
(O　▽　□　　　conversion (equation 2))

Fig. 3:
Polymerization of
4-Vinylbenzene-
thiol (2)
● O U.V.;
▼ ▽ dark, 22°C
■ □ dark, 50°C
(● ▼ ■ equation 1)
(O ▽ □ equation 2)

2.3. Polymerization in the dark

1 and 2 were polymerized at $22^{\circ}C$ and $50^{\circ}C$ excluding any light and initiator (Fig. 2, 3). It seems that the system contains enough thermochemical energy at room temperature to spontaneously produce active species in the dark. The decrease in intensity of the peaks due to $[CH_2=CH-]$ and $[-SH]$ are both proportional to the degree of conversion. However, for 2 although the decreasing intensity of the $CH_2=CH-$ peaks appears to be proportional to the conversion the intensity of the -SH peak is not only a function of the conversion. After 60 % conversion a ratio $[CH_2=CH-]$: $[-SH]$ = 1 : 2 was observed (compare part 3). The first-order plots of the polymerizations (Fig.2,3) are straight lines up to 50 - 70 % conversion. At higher conversion these systems became heterogeneous and therefore deviations from linearity are not unexpected.

3. Structure of the polymers

3.1. ^{1}H NMR

Poly-(thio-1,3-phenylenethylene)

Following structure
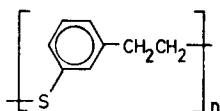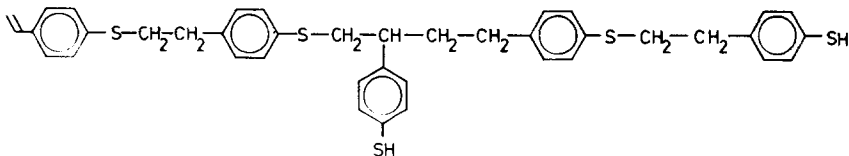

is strongly supported by
  a) synchronous decrease of $CH_2=CH-$ and -SH
     of 1 during the polymerization
  b) the pattern of the ^{1}H NMR-spectra
  c) the ^{13}C NMR (compare part 3.2.)

Poly-(thio-1,4-phenylenethylene)

After 60 % conversion the ratio$[CH_2=CH-]$:$[-SH]$= 1 : 2
was observed suggesting that chain growth also accurs
via simple carbon-carbon-bond formation:

3.2. ^{13}C NMR

Poly-(sulfonyl-1,3-phenylenethylene)

This polymer was synthesized by oxidation of poly-
(thio-1,3-phenylethylene)(NUYKEN et al. 1980). The
^{13}C NMR spectrum of poly-(sulfonyl-1,3-phenylethylene),
dissolved in nitromethane, shows signals at 135,65 -
121,94 ppm (aromatic C), at 51,91 ppm (Ar-$\underline{C}H_2$-) and
at 23,96 ppm (S-$\underline{C}H_2$-).

An anti-Markovnikov structure was concluded from the
^{1}H - off-resonance ^{13}C spectrum (triplet pattern).

Poly-(thio-1,4-phenylethylene)

The polymer, dissolved in CDCl$_3$, exhibits signals at
138,0 - 128,9 ppm (aromatic C) and only one signal in
the aliphatic region at 35,0 ppm. Obviously the two
signals are superimposed, since the signal becomes a
triplet in the ^{1}H off-resonance ^{13}C spectrum.

4. Experimental Part

The synthesis of 3-(1-hydroxyethyl)-benezenethiol and
3-vinylbenzenethiol have already been described
(O. NUYKEN et al.1980).

4-(1-hydroxyehtyl-benzenethiol)

A method similar to that described by Overberger
(C.G.OVERBERGER et al. 1956) was used.
4-aminoacetophenone was diazotized and than converted
into the ethyl p-acetylphenyl-xanthate (M.C.BOURGEOIS,
1899). The reduction with sodium borohydride was car-
ried out directly on the crude xanthate, yielding the
alcohol.
Yield: 40 %; b.p.: 88°C/0.2 Torr

^{1}H NMR (CDCl$_3$) δ (ppm): 1.35 (d,-CH$_3$); 3.50 (s,-SH);
                                      3.75 (s,-OH); 4.65 (q,-CH);
                                      7,20 (s,-C$_6$H$_4$-);

IR (CHCl$_3$) ν (cm^{-1}) : 3590 ssh (O-H); 3420m (O-H);
                                 3060 m (aromat. C-H); 2960 ssh
                                 aliphat. C-H); 2400 msh (S-H);
                                 1100 ssh (C-O); 815 sh (1.4-C$_6$H$_4$-);

4-vinylbenzenethiol

The 4-(1-hydroxyethylbenzenethiol) was distilled
(G.MANECKE et al. 1964; R.KERBER et al. 1978) over
Al$_2$O$_3$ 300°C (a method which is described for dehydrat-
ing) and purified by fractional distillation.
Yield: 60 %, b.p.: 40°C/0.4 Torr

^{1}H NMR (CDCl$_3$) δ (ppm): 3.45 (s,-SH); 5.20 (d,=CH$_2$);
                                     5,67 (d,= CH$_2$); 6.65 (dd,-=CH-);
                                     7,20 (m,-C$_6$H$_4$-);

Sample preparation and ^{1}H NMR kinetics

A described operation, including the ^{1}H NMR measurements
were performed in completely dark rooms.
A sodium vapour lamp (λ = 568 nm) was used as the indoor
light in the laboratory where the experiments were car-
ried out (Sanat-lamp, Durst/Bozen-Italy).

After fractionated destillation of $\underline{1}$ and $\underline{2}$ $CDCl_3$ was added (1:1), than the solution was degassed and transferred directly into the NMR tube using the apparatus shown in Fig. 4.
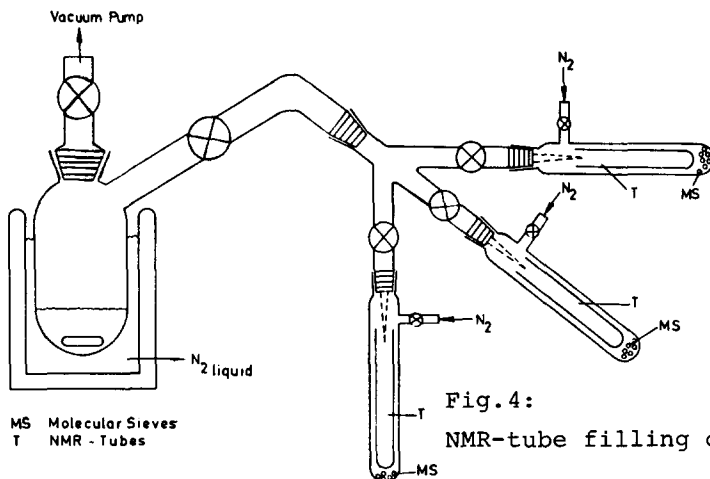

Fig.4:
NMR-tube filling device

MS   Molecular Sieves
T   NMR - Tubes

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