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Polymer Bulletin

New Sulfur-containing Polymers

3*. Poly(1-thio-3-(1-methylethylen)phenylene) and Poly(1-thio-4-(2-methylethylen)phenylene)

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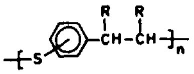
Dedicated to Professor Franz Patat on his 75th birthday

Summary

The polymerization of 2-(3-mercaptophenyl)propene (3) and 1-(4-mercaptophenyl)propene (4) was studied. The polymerization proceeds by an Anti-Markovnikov addition of the SH-group to the C=C-bond.

Introduction

Sulfur-containing polymers have attained a modest but significant position as speciality polymers. Their success in sealent and adhesive applications is due to their solvent and ozone resistance. Most of the commercial polysulfides are either aliphatic or aromatic; - only a few systems with mixed aliphatic-aromatic structures are known. (DAVIS et al, 1962). Polymers with the repeating unit



$R = H, CH_3$

can be synthesized from monomers which contain both (the SH and C=C) functional groups in one molecule, for example 1 - 4:

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* part 2, reference 3

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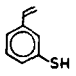
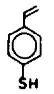


1



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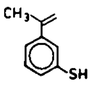


3

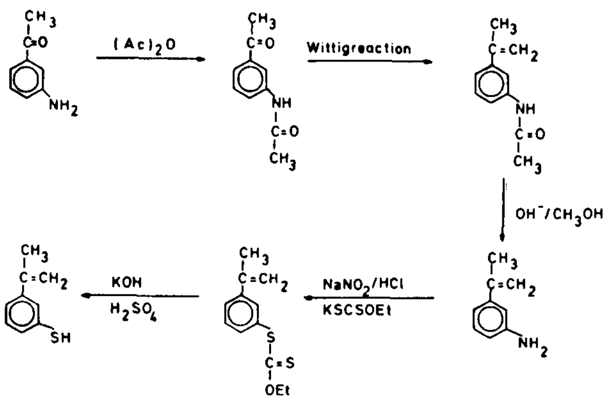
4

The polymerization of the monomers 1 and 2 has already been described (NUYKEN et al. 1980; NUYKEN et al.1981). It was shown that the polymerization of 1 and 2 is initiated by light but polymerization was also possible in the dark. Considering these results it was of some interest to polymerize the monomers 3 and 4 and to study the influence of the monomer structure on the rate of polymerization and the structure of the resultant polymer.

2. Syntheses of the monomers 3 and 4

The synthetic routes for 3 and 4 are shown in the reaction schemes I and II. It should be emphasised that the final step for both syntheses must be carried out in the dark to minimize polymerization of the desired product.

2-(3-mercaptophenyl)propene (3)



Reaction scheme I: synthesis of 3

a) Protection of the amino group:

Yield: 90 %

^{1}H NMR (Acetone-d_6): δ(ppm): 2,06 (s, CH_3); 2,51 (s, CH_3); 7,71 (m, C_6H_4); 9,31 (s, NH)

b) Conversion of the C=O into C=C (Wittig reaction):

In a 2l flask equipped with a stirrer, a nitrogen inlet, an Anschützadapter and a powder dosing funnel 198 g (0,55 mole) methyltriphosphoniumbromide and 0,54 g (0,0015 mole) crown ether were suspended in 750 ml 1,2-dimethoxyethane, 62 g (0,55 mole) potassium 1,1-dimethyl-ethanolate were then added in small portions under nitrogen. Immediately the typical yellow colour appeared. After 30 min 97 g (0,55 mole) 3-acetamidoacetophenone was added using the powder dosing funnel. After the addition stirring was continued for 2 h. The 1,2-dimethoxyethane and 2-methyl-2-propanol were then distilled off in vacuo (12 Torr). The residue was extracted with ether and the extract dried and evaporated. The crude product was used for the next stage in the preparation (hydrolysis of the amide) without further purification.

c) Hydrolysis of the amide

The result of the hydrolysis (FANTA et al. 1967) is 2-(3-aminophenyl)propene.

Yield: 38 %

b.p.: 74°C/0,2 Torr

IR($CHCl_3$); cm^{-1}: 3450, 3370 (NH); 3100, 1610, 895 ($C=CH_2$)

^{1}H NMR (acetone-d_6): δ(ppm): 2,06 (s, CH_3); 4,36 (s, NH_2); 5,03 (s, $=CH_2$); 5,32 (s, $=CH_2$); 6,81 (m, C_6H_4)

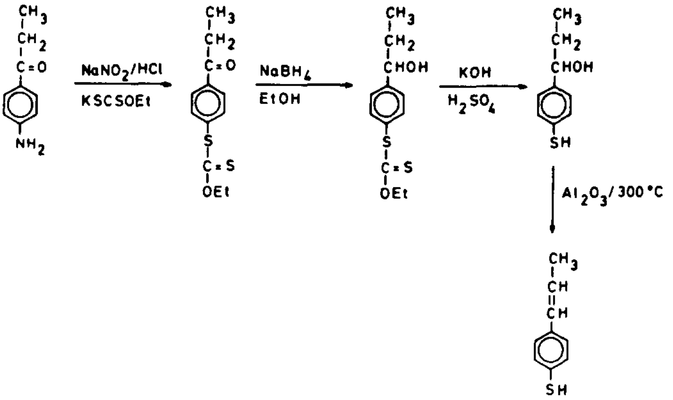
d) Xanthate reaction followed by hydrolysis (e) (NUYKEN et al. 1980):

Yield: 22 %

b.p.: 49°C/0,3 Torr

^{1}H NMR($CDCl_3$) δ(ppm): 2,08 (s,CH_3); 3,40 (s, SH); 5,06 (s, =CH_2); 5,32 (s, =CH_2); 7,15 (m, C_6H_4)

1-(4-benzenethiol)-propene (4)



Reaction scheme II: synthesis of 4

a) Xanthate reaction (NUYKEN et al. 1980)
The xanthate was used for the next stage of preparation without purification.

b) Reduction of the ketone:
The crude xanthate was dissolved in ethanol and $NaBH_4$/ethanol was added dropwise at 20°C. The mixture was stirred for a further 30 min at room temperature. The intermediate was a yellow solid.

c) Hydrolysis of the xanthate (NUYKEN et al. 1980):
After extraction with ether, drying and fractionation at high vacuum 1-(4-mercaptophenyl)propanol was isolated.

Yield: 33 %
b.p.: 108°C/0,5 Torr
IR ($CHCl_3$, cm^{-1}): 3590, 3420 (OH); 2580 (SH)
^1H NMR (acetone-d_6): δ (ppm); 0,80 (t, CH_3); 1,58 (m, CH_2); 3,90 (s, SH) 4,12 (s, OH); 4,45 (m, CH); 7,13 (s, C_6H_4)

d) Dehydration of the alcohol (MANECKE et al. 1964)
1-(4-mercaptophenyl)propene was isolated by fractional distillation.
Yield: 45 %
b.p. 50° /0,4 Torr
^1H NMR ($CDCl_3$): δ (ppm); 1,82 (d, CH_3); 3,35 (s,SH); 6,24 (m, CH=CH); 7,15 (m, C_6H_4)

3. Polymerization

A series of polymerizations of **3** and **4** were carried out in the dark at 50°C (Fig. 1). For comparison another series of polymerizations was initiated by irradiation from a high pressure mercury lamp (Fig.2).

The conversion of the monomers was followed by ^1H NMR spectroscopy using the CH_3 groups of the substituted C=C bond, which shifts from 2,08 (1,82) ppm in the monomer to 1,33 (1,17) ppm in the polymer for **3** (respectively **4**)

$$U\,[\%] = \frac{\int (CH_3)_{P,t}}{\int (CH_3)_{P,t} + \int (CH_3)_{M,t}} \cdot 100$$

$\int (CH_3)_{M,t}$ = Integral over the protons of the CH_3-group of the monomer at time t

$\int (CH_3)_{P,t}$ = Integral over the protons of the CH_3-group of the polymer at time t.

The first-order plots lead in all cases to straight lines up to 50 - 70 % conversion. However at higher conversion these systems became heterogeneous, which might explain the deviations from linearity. In agreement with this explanation polymerizations with lower monomer concentration show deviations from linearity at higher conversions.-

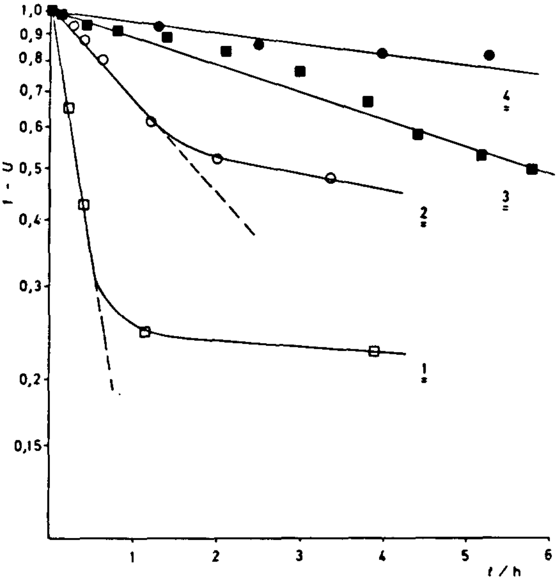


Fig.1: Polymerization of 1 - 4 at 50°C in the dark

As shown in Fig. 1 the polymerization rate decreases going from 1 to 4.

$$R_{p\ 1} > R_{p\ 2} > R_{p\ 3} > R_{p\ 4}$$

This can be explained by the difference in reactivity of the C=C bonds: monosubstituted bonds and the latter are more reactive than disubstituted olefins. The difference in reactivity between 1 and 2 is probably due to the higher resonance stabilization in 2. Photopolymerization of the four monomers (Fig. 2) is significantly faster than their thermal polymerization at 50°C. As expected, 1 and 2 react faster than 3 and 4. The slightly faster rate observed for 4 compared to

3 could be due to the photoisomerization of the 1,2-disubstituted olefin from the trans- into the cis form (The addition of the RS• (or RSH) on the cis-isomer seems to be less hindered than the addition on the trans-isomer).
The difference between the polymerisation rates of 1 and 2 is negligible.

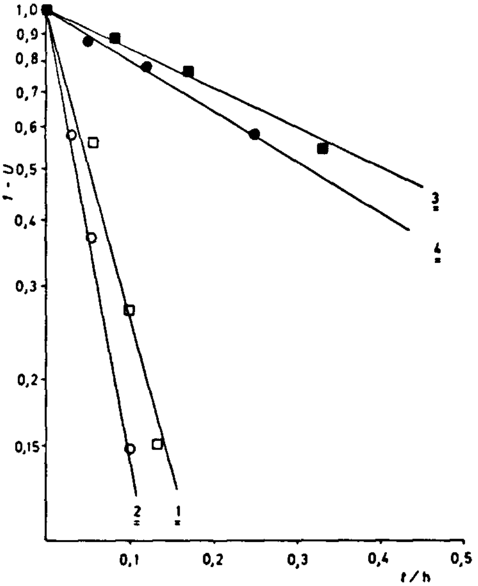


Fig.2: Photopolymerization of 1 - 4

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