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# Novel sulfur-containing telechelics with alternating aliphatic-aromatic structure units

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## Summary

Radical polyaddition of 1,3-dimercaptobenzene onto 1,5-hexadiyne yields sulfur containing polyenolthioethers. By using the method of unstoichiometric ratio not only the molar masses but also the functional end groups of the products can be controlled. The telechelics synthesized are soluble in common solvents such as benzene, toluene and chloroform.

## Introduction

The addition of mercaptanes onto unsaturated bonds can be catalysed by acids or bases, however, a radical mechanism is also possible. The radical addition yields anti-Markovnikov-products, alkylthioether in the case of the RSH addition onto C,C-double bonds and enolthioether in the case of the addition onto C,C-triple bonds.

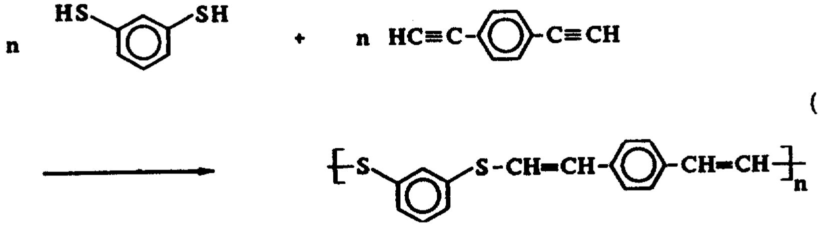
$$\mathrm{RSH} + \mathrm{H_2C{=}CH{-}R^1} \longrightarrow \mathrm{R{-}S{-}CH_2{-}CH_2{-}R^1} \qquad (1)$$

$$\mathrm{RSH} + \mathrm{HC{\equiv}C{-}R^1} \longrightarrow \mathrm{R{-}S{-}CH{=}CH{-}R^1} \qquad (2)$$

In the second reaction scheme a double addition of RSH onto the C,C-triple bond could be expected, however, this needs special conditions and is therefore an exception ( 1 ). Using bifunctional compounds it is possible to synthesize sulfur containing polymers. Meanwhile the radical addition of dimercaptocompounds onto diolefins is a well-described polyreaction ( 2-9 ), the analogeous reaction of dimercaptocompounds with C,C-triple bonds was almost unknown and has been used for polymerization only very recently.

## Polyenolthioether

Independent from each other two research groups ( 1, 10-12 ) have published details of the following reaction:



(3)

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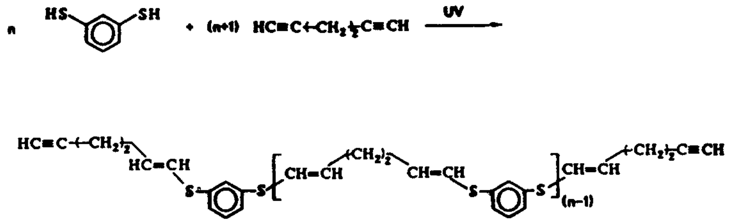
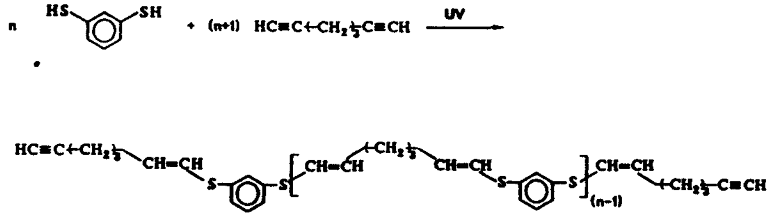
This reaction has some limitation due to solubility problems. In order to avoid these problems we have now replaced the aromatic by aliphatic dialkynes.

By this variation one yields interesting sulfur-containing polymers having alternating aliphatic-aromatic structure units.

In addition we have used the method of unstoichiometric ratio in order to synthesize telechelics with controlled molar masses.



**Polymer 1** ( 4 )



**Polymer 2** ( 5 )

## Experimental Part

### Materials

1,3-Dimercaptobenzene

This compound was synthesized following a description given by Vögtle ( 14 ).

1,5-Hexadiyne, 1,6-Heptadiyne

These compounds are commercially available. They were freshly distilled before use.

### Polymerization

The monomers were dissolved in benzene or toluene according to tables 1 and 2. These solutions were irridiated with the light of a 300 W UV-lamp for 8 to 10 hrs. After the removal of the solvent the polymers were dried in a vacuum oven. The polymer yield in all cases was close to 100 %.

### Characterization

For the characterization of the polymers the following instruments were used:

$^1$H NMR: Varian FT 80A; IR: Beckman IR 4240; DSC: DuPont 990 Thermal Analyzer; MS: Mat Bremen CH5; Vapor pressure osmometry ( VPO ): vapor pressure osmometer Knauer, calibrated with benzil

Molar masses were determined by end group analysis with $^1$H NMR-spectroscopy and by vapor pressure osmometry.

## Results

**Polymer 1:** prepared from 1,3-dimercaptobenzene and 1,5-hexadiyne

$^1H$ NMR ( $d_6$-benzene ), δ in ppm: 1.80 ( t, $-C\equiv C\underline{H}$ ); 2.00-2.50 ( m, $-C\underline{H_2}-$ ); 5.65-6.00 ( m, vinyl-H, cis ); 6.00-6.45 ( m, Vinyl-H, trans ); 7.00-7.70 ( m, aromatic H ).
cis : trans ≈ 1 : 2.
GC/MS: oligomers of masses 739, 519 and 298 could be separated and detected.
IR ( KBr ): 3295 $cm^{-1}$ ( s, ν ( $\equiv C-H$ )); 3040, 3005 $cm^{-1}$ ( w, ν ( $=C-H$ )) ; 2905, 2840 $cm^{-1}$ ( w, ν ( $-C-H$ )) ; 2100 $cm^{-1}$ ( w, ν ( $-C\equiv C-$ )); 1420 $cm^{-1}$ ( s, δ ( $-CH_2$ )); 950 $cm^{-1}$ ( m, δ ( $=C-H$ )).
DSC: Decomposition of the polymers were observed at temperatures above 295 °C.

Vapor pressure osmometry ( VPO ): The measurements were carried out in toluene solution.
The molar masses determined by VPO show an excellent agreement with those determined from $^1H$ NMR-spectroscopy ( table 1 ).

Solubility: The telechelics of structure **1** are soluble in benzene, toluene, chloroform and THF.

**Polymer 2** prepared from 1,3-dimercaptobenzene and 1,6-heptadiyne

$^1H$-NMR: ( $d_6$-benzene ), δ in ppm: 1.30-1.60 ( m, $CH_2-C\underline{H_2}-CH_2$ ); 1.70 ( t, $C\equiv C\underline{H}$ ); 1.85 -2.50 ( m, $C\underline{H_2}-CH_2-C\underline{H_2}$) 5.70-6.00 ( m, vinyl-H, cis ), 6.00-640 ( m, vinyl-H, trans ); 7.00-7.70 ( m, aromatic H ).
cis : trans ≈ 1 : 2
GC/MS: Oligomers of masses 795, 561 and 326 could be separated and detected.
IR ( KBr ): 3200 $cm^{-1}$ ( m, ν ( $\equiv C-H$ )); 3040 $cm^{-1}$ ( w, ν ( $=C-H$ )); 2910, 2850 $cm^{-1}$ ( s, ν ( $-C-H$ )); 2095 $cm^{-1}$ ( w, δ ( $-C\equiv C-$ )); 1450 $cm^{-1}$ ( s, δ ( $-CH_2-$ )); 945 $cm^{-1}$ ( w, δ ( $=C-H$ )).
DSC: Decomposition of the polymers of the structure **2** were observed at temperatures above 274 °C.

VPO : The molar masses determined by VPO measurements show a good agreement with those determined by $^1H$ NMR-spectroscopy ( table 2 ).

**Table 1**: Experimental results of the syntheses of polymer **1**

| molar ratio $-C\equiv CH$ : $-SH$ | calculated $\overline{P}_n$ | calculated $\overline{M}_n$ | measured $\overline{M}_n$ end group analysis | measured $\overline{M}_n$ VPO[a] and GC/MS[b] |
|---|---|---|---|---|
| 2 : 1 | 3 | 298 | 292 | 298[b] |
| 3 : 2 | 5 | 519 | 550 | 519[b] |
| 4 : 3 | 7 | 739 | 718 | 739[b] |
| 6 : 5 | 11 | 1189 | 1279 | — |
| 20 : 19 | 39 | 4265 | 3770 | — |
| 32 : 31 | 63 | 6900 | 5470 | 5500[a] |

**Table 2**: Experimental results of the syntheses of polymer **2**

| | | | measured $\overline{M}_n$ | |
|---|---|---|---|---|
| molar ratio -C≡CH : -SH | calculated $\overline{P}_n$ | calculated $\overline{M}_n$ | end group analysis | VPO a) and GC/MS b) |
| 2 : 1 | 3 | 327 | 350 | 327 b) |
| 3 : 2 | 5 | 561 | 547 | 561 b) |
| 4 : 3 | 7 | 795 | 1156 | 795 b) |
| 14 : 13 | 27 | 3139 | 2880 | 2900 a) |

## Discussion

The structure of the polymers **1** and **2** is supported by $^1$H NMR- and IR-spectroscopy but also by GC/MS measurements, which allowed to separate the first three members of homologous series of oligomers of type **1** and **2** respectively. Furthermore the ratios of aromatic to olefinic protons ( formed after the addition ) and to aliphatic protons also support the structures. Quantitative $^1$H NMR-spectroscopy was used to determine the functional end groups and to calculate the molar masses on the basis of this end group analysis. The theoretical values of the number average degree of polymerization are given by the following equation:

$$\overline{P}_n = \frac{1 + r}{1 + r - 2rx}$$

r = unstoichiometric ratio of the compounds or functional groups

$$\frac{\mathrm{RSH}}{\mathrm{R{-}C{\equiv}CH}} = r \leq 1$$

x = conversion of the functional group, in our case it has been assumed and proven experimentally to be equal to one.

Due to the fact, that the molar masses were controlled by the stoichiometric ratio of the components one has to assume an unusal mechanism. We have already suggested that even having radical intermediates this reaction has to be treated similar to an ordinary step growth reaction. Details on our mechanism view are already published ( 1, 13 ). All polymers synthesized by this method were soluble in benzene, toluene, chloroform and THF as long as an excess of SH-groups was avoided. In case of an excess of SH-groups in the starting mixture, the polymers became insoluble, due to the addition of the groups onto those C,C-double bonds which have been formed by the first addition step ( equ.2 ) ( 1, 13-15 ).

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## References

1. O. Nuyken, F. Siebzehnrübl, Phosphorus and Sulfur, in press
2. J. V. Braun, T. Platz, Ber. Dtsch. Chem. Ges. 67, 281 ( 1934 )
3. J. V. Braun, R. Murjahn, Ber. Dtsch. Chem. Ges. 59, 1202 ( 1926 )
4. C. S. Marvel, P. R. Chambers, J. Am. Chem. Soc. 70, 993 ( 1948 )
5. C. S. Marvel, P. H. Aldrich, J. Am. Chem. Soc. 72, 1978 ( 1950 )

6. C. S. Marvel, G. Nowlin, J. Am. Chem. Soc. 72, 5026 ( 1950 )
7. O. Nuyken, M. Hofinger, Polym. Bull. 4, 75 ( 1981 )
8. O. Nuyken, M. Hofinger, Polym. Bull. 4, 335 ( 1981 )
9. O. Nuyken, M. Hofinger, Polym. Bull. 4, 343 ( 1981 )
10. E. Kobayashi, T. Ohashi, J. Furukawa, Makromol. Chem. 187, 2525 ( 1986 )
11. E. Kobayashi, T. Ohashi, J. Furukawa, J. Polym. Sci. 25, 2077 ( 1987 )
12. Jap. Pat. 6,255,133 ( 1987 ), Mitsubishi Petrochemical Co. Ltd.; H. Kobayashi, T. Ohashi, M. Miyabayashi, Chem. Abstr. 107 , 50423p ( 1987 )
13. O. Nuyken, F. Siebzehnrübl, Makromol. Chem., in press
14. F. Vögtle, R. G. Lichtenthaler, M. Zuber, Chem. Ber. 106 , 719 ( 1983 )
15. A. Oswald, K. Griesbaum, J. Am. Chem. Soc. 86, 2877 ( 1964 )

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