

Unusual addition by the thiol-ene photopolymerization

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SUMMARY

The photoaddition of aromatic dithiols (1) onto aliphatic alkenes (2a - 2c) yielding polysulfides is studied. Polysulfides having anti-Markownikow and Markownikow moieties in the main chain are obtained by the reaction of dithiols (1) with ethyleneglycoldivinylether (2a). The unusual Markownikow orientation is explained on the basis of a radical cation intermediate.

INTRODUCTION

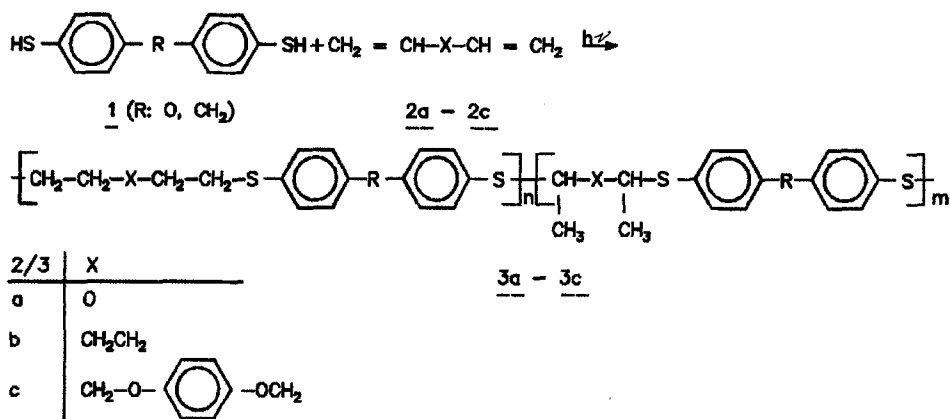
The addition of thiols onto olefins is a well known reaction (1) and it occurs at a stoichiometric ratio of bifunctional olefins ("enes", alkenes, etc.), and bifunctional thiols (mercaptans) to linear polysulfides (2, 3). The thiol-ene polymerizations proceed via a step growth addition mechanism propagated by a free radical chain transfer process (4). This includes the fact that it yields products of a definite composition, the anti-Markownikow product.

We found exceptions from this rule and we want to report on studies of the photopolymerization of aromatic dithiols with aliphatic dienes.

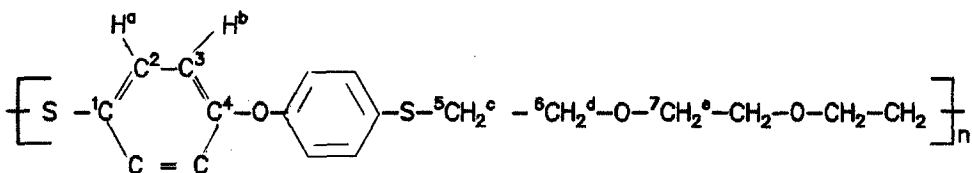
RESULTS AND DISCUSSION

4.4'-Dimercaptodiphenylether 1 (R=O) or 4.4'-dimercaptodiphenylmethane 1 (R=CH₂) were used as bifunctional thiols for the bifunctional enes 2a - 2c (Eq. 1). The reaction was carried out with a molequivalent mixture of 1 and 2 in tetrahydrofuran containing 1.0 wt% benzildimethylketal photoinitiator under irradiation with light of the wavelength 365 nm. In contrast to our previous investigations with aliphatic dithiols we found that the aromatic dithiols 1 react extremely slowly. Only after 18 hours the reaction is quantitative and the polythioethers are precipitate. The polymer 3 is soluble, for example, in chloroform and tetrahydrofuran respectively.

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The results of ¹H and ¹³C chemical shifts of the polymer 3a (R=O) are listed below in Table I.



(spectra were run in CDCl₃ with HMDS as the internal standard)

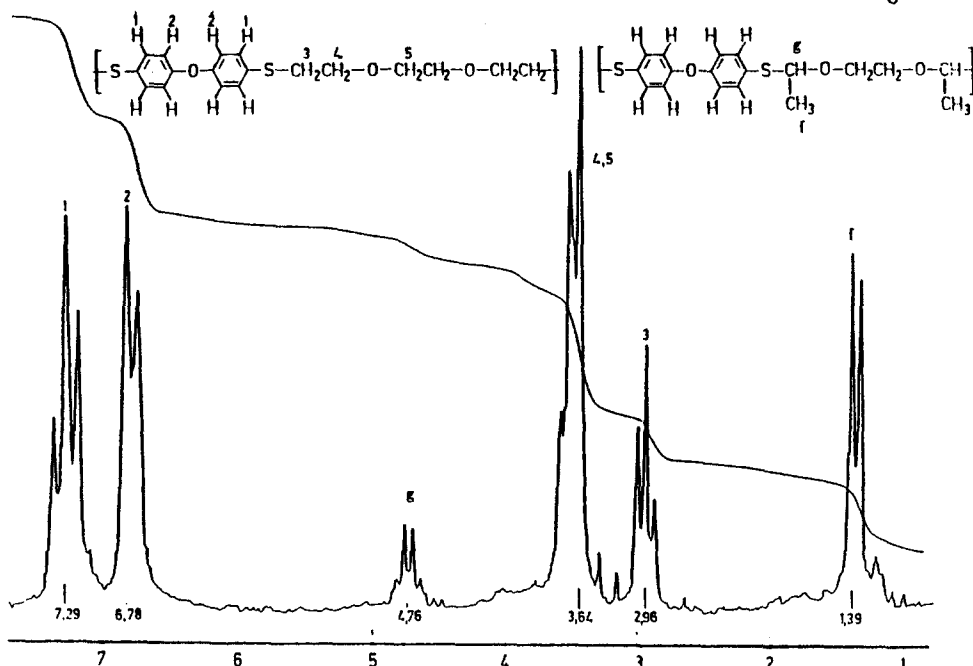
TABLE I
¹H and ¹³C chemical shifts of 3a (R=O)

C atom	δ [ppm]	H atom	δ [ppm]
1	136.62	a	7.29 (m)
2	132.62	b	6.78 (m)
3	119.61	c	2.96 (t)
4	156.50	d	3.64 (t)
5	27.98	e	3.64 (s)
6	70.62	(f)	1.39 (d)
7	71.59	(g)	4.76 (q)
(8)	22.64		
(9)	81.97		

In addition to the peaks of the "normal" anti-Markovnikov product two further peaks (¹H: (f, g) and ¹³C: C⁸, C⁹) are present. By means of the APT technique it can be shown that these peaks result from the structure -CH-CH₃. Fig. 1 is illustrate the ¹H NMR spectrum of the polymer 3a (R=O). Simi-

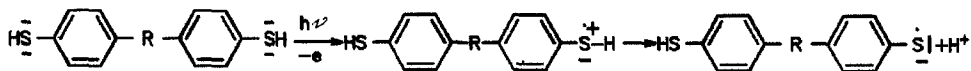
lar results have also been obtained in case of the dithiol 1 with $R=CH_2$. These results are consistent with literature reports on the reaction of 1,3-bismercaptobenzene with 1,4-butanedioldivinylether (5) in presence of AIBN.

FIGURE 1. 1H NMR spectrum of the polymer 3a ($R=O$) in $CDCl_3$



The photopolymerization of the alkenes 2b and 2c with dithiols 1 ($R = O, CH_2$) leads exclusively to the "normal" anti-Markownikow product.

We assume the following mechanism for the unusual orientation obtained by the photopolymerization (Eq. 2)



Under irradiation a radical cation is produced eliminating a proton. In case of an electron rich C=C-double bond, for example the alkene 2b, an electrophilic addition of thiol can take place.

It is interesting to note that the copolymerization carried out with mixtures of different aromatic and aliphatic dithiols with vinyl ethers indicated the Markownikow and anti-Markownikow composition (6).

ACKNOWLEDGEMENTS

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