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New Sulfur-containing Polymers
4*. The Structure of Some New Polysulfides

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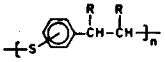
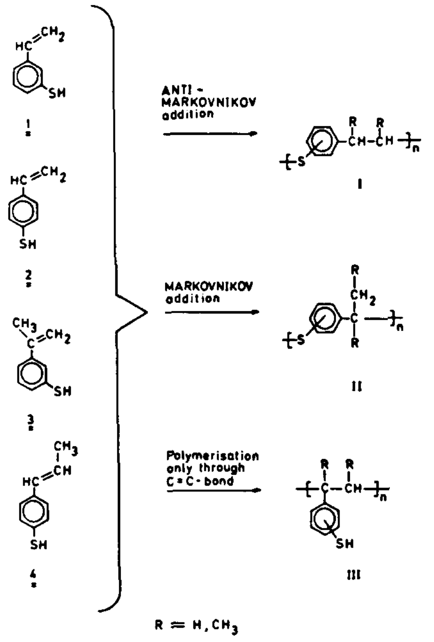
Summary

From ^{1}H NMR, ^{13}C NMR and $^{13}C - \{^{1}H\}$ off resonance experiments it was shown, that the main structural units are formed by an Anti-Markovnikov addition of the SH group to the C,C double bond.

Introduction

Polymers with the repeating unit  R = H,CH$_3$ have been described recently (NUYKEN et al. 1980, 1981). These polymers are synthesized from monomers with two functional groups per molecule (C=C and SH) such as 1 to 4. The generalised polymers which are theoretically possible from these monomers are shown. In addition to the single structures I, II, and III it is also possible that the polymer contains a mixture of these structures. To determine



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*part 3, reference 3

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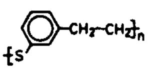
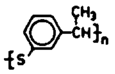
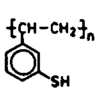
the precise structure of the polymers we have made a detailed analysis of their ^{13}C and ^{1}H NMR spectra.

Results

Polymer from 1:

Table 1: Expected signals for the different polymer structures possible from monomer 1

structure			
^{1}H NMR	CH_2 t CH_2 t	CH_3 d CH q	CH_2 d CH t
^{13}C NMR	$-CH_2-$ $-CH_2-$	$-CH_3$ $-CH-$	$-CH_2-$ $-CH-$
$^{13}C-\{^{1}H\}$ off reson.	t t	q d	t d

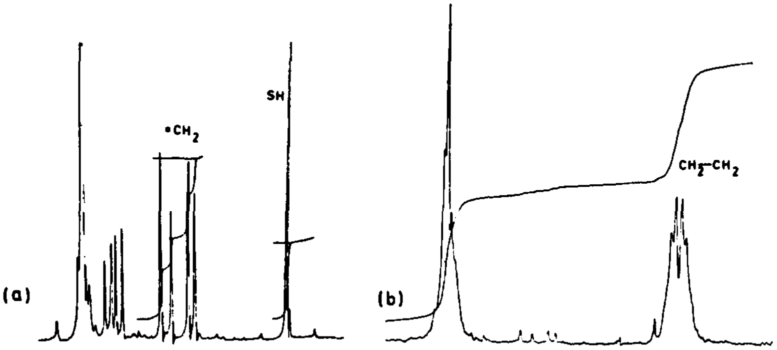


Fig. 1a: ^{1}H NMR of 1 (a) and of the polymer from 1 (b) (solvent: $CDCl_3$)

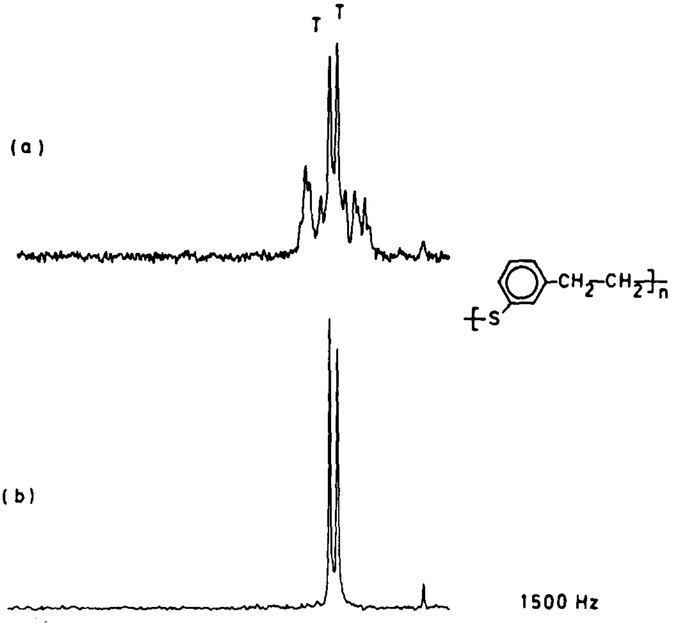


Fig. 1b: 22.53 MHz ^{13}C NMR spectrum of 1 (solvent: $CDCl_3$) using
a) off resonance proton decoupling
b) proton noise decoupling

Polymer from 2:

The only difference between 1 and 2 is the position of the SH group on the aromatic ring, therefore one would expect similar structures as shown in table 1.

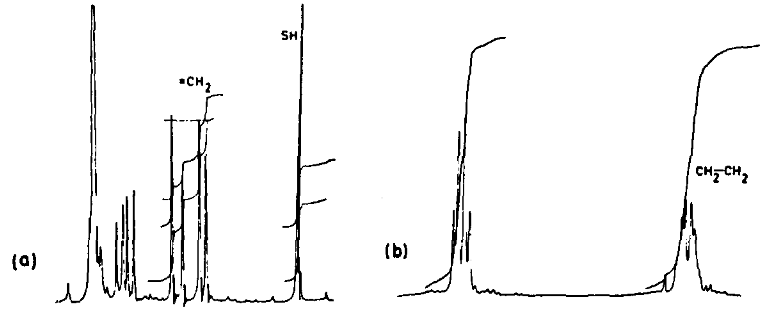


Fig. 2a: ^{1}H NMR spectra of **2** (a) and the polymer from **2** (b) (solvent: $CDCl_3$)

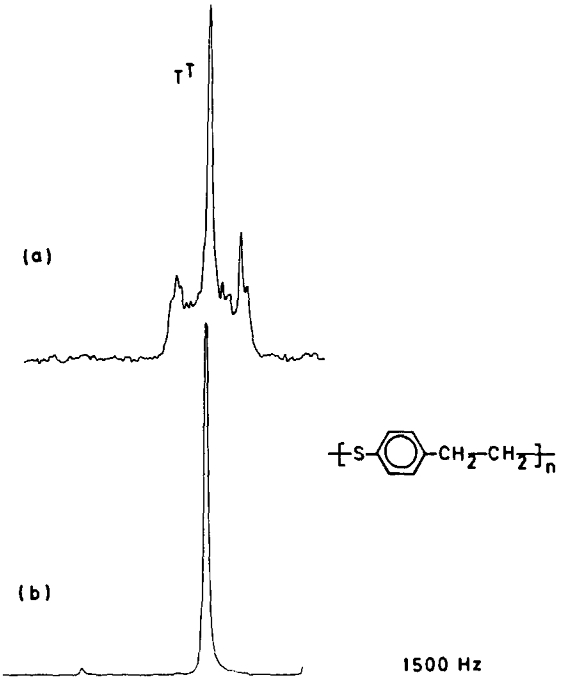


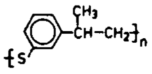
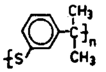
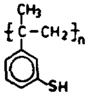
Fig. 2b: 22,53 MHz ^{13}C NMR spectrum of 2 (solvent:$CDCl_3$) using

a) off resonance proton decoupling

b) proton noise decoupling

Polymer from 3:

Table 2: Expected NMR signals for the different polymer structures possible from monomer 3

structure			
^1H NMR	CH_3 d CH m CH_2 d	CH_3 s twice that of the monomer signal	CH_3 s CH_2 s
^{13}C NMR	$-CH_3$ $-\overset{\vert}{C}H-$ $-CH_2-$	$-CH_3$ $-\underset{\vert}{\overset{\vert}{C}}-$	$-CH_3$ $-\underset{\vert}{\overset{\vert}{C}}-$ $-CH_2-$
$^{13}C-\{^1H\}$ off reson.	q d t	q s	q s t

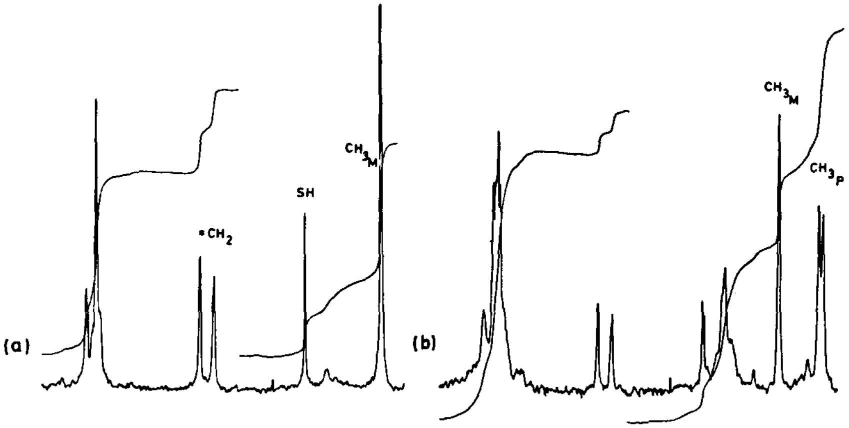


Fig. 3a: ^1H NMR of 3 (a) and of 3, after ∼ 50 % conversion (b) (solvent: $CDCl_3$)

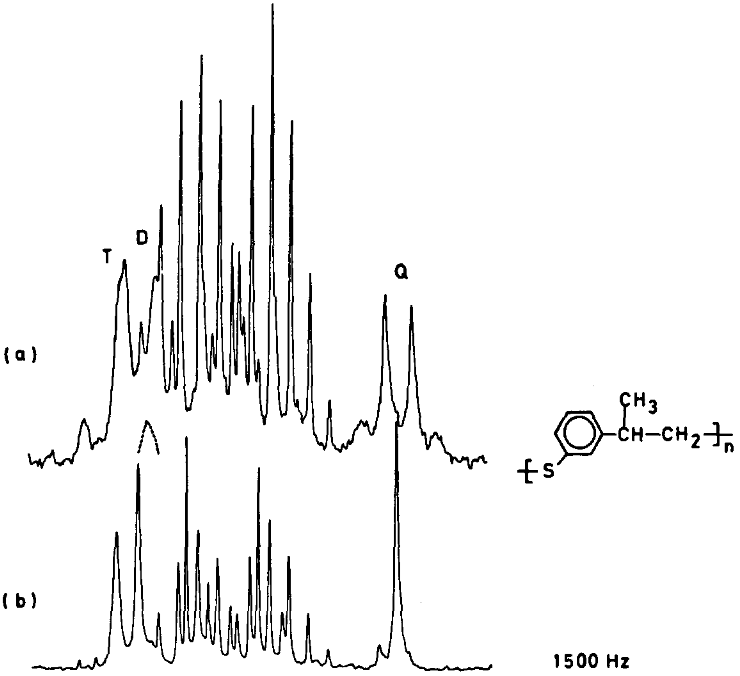
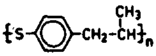
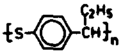
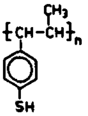


Fig. 3b: 22,53 MHz ^{13}C NMR spectrum of 3 (solvent: DMF - d_7) using
a) off resonance proton decoupling
b) proton noise decoupling

Polymer from 4:

Table 3: Expected NMR signals for the different polymer structures possible from monomer 4

structure			
^1H NMR	CH_3 d CH_2 d CH m	CH_3 t CH_2 m CH t	CH_3 d CH m CH d
^{13}C NMR	$-CH_3$ $-CH_2-$ $-\overset{|}{C}H-$	$-CH_3$ $-CH_2-$ $-\overset{|}{C}H-$	$-CH_3$ $-\overset{|}{C}H-$ $-\overset{|}{C}H-$
$^{13}C-\{^1H\}$ off res.	q t d	q t d	q d d

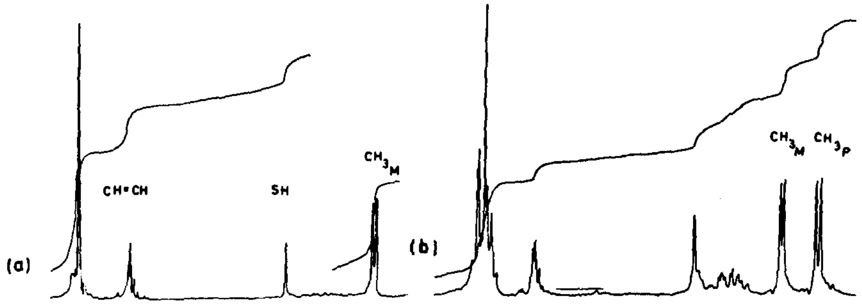


Fig. 4a: ^{1}H NMR of **4** (a) and of **4**, after ~50 % conversion (b) (solvent: $CDCl_3$)

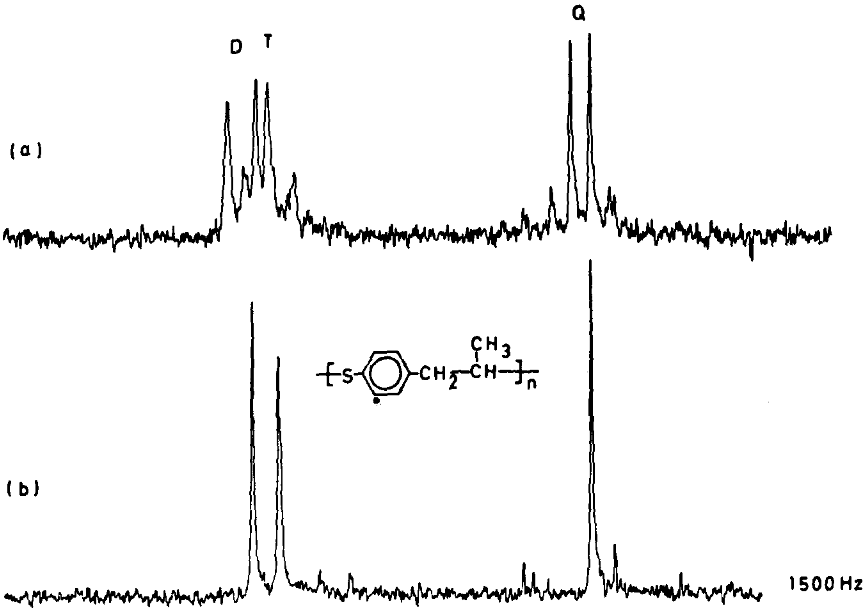


Fig. 4b: 22,53 MHz ^{13}C NMR spectrum of **4** (solvent: $CDCl_3$) using

a) off resonance proton decoupling

b) proton noise decoupling

Conclusion

Although the ^1H NMR of the polymers from 1 and 2, only suggests a $-CH_2-CH_2-$ unit (the symmetrical pattern around δ (ppm) : 3,0) the $^{13}C - \{^1H\}$ off resonance spectra (Fig. 1b and Fig. 2b) conclusively prove that only the Anti-Markovnikov addition product (I) is present in these polymers.

In the case of the polymer formed from 3 the ^1H NMR (Fig. 3a) clearly shows that Anti-Markovnikov product is the only detectable structure and the two experiments using ^{13}C NMR further corroborate this interpretation: the proton broad band decoupled spectrum shows only CH_3, CH_2 and CH carbon atoms and the $^{13}C-\{^1H\}$ off resonance spectrum shows very clearly a single quartet (CH_3), a single triplet (CH_2) and a single doublet (CH).

For the polymer from 4 structure II can be excluded because of the ^1H NMR. In order to distinguish between I and III one can take either an IR spectrum, which shows no SH absorption or the $^{13}C-\{^1H\}$ off resonance experiment, from both only structure I is possible. Thus it has been conclusively shown that for all four monomers the polymerization occurs exclusively via Anti-Markovnikov addition of the SH to the C=C group.

References:

1) NUYKEN, O., HOFINGER, M., KERBER, R., Polymer Bull. 2, 21 (1980)

2) NUYKEN. O., HOFINGER, M., Polymer Bull. 4, 75 (1981)

3) NUYKEN. O., HOFINGER, M., Polymer Bull. 4, 335 (1981)

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