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# New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)

## 9. A Demonstration of Chain Extension of α,ω-Polyisobutylene-diolefins with Dithiols

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## Abstract

The molecular weight of liquid telechelic polyisobutylene-diolefins was extended with the dithiol glycol-dimercaptoacetate in the presence of UV light. The mechanism of this polymerization was studied by model experiments.

## Introduction

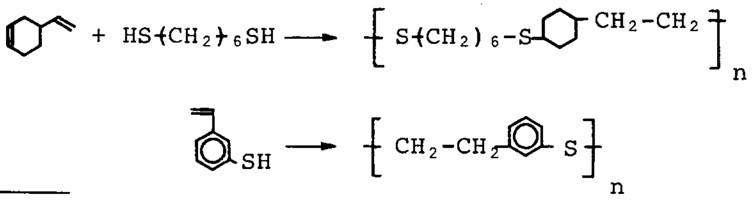
The addition of thiols to olefins has been known for many years (POSNER, 1905). It has been generally accepted that the process involves free radicals (GRIESBAUM, 1970; ABELL, 1973). Initiation occurs by homolysis of the thiol and can be accomplished by thermolysis of azo compounds or peroxides, by photolysis with UV-light, or by radiolysis (ABELL, 1973):

$$RSH \longrightarrow RS\cdot + H\cdot$$

$$RS\cdot + R'\text{-}CH{=}CH_2 \longrightarrow R'\text{-}\dot{C}H\text{-}CH_2\text{-}S\text{-}R$$

$$R'\text{-}\dot{C}H\text{-}CH_2\text{-}S\text{-}R + HSR \longrightarrow R'\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R + RS\cdot$$

The reaction between thiols and olefins catalyzed by peroxides or UV-light has been studied in detail and was applied to polymerization processes (MARVEL et al. 1951; NUYKEN et al. 1980).



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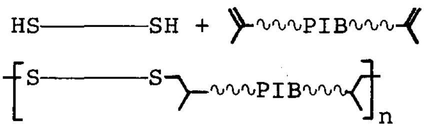
This note concerns the UV light induced chain extension of α,ω-polyisobutylene-diolefins with a dithiol i.e., glycol-dimercaptoacetate HS————SH:



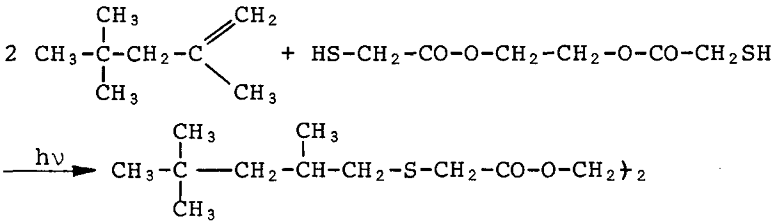
## Results and Discussion

### I. Model Experiments

Prior to extension studies with the telechelic polyisobutylene diolefin, model experiments have been carried out using a small mono-olefin, 2,4,4-trimethyl-1-pentene TMP, whose olefin group exactly mimics the structure of the terminal olefin group in our telechelic polyisobutylene-diolefin, and a well defined readily available small diene, 1,6-heptadiene.

### A) Experiments with 2,4,4-Trimethyl-1-Pentene

TMP has been found to react efficiently with glycol-dimercaptoacetate in the presence of UV-light at room temperature in less than 30 min.



The reaction has been followed by $^1$H NMR spectroscopy by determining the disappearance of the resonances associated with the vinyl protons at 4.6 and 4.8 ppm and the appearance of signals due to protons in alkyl groups between 2.8 and 1.0 ppm which arise as a consequence of the conversion of $-CH_2-C(CH_3)=CH_2$ into $-CH_2-CH(CH_3)-CH_2-$ groups.

### B) Experiments with 1,6-Heptadiene

Stoichiometric 1,6-heptadiene/glycol-dimercaptoacetate mixtures in the presence of UV light rapidly yielded a polymer with the anticipated overall structure:

$$\left[S-CH_2-CO-O-CH_2-CH_2-O-CO-CH_2-S-(CH_2)_7\right]_n$$

The molecular weight of the product is estimated to be ∿5000 i.e., n ∿ 20 (data obtained by GPC using a polystyrene calibration).

### II. Extension of Polyisobutylene-Diolefins with Dithiol

Encouraged by the results of model experiments, a series of extensions of telechelic polyisobutylene-diolefins with glycol-dimercaptoacetates have been carried out under conditions found to yield satisfactory results in model experiments. The polyisobutylene-diolefin $\overline{M}_n = 2,380$ and $\overline{M}_w/\overline{M}_n = 1.6$ was prepared by the inifer technique (KENNEDY et al. 1979). Table I shows the stoichiometric ratios used and molecular weights obtained.

Table I. Reaction between α,ω-Polyisobutylene-diolefin and Glycol-dimercaptoacetate

| $-SH/-C(CH_3)=CH_2$ | $\overline{M}_n$ | $\overline{M}_w$ | $\overline{M}_w/\overline{M}_n$ | Extension[a] $\overline{M}_n/\overline{M}_{n_o}$ | $\overline{M}_w/\overline{M}_{w_o}$ |
|---|---|---|---|---|---|
| 0.9 | 5840 | 12900 | 2.2 | 2.4 | 3.4 |
| 1 | 6760 | 14700 | 2.2 | 2.8 | 3.8 |
| 1.1 | 5480 | 11700 | 2.1 | 2.3 | 3.0 |

[a] The number-average and weight-average molecular weight of initial α,ω-polyisobutylene-diolefin are $\overline{M}_{n_o} = 2380$, $\overline{M}_{w_o} = 3840$

The initially liquid charges rapidly became very viscous and stirring became difficult. According to the molecular weight data shown in Table I the highest extension (i.e. 3.8) was obtained with 1:1 $-SH/-C(CH_3)=CH_2$. This observation corroborates independent analytical information according to which $\overline{F}_n$ (number average functionality) of the polyisobutylene diolefin is 2.0.

The relatively low extension obtained in these preliminary experiments are probably due to a combination of factors, i.e., rapid increase in the viscosity of the charge, unsuitably thick layers of samples preventing the efficient absorption of UV radiation, the use of a non-optimum UV sensitizer (benzophenone), and possibly some side reactions. Experiments are in progress to raise the degree of extension by improving mixing, using thinner layers of materials, searching for better sensitizers, etc.

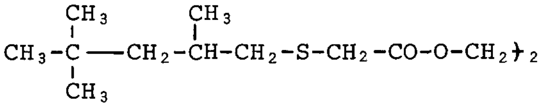
## Experimental

### I. Model Reaction

### 2,4,4-Trimethylpentene and Glycol-dimercaptoacetate

Two parts of 2,4,4-trimethyl-1-pentene (2.24 mg) and 1 part of glycol-dimercaptoacetate (2.0 mg) were dissolved in 5 ml $CDCl_3$, and a catalytic amount of benzophenone (sensitizer) was added. The mixture was irradiated by UV light (Sylvania sun lamp) at room temperature and the reaction was followed by $^1$H NMR spectroscopy.

Final product:



$$\mathrm{CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{---}CH_2\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CO\text{-}O\text{-}CH_2)_2}$$

$^1$H NMR(CDCl$_3$): $\delta$(ppm):4.3(4H,s,-S-CH$_2$-CO); 3.3(4H,s, -O-CH$_2$-); 2,8-1.0(34H,m,alkyl)

### 1,6-Heptadiene + Glycol-dimercaptoacetate

One part 1,6-heptadiene (960 mg) and 1 part glycol-dimercaptoacetate (2.10g) and a catalytic amount of benzophenone (2 mg) were dissolved in toluene and irradiated with UV light at room temperature. After a few minutes a noticeable increase of the viscosity indicated the onset of polymerization. The polymer was precipitated in methanol.

$^1$H NMR(CDCl$_3$): $\delta$(ppm): 4.3(4H,S,-S-CH$_2$-CO-); 3.2(4H,S, -O-CH$_2$-); 2.8-2.5(4H,t,-S-CH$_2$-CH$_2$-); 1.4-1.0(10H,m,alkyl)

## II. Extension of $\alpha,\omega$-Polyisobutylene-Diolefins

Different ratios of $\alpha,\omega$-polyisobutylene-diolefins ($\overline{M}_n$ = 2380) and glycol-dimercaptoacetate and a catalytic amount ($\sim$2 mg) of benzophenone were rapidly mixed in bulk. The viscosity of the mixture rapidly increased. After 20-30 min of UV irradiation the viscosity did not seem to increase further. The polymer was washed and dried.

$^1$H NMR spectra showed in addition to the typical signals of polyisobutylene, the signals due to the -S-CH$_2$-CO-(4.3 ppm) and -O-CH$_2$- (3.2 ppm) units. There was no evidence for the presence of olefinic endgroups.

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Financial support by NSF Grant DMR-77-27618 Polymer Program and the Deutsche Forschungsgemeinschaft (to O.N.) is gratefully acknowledged. We wish to thank Evans Chemetics, Darien, Connecticut 06820, for a sample of glycol-dimercaptoacetate.

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