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ADDITION POLYMERIZATION OF ALIPHATIC DITHIOLS WITH DIENE MONOMERS

E. KLEMM and ST. SENSFUSS

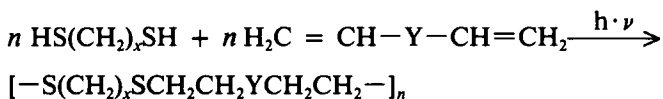
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ABSTRACT

The photoinitiated free radical polymerization of triethylenglycoldithiol and hydrochinonebisallylether or ethyleneglycoldivinylether leads to poly(thioethers) having anti-Markovnikov structure M_n : 14,000, 12,000 (VPO), respectively. The chain propagation is limited by a cyclic product (nearly 4%). Telechelics may be obtained by the use of nonequivalent molar ratio of the thiol/enemonomers. They are useful in preparation of block copolymers and networks, respectively. By means of ESR-spectroscopic investigations, it is shown that in dithiole/diene mixtures, which are free of daylight and oxygen, radicals are formed spontaneously. Using the spin-trapping technique, the existence of sulfur and carbon radicals could be proved unambiguously.

INTRODUCTION

A large number of photocross-linkable systems based on a polythiol plus a polyene have been described, and many patents have been issued in this general field [1, 2]. However, addition polymerization of a dithiol with compounds having only two carbon-carbon double bonds to a linear addition polymer has rarely been done [3–7].



The reaction was also sensitized by additives such as benzophenone or benzyldimethylketal under the irradiation of light of wavelengths 365 nm.

In this article we describe addition polymerization of aliphatic dithiols with different reactive dienes and report on the self-initiation mechanism of thiol/ene systems.

RESULTS AND DISCUSSIONS

The investigations were carried out with molequivalent mixtures of thiol/ene-compounds containing 1 wt% hydroquinone as stabilizer. In this way, dark storage stability was given. The photoinitiator concentration (benzyldimethylketal) amounted to 1.5 wt%. Table 1 shows the thiol/ene monomers used for polymerization. Table 2 summarizes the results of the reaction of triethyleneglycoldithiol 1 with three dienes (1', 2', 3') having a different reactivity.

TABLE 1. Diolefins and Dithiols Used for Polymerization

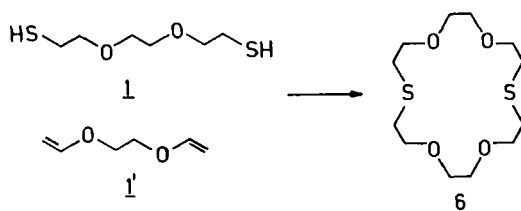
Dithiols		Diolefins	
$\text{HS}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{SH}$	<u>1</u>	$\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OCH}=\text{CH}_2$	<u>1'</u>
$\text{HS}(\text{CH}_2)_8\text{SH}$	<u>2</u>	$\text{CH}_2=\text{CH}-\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}=\text{CH}_2$	<u>2'</u>
$\text{HSCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{SH}$ CH ₃ CH ₃	<u>3</u>	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	<u>3'</u>
$\text{HSCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SH}$ CH ₃ CH ₃	<u>4</u>	$\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$ CH ₃ CH ₃	<u>4'</u>
$\text{HSCH}_2\text{CO}(\text{CH}_2)_4\text{OCCH}_2\text{SH}$ O O	<u>5</u>		

TABLE 2. Polyalkylene Sulfides from Triethyleneglycolthiol with Dienes Having Different Reactivity

$n \text{ HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH} + n \text{ CH}_2=\text{CH}-\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[10 \text{ min}]{365 \text{ nm, } h\nu}$						
$[-\text{CH}_2\text{CH}_2-\text{R}-\text{CH}_2\text{CH}_2-\text{S}-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{S}-]_n$ crystalline, colorless, soluble						
<i>R</i>	\bar{M}_n (VPO)	Polymer yield	T_m (Tg) [°C]	Analysis		
				C	H	S
$-\text{CH}_2\text{CH}_2-$	3040	63	17-47 (-4.5)	54.50 54.52	9.15 9.27	24.25 24.45
$-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2$	14000	95	30-57 (-35.4)	58.03 58.10	7.58 7.80	17.21 17.30
$-\text{OCH}_2\text{CH}_2\text{O}-$	12000	89	32-45 (-63.8)	48.62 48.32	8.16 7.91	21.63 22.11

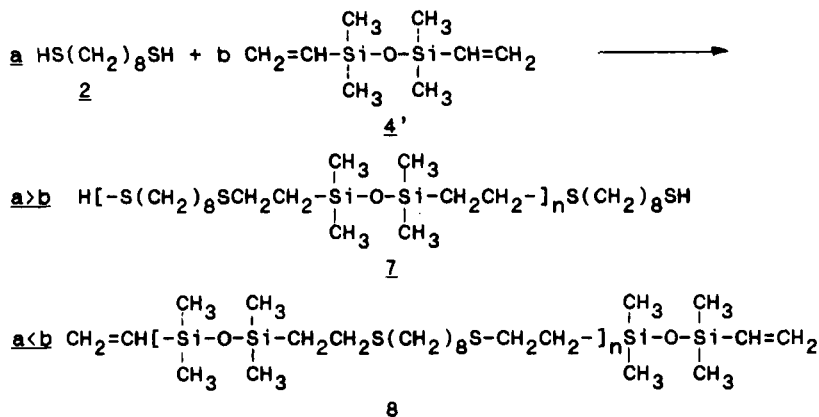
Initiator: benzophenone or benzilidimethylketal. I_0 : 0.266 mW/cm².

The structure of polymers is confirmed as the anti-Markovnikov-type addition product typical of a radical mechanism [8]. We found evidence of the chain-limiting termination processes by analysis of methanol-soluble fractions obtained from the parent solutions. Their proportion amounts to 3 wt%. From the reaction mixtures of triethyleneglycoldithiol 1 with ethyleneglycoldivinylether 1', we isolated the intramolecular addition product 6. The structure is in agreement with the crownether obtained by an independent synthesis.



Recently we reported that photoinitiation of the thiol/ene mixture with diaryliodonium salts leads to Markovnikov-type addition product [9].

Telechelics may be obtained by use of the nonequivalent mol ratio of the thiol/ene-monomers (Table 1). For example, the photoaddition of 1,8-dimercaptooctane 2 with 1,1,3,3-tetramethyl-1,3-divinylsiloxane 4' leads to SH- or vinyl-terminated telechelics 7 and 8.



DC and HPLC investigations showed that the telechelics consist of a mixture of oligomers with growing chain length. The distribution de-

depends on the molar ratio of the monomers (Tables 3 and 4). The structures of 7a-e and 8a, 8b are derived from NMR spectroscopy and from C, H, and S analysis.

The telechics exhibit \overline{M}_n values between 500 and 2000 g mol⁻¹. They are stable and useful in preparation of block copolymers, networks, and composites. Thus telechelics 7a-e react with diepoxides, for example, dianeddiglycidylether, within 3 h near 60°C and give high-molecular-soluble addition polymers. In the same way, the reaction is applicable in the case of diisocyanates, which leads to poly(thiocarbamates) [10]. Such thiol/ene systems are developed for preparation of special adhesives for optics [11].

TABLE 3. Some Telechelics 7 with SH End-Groups

	<u>7</u> 1.8-Dimercap-tooctaine <u>2</u>		Siloxane <u>4'</u>		Molar ratio		\overline{n}	\overline{P}_n	\overline{M}_n	$\overline{M}_n(\text{VPO})$ (calc.)	Tg
	g	mmol	g	mmol	a/b	<i>r</i>					
a	2.5	14.02	1.306	7.01	2:1	0.5	1	3	543	550	-7.2
b	2.0	11.21	1.394	7.48	3:2	0.66	2	5	908	900	-6.5
c	2.0	11.21	1.568	8.41	4:3	0.75	3	7	1272	1150	-5.8
d	2.0	11.21	1.672	8.91	5:4	0.8	4	9	1637	1620	4.0
e	2.0	11.21	1.742	9.34	6:5	0.83	5	11	2002	2050	8.0

C/H analysis of telechelics <u>7</u>	C (calc.)	H (calc.)
	C (exp.)	H (exp.)
a C ₂₄ H ₅₄ OS ₄ Si ₂ (543)	53.07	10.02
	53.22	9.97
b C ₄₀ H ₉₀ O ₂ S ₆ Si ₄ (907.8)	52.92	9.99
	53.21	9.86
c C ₅₆ H ₁₂₅ O ₃ S ₈ Si ₆ (1272)	52.89	9.91
	53.13	9.89
d C ₇₂ H ₁₆₁ O ₄ S ₁₀ Si ₈ (1636)	52.84	9.92
	52.64	10.15
e C ₈₈ H ₁₉₇ O ₅ S ₁₂ Si ₁₀ (2001)	52.82	9.92
	52.26	9.24

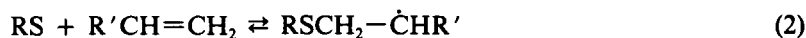
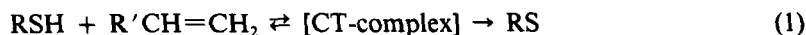
TABLE 4. Some Telechelics 8 with $-\text{CH}=\text{CH}_2$ End-Groups

<u>8</u>	1.8-Dimercap- tooctane <u>2</u>		Siloxane <u>4'</u>		Molar ratio		\bar{n}	\bar{P}_n	\bar{M}_n	$\bar{M}_n(\text{VPO})$ (calc.)
	g	mmol	g	mmol	a/b	r				
a	0.9568	5.365	2	10.729	1:2	0.5	1	3	551	608
b	1.5946	8.941	2	10.729	5:6	0.833	5	11	2010	2100
C/H analysis of telechelics <u>8</u>						C (calc.)	H (calc.)			
						C (exp.)	H (exp.)			
a	$\text{C}_{24}\text{H}_{55}\text{O}_2\text{S}_2\text{Si}_4$ (552.2)					52.20	10.04			
						52.45	9.96			
b	$\text{C}_{88}\text{H}_{199}\text{O}_6\text{S}_{10}\text{Si}_{12}$ (2011)					52.55	9.97			
						53.04	10.18			

THE SPONTANEOUS FORMATION OF RADICALS

All the SH/ene combinations we used show a more or less strong spontaneous dark reaction under formation of polymers (without initiator and without light!). Oxygen has no significant influence on the reaction. In the literature this phenomenon is described on the basis of a "molecule assisted homolysis" [12].

Evidence for the spontaneous formation of radicals is not known. We investigated the reaction by means of UV and ESR spectroscopy. We have shown by UV and DSC measurements that a charge transfer interaction takes place between bismercaptane and diene at the beginning of this spontaneous dark reaction [13]. The next step is electron transfer and formation of a thiyl radical. The thiyl radical induces the addition polymerization:



A direct proof of the existence of radicals [Eq. (1)] resulting from the dark reaction is not given in the literature.

We used 1:1 mixtures of 1,5-hexadiene or ethyleneglycoldivinylether with triethyleneglycoldithiol for the ESR spectroscopy. The spin-trap reagent was nitrosodurene (2,3,5,6-tetramethylnitrosobenzene). According to Eq. 2-3) one thiyl radical and one carbon radical should be formed in each case, giving radicals I-III with nitrosodurene.

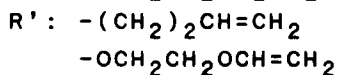
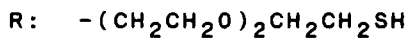
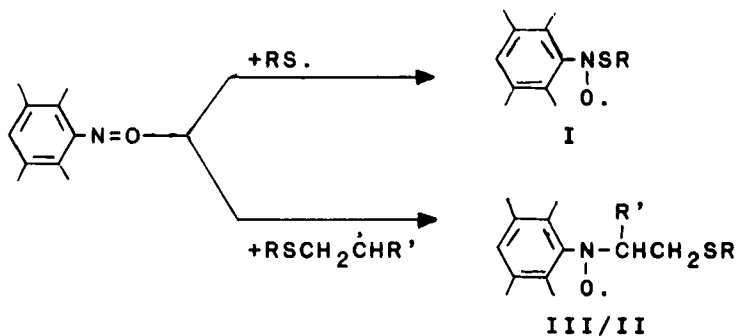


Figure 1 shows the spectrum of the mixture of monomers 1 and 3' 30 s after the homogenizing and 5 min afterward. The spectrum is composed of six signals of the carbon radical III and three signals of the thiyl radical I. The measurements were carried out in the absence of light and oxygen. The values of the coupling constant a_N and a_H are given in Table 5. The data are in good agreement with those described in the literature for aliphatic S-radical and sec. C-radical [14]. We obtained the same results by experimenting in the presence of oxygen. An initiation mechanism according to: $\text{R SH} + \text{O}_2 (\text{air}) \rightarrow \text{RS}\cdot + \text{HOO}\cdot$ must be excluded [15].

ESR investigations of triethyleneglycoldithiol 1 with nitrosodurene as spin trap show no type of radical whether or not oxygen is present. Only with the addition of diene can we identify the radicals.

APPLICATIONS

The addition polymerization described above was investigated for adhesives or coatings with low shrinking and stress. Thiol/ene systems were developed for the preparation of adhesives for optical systems.

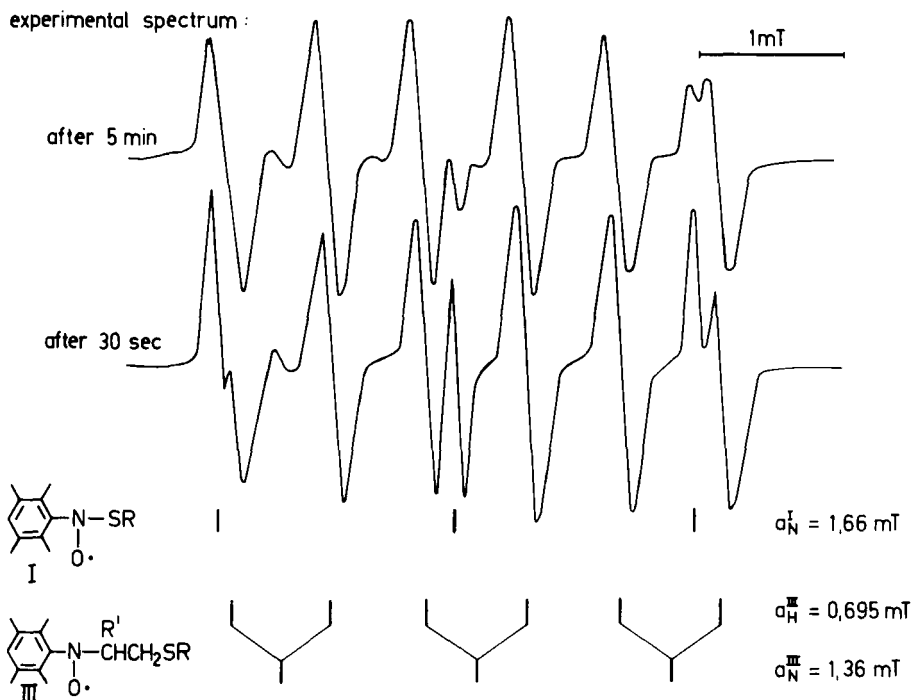


FIG. 1. ESR spectrum of homogeneous mixture of monomers I and 3' (1:1, without oxygen and light) in dependence on the time.

TABLE 5. Hfs-Coupling Constants a_N and a_H of Spin Adducts of Nitrosoduren in Molequivalent Dithiol/Diene-Mixtures

Monomers	Radical	Coupling constants (mT \pm 0.01mT)	Literature [14]
<u>1/3'</u>	III	$a_N^{III} = 1.36$ $a_H^{III} = 0.695$ (1H)	$\cdot\text{CH}(\text{CH}_3)_2: a_N = 1.372$ $a_H = 0.692$
	I	$a_N^I = 1.66$	$\cdot\text{S}(\text{CH}_2)_2\text{CH}_3: a_N = 1.682$
<u>1/2'</u>	II	$a_N^{II} = 0.128$ $a_H^{II} = 0.600$ (1H)	
	I	$a_N^I = 1.66$	

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