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1-Butadienyl Sulfide Polymerization

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ABSTRACT

1-Butadienyl sulfides, mainly cis in configuration, are obtained by
the base-catalyzed addition of mercaptans to vinylacetylene. bis-1-
Butadienyl sulfides are readily polymerizable using azo catalysts,
but mono-1-butadienyl sulfides are not, nor do they copolymerize
with styrene or butadiene. They have a high Q-value and copolymer-
ize well with other high Q monomers such as chlorostyrene and
chloroprene. bis-1-Butadienyl sulfides were made by reacting a
dithiol, such as bis-4-mercaptophenyl ether, with vinylacetylene
or by a two-step process using mercaptoethanol followed by treat-
ment of 2-hydroxyethylthiobutadiene with diisocyanate. The poly-
mers were largely of 1,4-trans polydiene structure.

INTRODUCTION

Russian chemists [1] have been active in the base-catalyzed addition
of thiols to vinylacetylene. They obtained cis-rich terminally substi-
tuted butadienes and reported that the addition occurred at the ethynyl
group rather than by 1,4-addition followed by bond shifts. Their prod-
ucts did contain traces of allenes and acetylenes and 2-substituted
butadienes. From the reaction with sodium sulfide, bis-1-butadienyl
sulfide was obtained. trans-Butadienyl sulfides have been made by

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others [2] by the reaction of sulfenyl chloride with butadiene. No information is available on the polymerization of these monomers.

EXPERIMENTAL

Addition of Thiols to Vinylacetylene

Mercaptoethanol (2.34 g, 0.03 mol) and potassium hydroxide (0.56 g, 0.01 mol) were dissolved in ethanol (15 mL) and chilled in Dry Ice while vinylacetylene (1.56 g, 0.03 mol) was dissolved. The solution was heated in a pressure vessel at 90° for 1 day. The product was dissolved in methylene chloride, rinsed with water, and distilled in the presence of a little inorganic base. The 1-(2-hydroxyethylthio) butadiene (Ic) boiled at 85°C at 0.5 mm and melted at 11-12°C. The yield was 70%. Gas chromatography on a diethylene glycol succinate column showed it to be 96% cis and 4% trans. The retention time of the trans isomer was 93% of that of the cis isomer.

The reaction of thiophenol with vinylacetylene was carried out by the literature procedure [1]. It was distilled, bp 55°C at 1 mm, and by infrared evidence was 55% the cis isomer, 29% trans, and 16% 4-phenylthio-1-butyne. There was a trace of allenic structure.

The reaction with 4-mercaptophenol was carried out in the same manner and occurred at the thiol group first. If the temperature was raised to above 100°C, the hydroxyl group added a second mole of vinylacetylene. The 1-(4-hydroxyphenylthio) butadiene was not distilled. It was a solid at room temperature.

The reaction of bis-4-mercaptophenyl ether with vinylacetylene was carried out in hexane and the bis-butadienyl derivative was a white solid which turned yellow and polymerized if allowed to stand in air at room temperature. The infrared spectrum showed the presence of a small amount of acetylenic structure.

2-(1-Butadienylthio)ethyl Acrylate (XI)

A mixture of methyl acrylate (0.4185 g) and Ic (0.4436 g) was heated overnight at 60°C in an open vial with diphenylamine (7.4 mg) and sodium methylate (21.5 mg). The formation of methanol was observed by NMR. The sample was centrifuged, AIBN added, and heated 3 h at 65°C. It had gelled and was a cross-linked polymer.

Copolymerization of Ic

A mixture of Ic and chloroprene containing Vazo 33 W was shaken at 40°C in the absence of air with 0.1 M aqueous neutral phosphate buffer.

A mixture of Ic and chlorostyrene containing AIBN was heated at 65°C in the absence of air.

RESULTS

We have added aromatic bis-thiols to vinylacetylene and obtained bis-1-butadienyl sulfides which we found to be highly polymerizable even at room temperature. We have also added hydroxyl-containing mercaptans to vinylacetylene and post-reacted the products with di-isocyanates to obtain other bis-butadienyl sulfides which also are rapidly curable.

$$RSH + CH_2=CHC\equiv CH \xrightarrow{\text{base}} RSCH=CHCH=CH_2 \qquad I$$

mainly cis
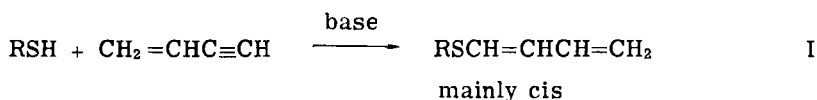
    a. $RSH = 4,4'-HSCH_2C_6H_4OC_6H_4SH$
    b. $RSH = 4-HSCH_2C_6H_4CH_2SH$
    c. $RSH = HOCH_2CH_2SH$
    d. $RSH = 4-HOC_6H_4SH$
    e. $RSH = C_6H_5SH$

$$R'NCO + Ic \xrightarrow{T12} R'NHCO_2CH_2CH_2SCH=CHCH=CH_2 \qquad II$$
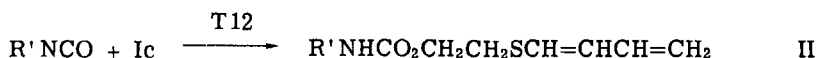
    a. $R'NCO = C_6H_5NCO$
    b. $R'NCO = CH_2(C_6H_4NCO)_2$
        $T12 = (C_4H_9)_2Sn(O_2CC_{11}H_{23})_2$

$$R'NCO + Id \longrightarrow R'NHCO_2C_6H_4SCH=CHCH=CH_2 \qquad III$$
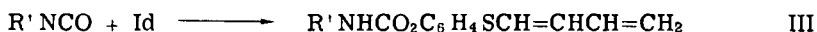
The bis-butadienyl sulfide, Ia, made from bis 4-mercaptophenyl ether, polymerized spontaneously at room temperature unless an anti-oxidant such as diphenylamine was added. If not, the initially white crystalline solid changed in a short time to a yellow insoluble polymer. The polymer was brittle solid but was a strong adhesive for phosphatized steel. After cure at 90°C, a lap shear strength of greater than 1000 psi was realized. An extraction was made of the polymer and the small amount of material soluble in tetrahydrofuran was found to contain little if any dimer but rather low molecular weight polymer.

A differential scanning calorigram (Fig. 1a) made at the heating rate of 2°/min showed an exotherm amounting to 10.8 kcal/mol. It began at about 45°C and was completed by 65°C. Between 90 and 130°C there was a second exotherm amounting to 4.1 kcal/mol. The relative
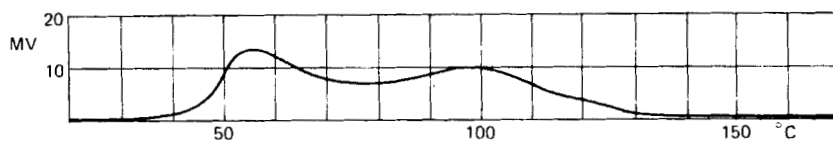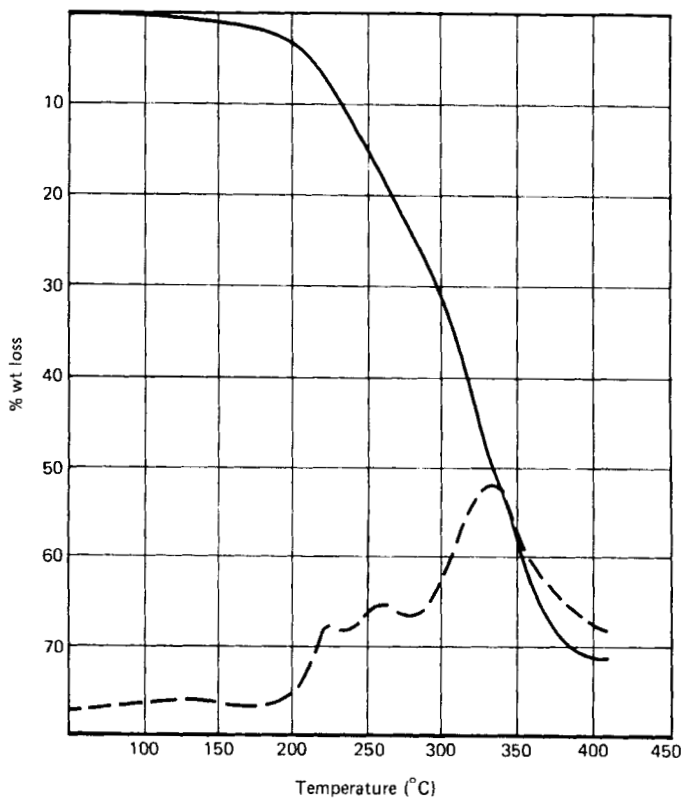
FIG. 1a. DSC of Ia, scan speed 2°/min.

FIG. 1b. TGA curve of IIb polymer under N_2. Derivative curve dashed.

size of the exotherms depended on the scanning rate. Weight loss starting at 200°C was observed by thermal gravimetric analysis (Fig. 1b).

The urethane, IIb, also a bis-butadienyl sulfide, was made from bis-4-isocyanatophenylmethane (MDI) using a liquid commercial grade which was miscible with 1-(2-hydroxyethyl)thiobutadiene (Ic). There was a small exotherm upon addition of the tin catalyst, but the sample returned to room temperature. It then changed to a colorless tough rubber within an hour's time. The rubber swelled in tetrahydrofuran. Crystalline MDI is not readily soluble in Ic, but the pasty mixture gave satisfactory bonding of steel plates after heating at 90°C. The differential scanning thermogram of the pasty mixture showed an exotherm beginning at 50°C. The second exotherm was small and began at 170°C.

The urethane IIa, a monobutadienyl sulfide, was a crystalline solid at room temperature. It polymerized incompletely on heating overnight at 65°C with AIBN. The polymer was soluble in tetrahydrofuran and by gel phase chromatography (GPC) had a M_w of 33,000 (Fig. 2). The GPC curve showed the presence of monomer and dimer as well. The polymer had an infrared absorption band at 975 cm^{-1}, attributed to a trans-1,4-diene polymer. Copolymerization with styrene was attempted with the following result. Polymerization occurred when IIa was dissolved in an equal weight of styrene and heated at 65°C with
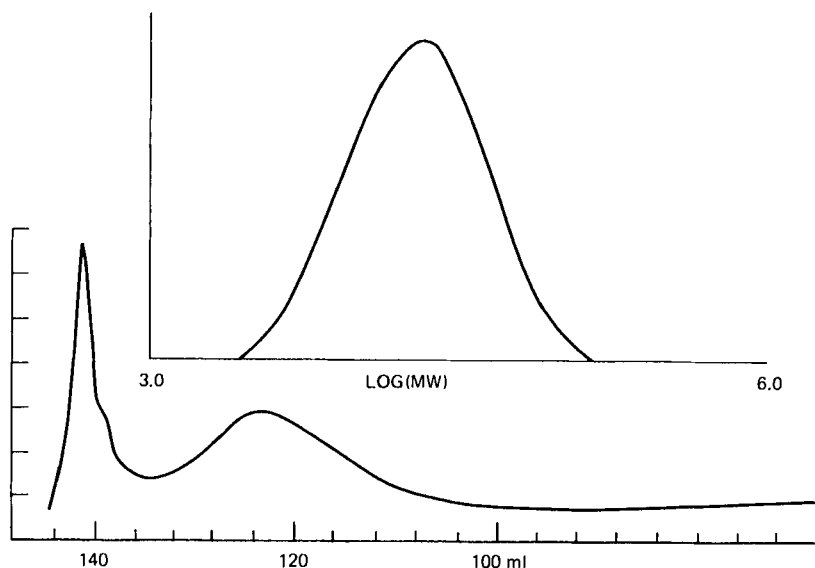

FIG. 2. GPC of homopolymer of IIa with refractive index detector. Inset: Molecular weight distribution (neglecting monomer), $\overline{M}_n$ = 20,000; $\overline{M}_w$ = 33,000.
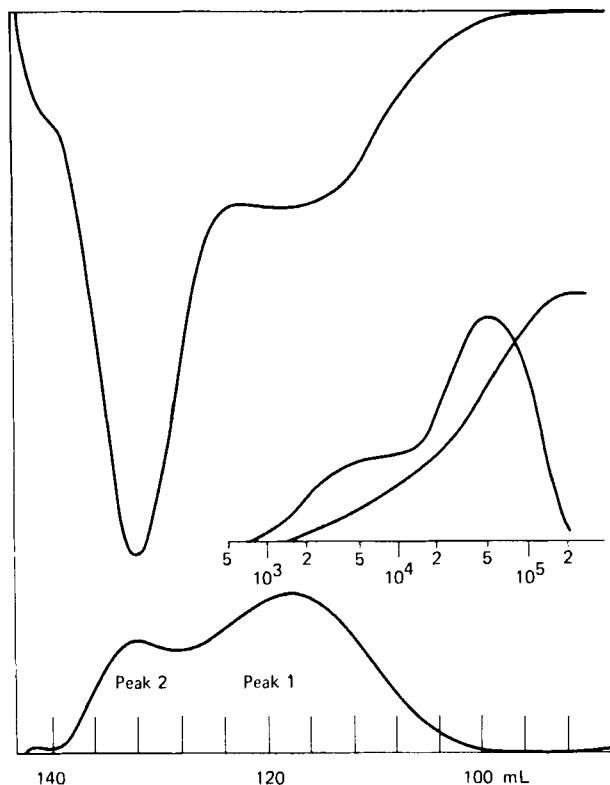
FIG. 3. GPC of copolymer of IIa and styrene with detection by re-
fractive index (lower curve) and UV absorption at 254 nm (upper curve,
inverted). Inset: Molecular weight distribution.

AIBN overnight. The solution became only slightly viscous and a 20%
yield was obtained of a tan powder insoluble in methanol. This polymer
contained 61 mol% of polymerized IIa whereas the monomer mixture
contained 30 mol%. The GPC (Fig. 3) indicated a very nonuniform
composition. There was some polymer of molecular weight 5,100 and
some of molecular weight 44,000. The ratio of UV optical density to re-
fractive index increment for the two peaks indicated that the low molecu-
lar weight polymer was more strongly absorbing at 254 nm. The high
molecular weight polymer (Peak 1 in Fig. 3) amounted to 71.4% of the
yield and consisted of 90% styrene.

An additional quantity of the low molecular weight polymer was re-
covered by evaporation of the precipitation liquor. The infrared ab-
sorption band at 975 cm^{-1} indicated that it was mainly of trans-1,4-
polydiene structure.

Compound Ic itself underwent free radical polymerization with dif-
ficulty. Prolonged heating at 65°C with AIBN gave incomplete con-
version to a polymer of molecular weight less than 5000. It probably
underwent self-transfer as alcohols are wont to do. The polymer
was soluble in methanol and gave a soft, colorless, nontacky film on
drying. It had a T_g of -74° by the torsion pendulum test with an indi-
cation of another transition at +31° (indefinite).

The unpurified 1-phenylthiobutadiene (Ie) was used as a model for
Ia. It was not readily polymerizable although a resinous residue was
obtained on distillation. GPC showed that the molecular weight was
less than 3000. The infrared spectrum showed that the polymer was
mainly of trans-1,4-diene configuration. After being rinsed with
hexane to remove a small amount of dimer, the film was no longer
tacky. A polymer of similar structure but higher molecular weight
(9000) was obtained by prolonged β-ray exposure (100 mrad). Con-
version was incomplete even then. Heating with AIBN at 65°C gave a
similar result. The polymer was yellow.

Radiation polymerization of the monobutadienyl sulfides with β-rays
was incomplete after the very large dose of 60 mrad whereas the bis-
butadienyl sulfides polymerized spontaneously. For comparison, the
corresponding vinyl sulfides were made. These also required large
β-ray doses (30-40 mrad) for cure. In general, it is preferable to use
azo catalysts to polymerize either vinyl or butadienyl sulfides.

A copolymer of Ie was obtained with chloromaleic anhydride using
AIBN at 60°C. The infrared spectrum of a sample which was preci-
pitated with ether showed two anhydride absorption bands, one satu-
rated and one unsaturated. The polymer was dark in color and some
dehydrohalogenation had evidently occurred. Again the molecular
weight by GPC was low. Conversion was again incomplete.

Copolymerization of Ia with N-phenylmaleimide gave a heat-resis-
tant and cross-linked polymer.

We were not able to copolymerize Ic with styrene or butadiene, but
we did copolymerize it in a 5% amount with isoprene in emulsion. The
solubility of Ic in water at 60°C is less than 2% but it is self-emulsifi-
able. The copolymer was a soft elastomer which cross-linked on dry-
ing and could be cross-linked in tetrahydrofuran solution by the addi-
tion of toluenediisocyanate.

Monomer Ic copolymerized readily with chlorostyrene, a monomer
with a higher Q-value than styrene. The chlorostyrene which was used
was a 60:40 o/p-isomer mixture. The Q-value of Ic appeared (Fig. 4)
to be larger than that of chlorostyrene. It was much larger than that
of vinyl sulfides (which have Q-values in the region of 0.43) [3]. The
monomer Ic was readily copolymerized with chloroprene in emulsion
or under precipitating conditions in alcohol. Butadiene itself polymer-
izes well under these conditions but not in solution [4]. The copolymer
composition curve of Fig. 5 was based on assay of residual monomer
by GC in the case of copolymers which are richer in Ic and were some-
what difficult to reprecipitate without loss. The trans isomer was
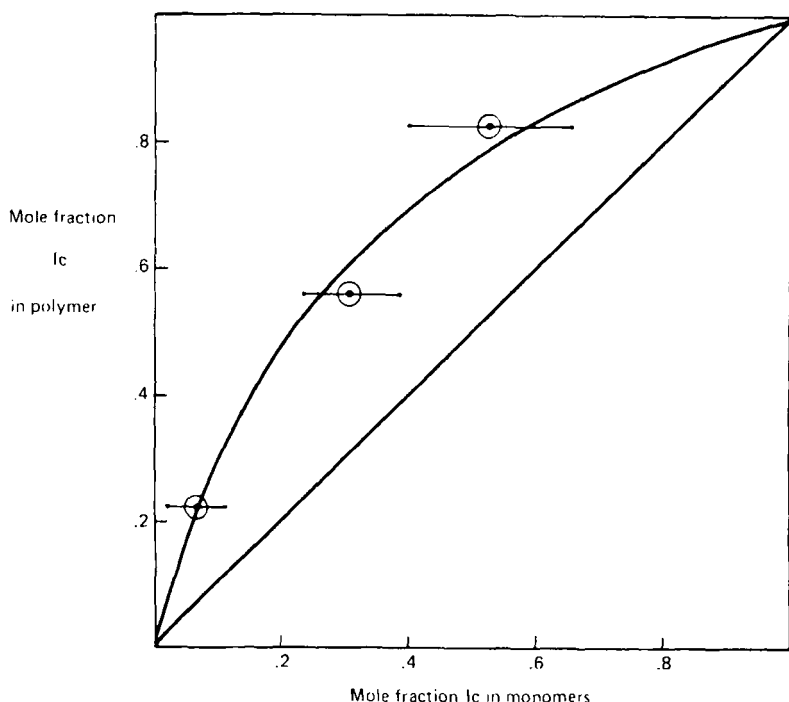slightly enriched in the residual monomer.

FIG. 4. Copolymerization of Ic with chlorostyrene (M_2) $(60{:}40$ m,p-isomer mixture) using AIBN at 65°C. Found: $r_1 = 3.27$, $r_2 = 0.24$. Calculated: $e_1 = 0.15$, $Q_1 = 4.16$. Given: $e_2 = -0.35$, $Q_2 = 1.18$.

We transesterified methyl acrylate with Ic using a basic catalyst. The product, 1-butadienylthioethyl acrylate, gave a cross-linked polymer which may have resulted from consecutive polymerization, first of the butadienyl sulfide and then of the pendant acrylate groups.

Ring closure of Ic to a 1,3-oxathiolane (IV) may occur under acid catalysis. Compound IV was not formed as an impurity in distilled Ic because the distillation was done in the presence of a small amount of base. When Ic was treated with acid, methyl groups appeared in the NMR spectrum in the allylic region (1.6 ppm). It was noted, however, that the water layer resulting from treatment of a chloroform solution with aqueous acid became first pink and then violet. There was little color in the chloroform layer. A test was made with 20% DC1 in D_2O and the D_2O layer examined in NMR. It was brown in color. The main band was at 4.2 ppm and was attributed to Compound V. Both Compounds IV and V are expected products of protonation of the diene. The relative amounts of IV and V formed would depend on the presence of water to stabilize the sulfonium ion. Confirmation of the hypothesis
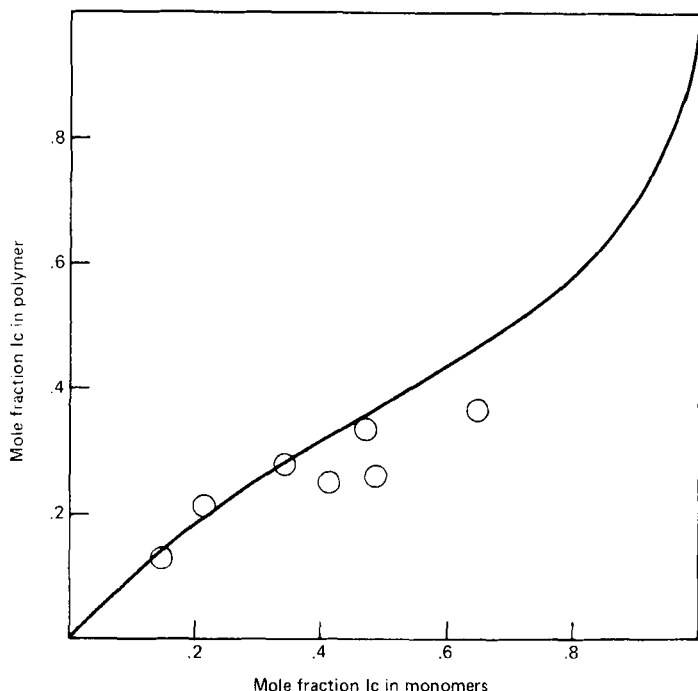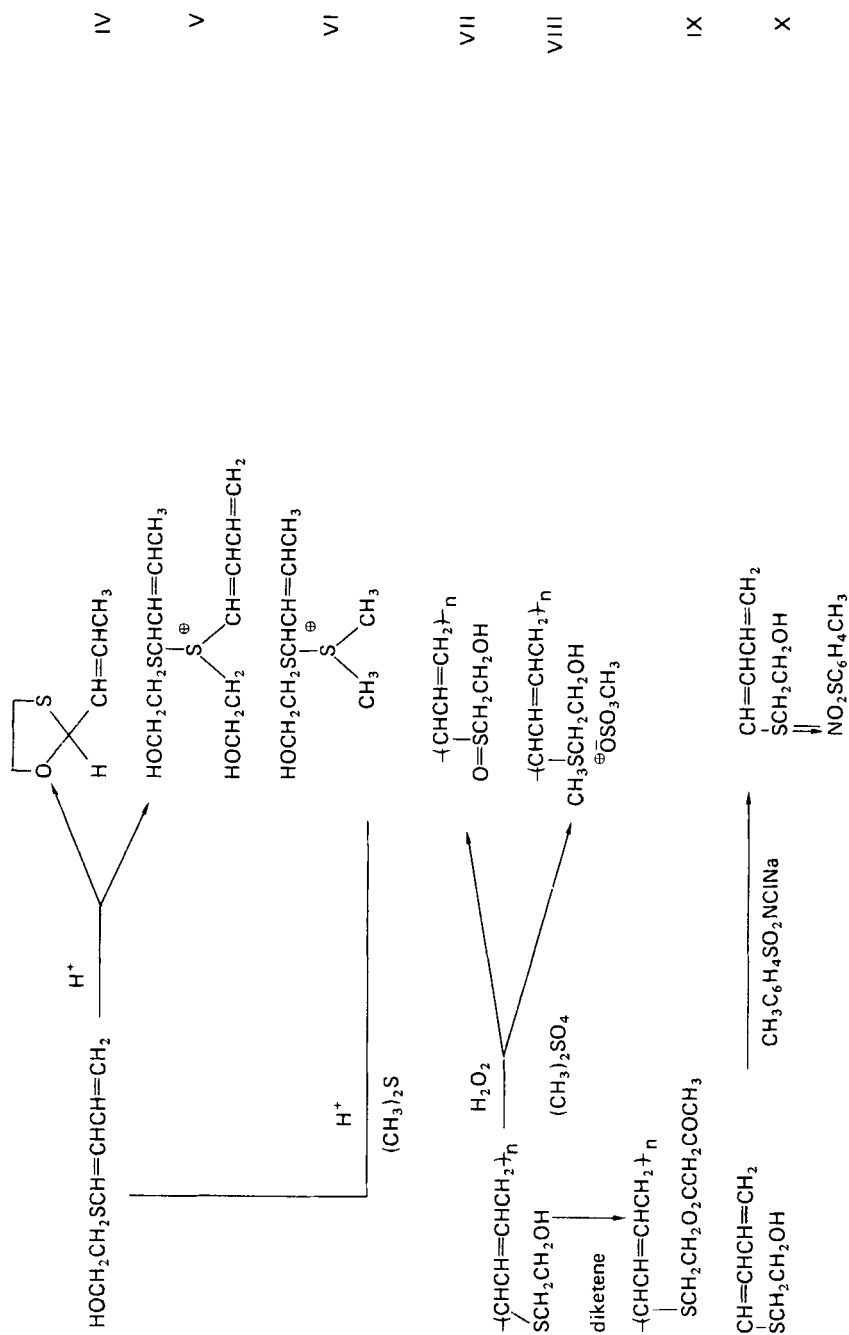
FIG. 5. Copolymerization of Ic with chloroprene (M_2) using Vazo 33 W at 40°C. Found: $r_1 = 0.2$, $r_2 = 1$. Calculated: $e_1 = -1.29$, $Q_1 = 7.26$. Given: $e_2 = -0.02$, $Q_2 = 7.26$.

was obtained by adding dimethyl sulfide, a better nucleophile than Ic. Now the main NMR band was at 3.0 ppm, the location of a methylsulfonium group. A precipitate was obtained when some potassium picrylsulfonate was added.

Why the vivid colors are formed along with V was not explained, but it was found that phenyl vinyl sulfide also gave a violet color when treated with acid. Compound Ic was slowly converted at room temperature with iodine or trifluoroacetic acid to a low molecular weight polymer which contained hydroxyl groups. The infrared spectrum showed the presence of some trifluoroacetate ester.

The reaction products were made of the homopolymer of Ic with hydrogen peroxide, with methyl sulfate, and with diketene. The derivatives VII and VIII were water-soluble. We tested them as reactants for paper, but they did not cure significantly. The property which had been expected to be improved was wet extension. The derivative of monomeric Ic with Chloramine T was also ineffective when cured in paper.

$HOCH_2CH_2SCH=CHCH=CH_2$

IV

V

VI

VII

VIII

IX

X

H^+

$HOCH_2CH_2SCHCH=CHCH_3$

$HOCH_2CH_2S^{\oplus}CH=CHCH=CH_2$

$HOCH_2CH_2SCHCH=CHCH_3$ / $S^{\oplus}(CH_3)(CH_3)$

$(CH_3)_2S$

H^+

$(CH_3)_2SO_4$

H_2O_2

$+CHCH=CH_2+_n$ / $O=SCH_2CH_2OH$

$+CHCH=CHCH_2+_n$ / $CH_3SCH_2CH_2OH$ $^{\oplus}\overline{O}SO_3CH_3$

$+CHCH=CHCH_2+_n$ / SCH_2CH_2OH

diketene

$+CHCH=CHCH_2+_n$ / $SCH_2CH_2O_2CCH_2COCH_3$

$CH_3C_6H_4SO_2NClNa$

$CH=CHCH=CH_2$ / SCH_2CH_2OH

$CH=CHCH=CH_2$ / SCH_2CH_2OH

$NO_2SC_6H_4CH_3$

DISCUSSION

It is clear that monobutadienyl sulfides are not very polymerizable. Part of the trouble may have been due to small amounts of allenic and acetylenic impurities, absorbing at 1975 and 629 cm^{-1}, respectively, but these structures were present in the bis-butadienyl sulfides also. A surprising observation was that the purity of the monomer was improved by exposure to 10 mrad γ-ray irradiation under a nitrogen stream. It was concluded that the by-products revert to the starting materials. The diene was 70 to 90% cis depending on the solvent in which the preparation was carried out. The estimate was based on a measured ratio of 1.47 for the optical densities of cis (768 cm^{-1}) and trans (978 cm^{-1}) bands in other compounds. The 90% value seems higher than the composition of the equilibrium mixture and has been cited [1] as evidence for the formation (which we confirm) of 3-methylbutadienyl hydroxyethyl sulfides from the base-catalyzed addition of mercaptoethanol to 3-methylbutenyne.

The low molecular weight character of polymers of monobutadienyl sulfides suggests degradative chain transfer or a high termination rate. It has been reported [5] that after α-methylthiophene was irradiated at room temperature in a solid medium, the ESR signal of a stable radical developed over a period of hours.

There is a surprising contrast between the high polymerizability of the bis-butadienyl sulfides and the sluggish polymerization of the mono-butadienyl sulfides. We do not attribute the difference to a Trommsdorff effect because the addition of small amounts of glycol diacrylate did not increase the polymerization rate of a monobutadienyl sulfide. When Ic was treated with a one-quarter equivalent of toluenediisocyanate, it polymerized slowly. The polymer was soluble and did have a molecular weight of 45,000, but no doubt it had a branched structure.

It should not have been a surprise that we could not make random copolymers of the monobutadienyl sulfides with styrene. The Q-values of butadienyl sulfides would be expected to be high because of the doubly resonance-stabilized nature of the monomer. The high Q-value of 1-butadienyl sulfides (Figs. 4 and 5) is more typical of that of a 1-substituted diene than of a vinyl sulfide. Thus, 1-acetoxybutadiene was reported [6] to be much much more reactive than acrylonitrile and 1-cyanobutadiene than butadiene.

The cis-1-substituted butadienes make better monomers than the trans isomers, because unlike the trans isomers they are sterically hindered from undergoing self-addition in the Diels-Alder reaction.

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