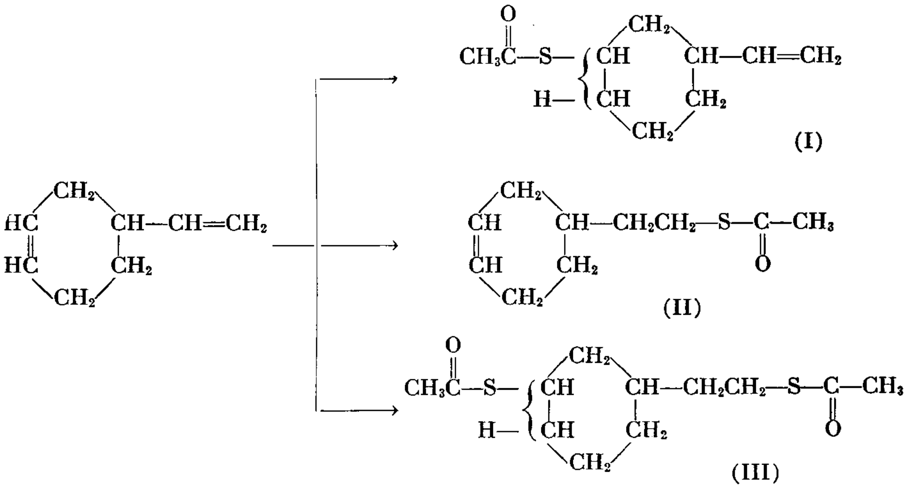
JOURNAL OF POLYMER SCIENCE VOL. XXVI, PAGES 23-28 (1957)

Polyalkylene Sulfides. XIII. Polymers from 4-Vinyl-1-cyclohexene and *d*-Limonene*

C. S. MARVEL and L. ELMER OLSON
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

It has been found that polyalkylene sulfides made from nonconjugated diolefins with branching in the chain have some rubber-like properties.[2,3] The work described in this communication was undertaken to attempt to use two readily available nonconjugated diolefins, 4-vinyl-1-cyclohexene and *d*-limonene, as sources for such polymers.

4-Vinyl-1-cyclohexene was found to react with thiolacetic acid to yield one di- and two monoaddition products:



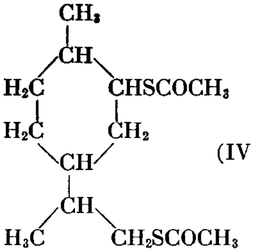
Structure I was assigned to the monoadduct boiling at 117–119° at 13 mm. on the basis of strong infrared absorption bands at 995 and 913 cm.$^{-1}$ which are characteristic of a terminal vinyl group. These bands were not exhibited by the isomer (II), which boiled at 125–127° at 13 mm. Both

---

* Abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree by L. Elmer Olson to the Graduate College of the University of Illinois. The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the government synthetic rubber program. For the preceding communication on this topic, see reference (1).

monoadducts and the diadduct (III) gave the strong absorption band at 953 cm.$^{-1}$ which is characteristic of a thiol ester. In the reaction to yield a monothiol ester, the ratio of isomers formed is approximately 2 parts of I to 3 parts of II. All three of the adducts were hydrolyzed to yield the corresponding mercaptans.

d-Limonene was converted by the addition of thiolacetic ester to the dithiol ester, which was assigned structure IV on the basis of an expected



(IV)

free radical reaction. The corresponding dimercaptan was formed when this ester was hydrolyzed.

Polyalkylene sulfides were prepared from the new dimercaptans and biallyl and from the dimercaptans and the diolefins from which they had been prepared. Also the unsaturated monomercaptan from vinylcyclohexene was polymerized alone. All of the polymers had inherent viscosities in the 0.12–0.36 range and were soft and sticky.

EXPERIMENTAL

Thiolacetic acid was prepared, using the method of Ellingboe,[4] in 58% yield, b.p. 86–87° (atmos.), n_D^{20} 1.4635.

The 4-vinyl-1-cyclohexene was Eastman practical grade which was distilled through a 12 inch glass helices packed column, b.p. 124° (atmos.), n_D^{20} 1.4653.

The *d*-limonene was obtained from Clinton Foods, Incorporated, and was distilled through a 12 inch glass helices packed column at a reflux ratio of 5 to 1 and the material boiling 174–176° (743 mm.), n_D^{20} 1.4726 was used.

Monothioacetate from 4-Vinyl-1-cyclohexene. 433 g. (4.0 moles) of 4-vinyl-1-cyclohexene distilled five weeks previously was placed in a 1 l. three-necked round-bottomed flask equipped with a reflux condenser, separatory funnel, and a motor-driven glass stirrer. Through the separatory funnel was added slowly with stirring 304.4 g. (4.0 moles) of freshly distilled thiolacetic acid. The temperature of the mixture rose to 60° and then the mixture was allowed to cool to room temperature while stirring was continued. The mixture was then placed in quartz flasks under an ultraviolet lamp for four hours. The mixture was distilled under 100 mm. of pressure with recovery of 170 g. (mainly 4-vinyl-1-cyclohexene). The distillation was continued under reduced pressure to give the six fractions in the following list:

Fraction No.	B.p. (°C.)/13 mm.	Wt., g.	n_D^{20}
1	110	11.3	1.5118
2	110–118	109.1	1.5085
3	119–124	65.4	1.5105
4	125–127	121.5	1.5108
5	128–129	14.8	1.5118
6	197–198	189.3	1.5012

The distillation of fractions 1–5 was carried out in a 2 ft. heated, glass helices packed column with a take-off reflux ratio of 1 to 7. Fraction 6, which is the diaddition product of thiolacetic acid and 4-vinyl-1-cyclohexene, was distilled through a 8 inch heated Vigreux column. Samples from fractions 2 and 4 were submitted for infrared analysis. Fraction 2 showed strong absorption at 995 and 913 cm.$^{-1}$ which are characteristic of a terminal vinyl group. These bands were not present in the spectrum of fraction 4. The thiolacetic acid appears to add to the vinyl and endocyclic double bonds of 4-vinyl-1-cyclohexene in a ratio of 3 to 2. This addition does not occur readily when freshly distilled vinylcyclohexene is used. Apparently the peroxides formed in the olefin on standing catalyze the addition of thiolacetic acid. Portions of fraction 2 and 4 were submitted for elemental analysis.

ANALYSIS: *Calcd. for* $C_{10}H_{16}SO$, C, 65.16, H 8.75, S 17.40. *Found Fraction 2,* C 65.59, H 8.74, S 18.01. *Fraction 4,* C 65.30, H 8.53, S 17.22.

4-β-Mercaptoethyl-1-cyclohexene. In a 500 ml. round-bottomed flask were placed 250 ml. of 10% sodium hydroxide and 36.8 g. (0.2 mole) of the acetate of fraction 2 above. The flask was fitted with a condenser and the mixture refluxed for ten hours. The mixture was made neutral with hydrochloric acid and extracted three times with 100 ml. of benzene. The benzene was dried overnight over anhydrous calcium chloride and the calcium chloride was then removed by filtration. About 0.05 g. of hydroquinone was added and the benzene was removed under reduced pressure. The unsaturated mercaptan was distilled under reduced pressure boiling at 46–48° (0.2 mm.); $n_D^{20.5}$ 1.5081; d_4^{25} 1.008. The yield was 12.2 g. or 43% of the theoretical amount.

ANALYSIS: *Calcd. for* $C_8H_{14}S$, C 67.54, H 9.92, S 22.54. *Found,* C 67.12, H 9.86, S 22.03.

1(or 2)-Mercapto-4-vinylcyclohexane. This mercaptan was prepared as above starting with fraction 4 from the monoadduct of thiolacetic acid and vinylcyclohexane. It boiled at 84–87° under 15 mm. pressure, n_D^{20} 1.5103.

Diacetate of β-Mercaptoethyl-3(or 4)-mercaptocyclohexane. In a 1 l. three-necked flask fitted with a condenser, stirrer, thermometer, and separatory funnel was placed 216.2 g. (2.0 moles) of 4-vinyl-1-cyclohexene which had been distilled five weeks earlier. 5 moles (380.0 g.) of thiolacetic acid which had been distilled five weeks earlier was added dropwise with stirring to the 4-vinyl-1-cyclohexene at a rate so that the temperature of the mixture in the flask did not rise above 90°. The addition took five hours. The reaction mixture was allowed to stand overnight and was practically colorless. The flask was fitted with a Claissen distillation head and condenser and the mixture was distilled under reduced pressure:

Fraction No.	B.p., °C.	Pressure, mm.	Yield
1	25–29	80–23	152.4 g.
2	134–144	15	141.2 g. (0.82 mole)
3	193–205	15	286.0 g. (1.1 moles)

Fraction number 1 was mainly unreacted thiolacetic acid while fraction number 2 was mixed monothioacetates. Fraction number 3 was redistilled through a 8 inch heated Vigreux column. The ester boiled at 206–208°/16 mm., n_D^{20} 1.5308, d_4^{25} 1.103. The yield was 276.2 g. or 53% of the theoretical amount. The dithioester had a light yellow color.

ANALYSIS: *Calcd. for* $C_{12}H_{20}S_2O_2$, C 55.35, H 7.74, S 24.62. *Found,* C 55.30, H 7.88, S 24.72.

β-Mercaptoethyl-3(or 4)-mercaptocyclohexane. 78 g. (0.3 mole) of the diacetate of β-mercaptoethyl-3(or 4)-mercaptocyclohexane was placed in a 1 l. flask fitted with a reflux condenser. Then 32 g. (0.68 mole) of sodium hydroxide dissolved in 500 ml. of water was added and the mixture refluxed for twenty-four hours. The mixture was then cooled, made acid with concentrated hydrochloric acid, and extracted with 100 ml. of diethyl ether. The ether extract was dried overnight over anhydrous magnesium sulfate. The drying agent was then removed by filtration and the ether removed on a steam bath. The mercaptan was distilled through a 4 inch Vigreux column under reduced pressure to give 41.7 g. (79%) of β-mercaptoethyl-3(or 4)-mercaptocyclohexane, b.p. 139–143° (13 mm.). Redistillation gave 35.6 g. of water white liquid of b.p. 144–146° (15 mm.), n_D^{20} 1.5422.

ANALYSIS: *Calcd. for* $C_8H_{16}S_2$, C 55.46, H 7.78, S 24.88. *Found,* C 55.30, H 7.88, S 24.72.

Diacetate of 1-(α-Methyl-β-mercaptoethyl)-3-mercapto-4-methylcyclohexane from d-Limonene. To 272.5 g. (2.0 moles) of *d*-limonene in a 1 l. three-necked flask fitted with a motor-driven glass stirrer, separatory funnel, and condenser was added slowly 380.0 g. (5.0 moles) of thiolacetic acid through the separatory funnel. The thiolacetic acid was added at such a rate that the temperature of the mixture did not rise above 90°. After all the thiolacetic acid was added (two hours), the mixture was allowed to cool and was placed in a quartz flask and irradiated with ultraviolet light. The mixture initially warmed up but returned to room temperature after two hours. The mixture was then distilled under reduced pressure and three fractions separated. The first fraction, b.p. 42–48° (90–100 mm.), was 103.9 g. (1.36 moles) of thiolacetic acid, the second 63.9 g. (0.34 mole) of crude monoaddition product, b.p. 134–138° (13 mm.), and the third was 460.5 g. (1.60 moles) of the diaddition product, b.p. 159–164° (14 mm.). A portion of the third fraction was redistilled boiling at 147° (0.4 mm.), n_D^{20} 1.5262. The ester has a light yellow color.

ANALYSIS: *Calcd. for* $C_{14}H_{24}S_2O_2$, C 58.29, H 8.39, S 22.23. *Found,* C 58.09, H 8.47, S 22.47.

1-(α-Methyl-β-mercaptoethyl)-3-mercapto-4-methylcyclohexane. Into a 1 l. round-bottomed flask fitted with a condenser was placed 40.8 g. (0.2 mole) of the diacetate of α-methyl-β-mercaptoethyl-3-mercapto-4-methylcyclohexane (from *d*-limonene), 20 g. (0.425 mole) of sodium hydroxide, and 350 ml. of water. The mixture was refluxed for forty-eight hours, cooled, acidified with 20 ml. of concentrated hydrochloric acid, and extracted with 100 ml. of diethyl ether. The ether extract was dried overnight over anhydrous magnesium sulfate, filtered, and the ether removed on a steam bath. The mercaptan was then distilled under reduced pressure to give 28.8 g. (70.5%) of α-methyl-β-mercaptoethyl-3-mercapto-4-methylcyclohexane (from *d*-limonene), b.p. 149–156° (10 mm.). Redistillation gave as boiling point 151° (10 mm.), n_D^{20} 1.5312.

ANALYSIS: *Calcd. for* $C_{10}H_{20}S_2$, C 58.76, H 9.86, S 31.37. *Found,* C 58.76, H 9.69, S 31.39.

The structure of this product is assumed from the free radical non-Markownikoff addition of thiolacetic acid to the double bonds of *d*-limonene.

Polymerizations

Polymerizations were carried out by making 50 ml. of 2% MP-635-S[5] 0.02 molal in sodium acetate and adding 1 ml. of a catalyst-activator solution containing 0.073 g. ammonium persulfate, 0.037 g. of sodium bisulfite, and 0.002 g. of copper sulfate pentahydrate and buffering to pH 3.4 with acetic acid. 5 ml. of carefully balanced equimolar quantities of dimercaptan and diolefin were added to the emulsifier in a 4 ounce bottle and the mixture tumbled four days at 30°. The emulsion was then broken and the polymer isolated. Considerable difficulty was encountered with the breaking of the polymerization emulsion during the reactions and this was deemed to be an important factor in the production of low molecular weight material.

Polymerization of 4-β-Mercaptoethyl-1-cyclohexene. In this polymerization 5 ml. of the unsaturated mercaptan was used in place of the balanced mixture of dimercaptan and diolefin mentioned above. A yield of 63% of polymer with an inherent viscosity of 0.12 (chloroform solution) was obtained.

1-(β-Mercaptoethyl)-3(or 4)-mercaptocyclohexane and Biallyl. Using the standard procedure above, polymers with an inherent viscosity of 0.4 (in chloroform) were obtained in 90–95% yields. These polymers were apparently identical with those prepared by the reaction of hexamethylene dimercaptan and vinylcyclohexene.[3]

β-Mercaptoethyl-3(or 4)-mercaptocyclohexane and 4-Vinyl-1-cyclohexene. Using standard procedures this gave a soft polymer with an inherent viscosity of 0.36 (in chloroform solution) in 72% yield.

ANALYSIS: *Calcd. for* $C_8H_{14}S$, C 67.54, H 9.92, S 22.54. *Found,* C 67.32, H 9.86, S 22.24.

1-(α-Methyl-β-mercaptoethyl)-3-mercapto-4-methylcyclohexane and d-limonene. Using the standard procedure, an 82% yield of polymer with 0.33 inherent viscosity in chloroform solution was obtained. When 3% of emulsifier was used, the yield improved to 92% and the inherent viscosity to 0.41. Both polymeric materials were very viscous sticky materials.

ANALYSIS: *Calcd. for* $C_{10}H_{18}S$, C 70.52, H 10.65, S 18.83. *Found,* C 70.49, H 10.75, S 18.51.

We are indebted to Mrs. Elizabeth Leighly for the infrared absorption spectra determinations and their interpretation and to Clark Microanalytical Laboratories and Micro-Tech Laboratories for the elemental analyses.

References

(1) C. S. Marvel, C. W. Hinman, and H. K. Inskip, *J. Am. Chem. Soc.*, **75**, 1997 (1953).

(2) C. S. Marvel and H. E. Baumgarten, *J. Polymer Sci.*, **6**, 127 (1951).

(3) C. S. Marvel and C. W. Roberts, *J. Polymer Sci.*, **6**, 717 (1951).

(4) E. K. Ellingboe, *Organic Syntheses*, Vol. 31, Wiley, New York, 1951, p.105.

(5) A mixed sixteen-carbon sodium alkanesulfonate emulsifier obtained from Dr Stanley J. Detrick, E. I. du Pont de Nemours & Co.

Synopsis

4-Vinyl-1-cyclohexene and *d*-limonene have been converted to dimercaptans by the addition of thiolacetic acid and subsequent hydrolysis. These dimercaptans have been added to the original nonconjugated diolefins to give low melting highly viscous polymers. In the case of 4-vinyl-1-cyclohexene two monoaddition products of thiolacetic acid have been isolated and characterized. The ratio of the two products indicates two parts of adduct to the cyclohexene double bond to three parts of adduct to the vinyl group double bond are produced in the addition reaction.

Résumé

Le 4-vinyl cyclohexène-1 et le *d*-limonène ont été transformés en dimercaptans par addition d'acide thioacétique et hydrolyse subséquente. Ces dimercaptans ont été additionnes aux dioléfines non-conjugées initiales et fournissent des polymères fortement visqueux de point de fusion bas. Dans le cas du 4-vinyl cyclohexène-1 deux produits de monoaddition de l'acide thioacétique ont été isolés et caractérisés. Le rapport des deux produits indique deux additions à la double soudure cyclohexénique pour trois additions à la double soudure vinylique.

Zusammenfassung

4-Vinylcyclohexen-1 und *d*-Limonen wurden durch Addition von Thiolessigsäure und darauffolgender Hydrolyse in Dimerkaptane verwandelt. Diese Dimerkaptane wurden zu den ursprünglichen, nicht-konjugierten Diolefinen zugefügt, und ergaben niedrig schmelzende, hochviskose Polymere. Im Falle von 4-Vinylcyclohexen-1 wurden zwei Monoadditionsprodukte von Thiolessigsäure isoliert und charakterisiert. Das Verhältnis der beiden Substanzen zeigt, dass in der Additionsreaktion zwei Teile Addukt zu der Cyclohexen-Doppelbindung zu drei Teilen Addukt zur Vinylgruppen-Doppelbindung erzeugt werden.

Received January 4, 1957