2-octanone,[22] b.p. 61–62° (7 mm.), n^{20}_D 1.4230, d^{20}_{20} 0.8328; *MR* obsd. 43.61, *calcd.* 43.81. A characteristic carbonyl band at 5.82 μ was shown in the infrared spectrum by this material.

The product gave a yellow 2,4-dinitrophenylhydrazone, m.p. 61.8–62.3° (ethanol), and a semicarbazone, m.p. 131.5–132.5° (ethanol).

DL-2,6-Dimethyl-2-octanol (IV). (A) Grignard Reaction on DL-6-Methyl-2-octanone.—A Grignard reagent was prepared from methyl iodide (14.2 g., 0.1 moles) and magnesium shavings, (3.65 g., 0.15 moles) in ether (200 ml.). With stirring added DL-6-methyl-2-octanone (10 g., 0.07 mole) in ether (50 ml.) over 1 hr. Stirred an additional 2 hrs. and then added satd. ammonium chloride until a clean separation of salts occurred. The salts were filtered and washed with ether (50 ml.). The combined ether layers were dried, filtered and distilled. There was obtained 7.0 g. (62.4%) of DL-2,6-dimethyl-2-octanol,[23] b.p. 75–76° (7.0 mm.), n^{20}_D 1.4336, d^{20}_{20} 0.8273; *MR* obsd. 49.57, calcd. 49.93. A characteristic hydroxyl band at 2.96 μ in the infrared spectrum was shown by this product.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.83; H, 13.92. Found: C, 75.32; H, 13.61.

There was obtained a phenylurethane of m.p. 84.0–85.0° (petr. ether).

Anal. Calcd. for $C_{16}H_{27}NO_2$: C, 73.60; H, 9.81; N, 5.29. Found: C, 73.61; H, 9.24; N, 5.61.

B. Reduction of Myrcenol.—Myrcenol (15.4 g., 0.10 mole) in absolute ethanol (70 ml.) was hydrogenated in the presence of 5% platinum–charcoal catalyst (0.5 g.) at room temperature and 3 atm. After the hydrogen uptake had ceased (2.5 hr., 98% theory) the catalyst was filtered off and the filtrate distilled through the modified Podbielniak column. There was obtained 13.4 g. (85%) of tetrahydromyrcenol, b.p. 83° (12.0 mm.), n^{20}_D 1.4332, d^{20}_{20} 0.8275. The infrared spectrum was identical with the spectrum of authentic DL-2,6-dimethyl-2-octanol. A phenylurethane, m.p. 83.5–84.5°, failed to depress a sample of authentic DL-2,6-dimethyl-2-octanol phenylurethan.

Acknowledgments.—The authors wish to express their appreciation to Dr. David Davidson of Brooklyn College for valuable discussions during the course of this work. We are also grateful to Mr. Erwin Sommer of our analytical department for infrared and ultraviolet determinations.

EAST RUTHERFORD, N. J.

---

[22] Sutherland has obtained a partially active 6-methyl-2-octanone b.p. 70–71° (10 mm.), n^{25}_D 1.420, d^{25}_4 0.822, $[\alpha]_D$ +1.4° (not optically pure) by the ozonolysis of partially active 2,6-dimethyloctene-1. He also reports a 2,4-dinitrophenylhydrazone, m.p. 61–62°, and semicarbazone, m.p. 130.5–131.5°. The above constants and the derivatives are in excellent agreement with the DL-isomer in this work. M. D. Sutherland, THIS JOURNAL, **75**, 5945 (1953).

[23] Sutherland, *cf.* ref. 22, has reported a partially active 2,6-dimethyl-2-octanol. This alcohol was obtained from a chloride prepared from 2,6-dimethyl-2-octene, $[\alpha]^{25}_D$ +2.44°. He reports b.p. 80.5° (10 mm.), n^{25}_D 1.4220, d^{25}_4 0.8023, phenylurethan, m.p. 83–83.5°.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

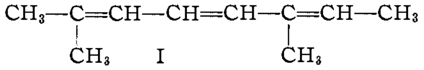
Polyalloöcimene[1]

BY C. S. MARVEL, P. E. KIENER[2] AND E. D. VESSEL

RECEIVED MARCH 27, 1959

Alloöcimene has been polymerized to a linear soluble polymer by use of triisobutylaluminum–titanium tetrachloride catalyst. The tentative structure and some properties of the polymer are discussed.

The recent note by Jones[3] describing the acid-catalyzed cyclopolymerization of alloöcimene (2,6-dimethyl-2,4,6-octatriene) (I) has prompted us to report work which has been done in this Laboratory on the polymerization of this triene by a triiosbutylaluminum–titanium tetrachloride catalyst system. In view of the published work on this catalyst system,[4] it is surprising that such a substituted triene can be converted to a high polymer with this catalyst.



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH=CH-\underset{CH_3}{\underset{|}{C}}=CH-CH_3$$

I

Alloöcimene which has been distilled over sodium in a nitrogen atmosphere readily polymerizes in heptane solution containing a catalyst prepared from a solution of three moles of triisobutylaluminum to one mole of titanium chloride. The polymerization goes best at about −15° and yields a white, fibrous, soluble polymer melting over the range of 120-154° which has an inherent viscosity of 1.0-1.2. The polymer is sensitive to oxygen, but if stablized with a little phenyl-β-naphthlyamine it can be stored for as much as a year without change as evidenced by the infrared spectrum.

Titration of the polymer with perbenzoic acid has demonstrated that two double bonds remain in the polymer for each ten carbon recurring units. The infrared spectrum shows strong bands at 970-965 cm.$^{-1}$ which are characteristic of *trans*-olefins and also at 1660-1650 cm.$^{-1}$ which are characteristic of double bonds. The ultraviolet spectrum of the polymer shows a λ_{max} at 245 mμ with an extinction coefficient of 5549. This λ_{max} is somewhat higher than would be expected for a simple conjugated system of double bonds which usually shows a λ_{max} of 232. The low extinction coefficient supports the view that this conjugated structure does not occur in every recurring unit.

Pyrolysis of a sample of the polymer by heating it to 205–210° gave about a 70% yield of alloöcimene which was identified by its infrared absorption spectrum.

Ozonolysis of the polymer gave 57-58% of the theoretical yield of acetone and 22% of the theoretical yield of glyoxal based on a C_{10} recurring unit. There was also obtained a low molecular weight polyaldehyde (inherent viscosity 0.05) corresponding to the composition (C_5H_8O). The yield of acetone is such that it seems probable the isopropylidene group is not affected by the polymerization.

---

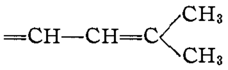
[1] This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.

[2] Fellow, Fundacion Creole, Caracas, Venezuela.

[3] J. F. Jones, *J. Polymer Sci.*, **33**, 513 (1958).

[4] For a review, see J. K. Stille, *Chem. Revs.*, **58**, 550 (1958).

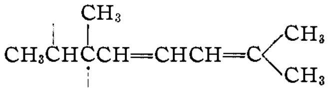
The isolation of 22% of glyoxal shows that at least that ratio of the recurring unit must contain the grouping



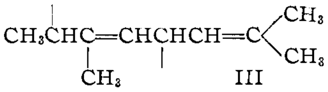
$$=CH—CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$$

and this would account for the ultraviolet spectrum of the polymer. The polymeric aldehyde $(C_5H_8O)_n$ shows two C–CH_3 groups per C_5-unit. This evidence thus suggests the recurring unit II in the polymer.

Since the isopropylidene group remains in the polymer, the second possible recurring unit could involve a 1,4-type of polymerization to give the recurring unit III. If these two units are present to the extent of about 40–50% of II and 60-50% of III, the experimental observations reported above can be explained. The exact manner of these groups and the exact ratio will have to be determined by further work.



II



III

The polyalloöcimene which we have prepared is amorphous or of a very low degree of crystallinity. Clear and fairly tough films can readily be prepared from it by hot pressing at 150° using a platen pressure of 500 lb. for one-half minute.

A comparison of some properties of such a pressed film with corresponding films of Marlex (Phillips Petroleum Co. polyethylene) and Hifax (Hercules Powder Co. high density polyethylene) is given in Table I. Polymer film strips one-half inch wide and one inch in length were tested on a model TTB Instron tester at an elongation rate of 10% per minute.

TABLE I

SOME PROPERTIES OF POLYALLOÖCIMENE FILMS

	Polyallo-ocimene[a]	Marlex	Hifax
Tensile strength at break (lb. per sq. inch)	4053	2500–4200	2000–4000
Elongation, %	3.1	680–1200	400–1000
Modulus (lb. per sq. inch)	181,880	120,000	80,000

[a] Average of five determinations.

Experimental

Commercial alloöcimene supplied by the Naval Stores Division of the Glidden Co. was distilled repeatedly under reduced pressure through a long column of glass helices and the fraction boiling at 80–82° at 15 mm. was collected. This fraction was then distilled from sodium wire in a nitrogen atmosphere before use in the polymerization experiments. The ultraviolet spectrum showed three peaks: λ_{max} 274 (ϵ 41,577), 267 and 286 mμ. The literature[5] describes the λ_{max} at 278 mμ with extinction coefficient at 42,871. This indicates our monomer was about 96–97% pure. Polymer formation was not satisfactory with monomer which was less pure than this as determined by the ultraviolet spectrum.

Polymerization.—The catalyst was prepared by dissolving 0.277 g. of triisobutylaluminum (Hercules Powder Co. product) in 20 ml. of dry heptane and then adding 0.085 g. of titanium tetrachloride. The mixture was then cooled to −15° and 20 ml. of pure alloöcimene (previously cooled to −15°) was added by injection through a rubber gasket. The catalyst solution was prepared and handled in a dry-box filled with highly purified nitrogen. The polymerization mixed was allowed to stand at −15° for three days. The reaction mixture was then poured into about 150 ml. of methanol. The polymer was isolated, redissolved in benzene and again precipitated by pouring into excess methanol to which had been added a few drops of a saturated solution of phenyl-β-naphthylamine in methanol. The polymer was collected on a filter and washed with more methanol (containing a little antioxidant). The polymer was purified by repeating this process two or three times and then it was finally dried at 50° under reduced pressure. The conversion was about 96%. The polymer starts to soften at about 120° and becomes completely liquid at about 145°.[6] The inherent viscosity determined in an Ostwald-type viscosimeter on a solution of 0.25 g. of polymer in 100 ml. of benzene varied from 1.0 to 1.2 in different samples. The ultraviolet absorption was measured in cyclohexane and showed λ_{max} 244–245 mμ, ϵ 5549. The infrared spectrum (chloroform solution) showed peaks at 1660–1650 and 970–965 cm.$^{-1}$ (Fig. 1).

Some of the many experiments on polymerization are described in Table II. Unless noted otherwise 20 ml. of monomer in 20 ml. of heptane was used with 0.277 g. of triisobutylaluminum and 0.085 g. of titanium tetrachloride molar ratio (Al/Ti = 3.2).

TABLE II

POLYMERIZATION OF ALLOÖCIMENE

Sample	Purity of monomer, %, found by ultraviolet absorption	Temp., °C.	Conversion, %	Viscosity of polymer
V-11	..	25	79.3	0.51
V-12	..	−15	77.5	1.12
A-3	90	−15	No polymer	
A-4	95	−15	87.5	..
PA-2	99	−15	90.7	..
PA-3	97	−15	94.7	1.01
PA-4[a]	93	−18	..	0.94
PA-5	About 100	−18	96	1.2

[a] This was a 5-g. run of alloöcimene with proportionate amount of catalyst. Changing the Al/Ti ratio from 3/1 to 1/1 always led to a polymer of lower viscosity (0.2 to 0.4).

Titration with Perbenzoic Acid.—The standard perbenzoic acid solution was prepared by the method of Kergomard and Bigou[7a] and the titration was performed by the procedure of Kolthoff and Lee.[7b]

A 75-ml. sample of perbenzoic acid solution in chloroform-benzene mixture was diluted to 100 ml. and used for titration to determine its strength. Then two solutions containing known quantities of polymer (PA-2) and the same amount of perbenzoic acid were prepared and titrated after being allowed to stand.

The results are summarized in Table III.

It is often found that more perbenzoic acid than the theoretical amount is used in such titrations.[8] Longer standing of the oxidation mixtures did not change the results.

Ozonization of Polyalloöcimene.—A solution of 5 g. of polymer (PA-3) in 250 ml. of dry methylene chloride was cooled to −15 to −20° and a current of ozonized oxygen containing 4–5% of ozone was passed through the solution for about 13 hours. The solvent was then removed under reduced pressure and the residue was dissolved in 60 ml. of glacial acetic acid. A suspension of 8 g. of zinc dust in water was added slowly with vigorous stirring and the

---

[5] R. T. O'Connor and L. A. Goldblatt. *Anal. Chem.*, **26**, 1726 (1954); W. Alder, A. Dreike, H. Espenbach and W. Wicker, *Ann.*, **609**, 1 (1957).

[6] All melting points recorded in this paper are uncorrected.

[7] (a) A. Kergomard and J. Bigou, *Bull. soc. chim. France*, 486 (1956); (b) I. M. Kolthoff and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947).

[8] W. R. Bragg, *Bull. soc. chim.*, **19**, 911 (1952).

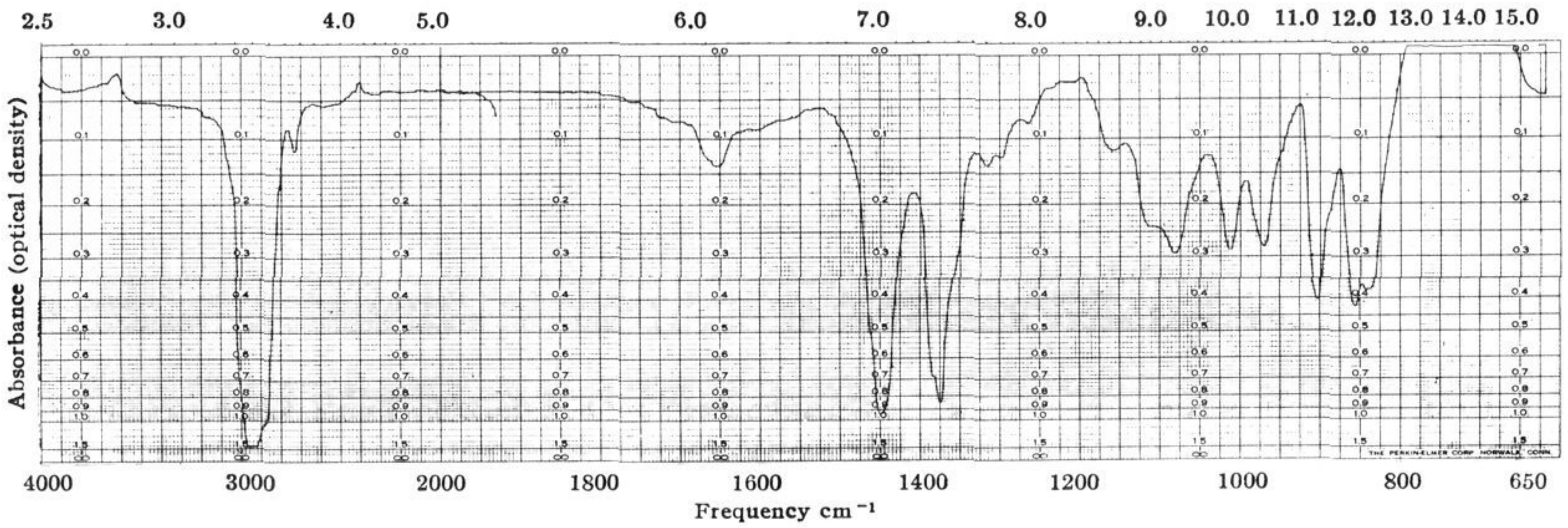


Fig. 1 (upper).—Polyalloöcimene.

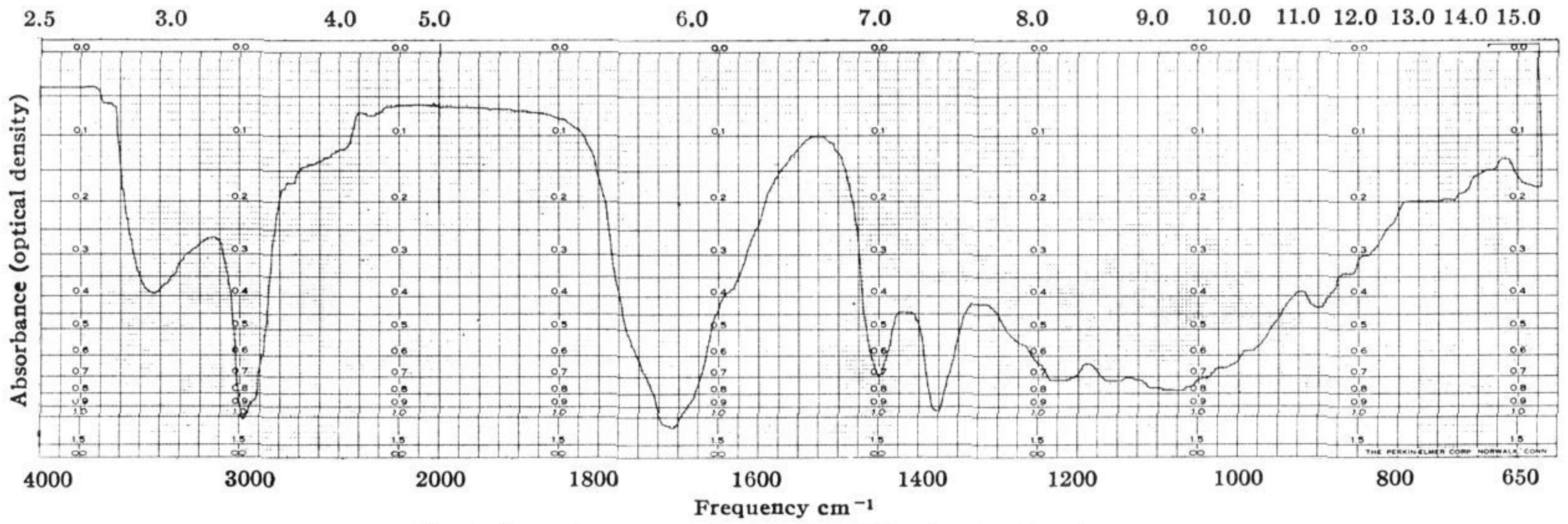


Fig. 2 (lower).—6-month old air oxidized polyalloöcimene.

reaction mixture was cooled. A slow stream of nitrogen was passed through the solution and a reflux condenser, then through a cold trap cooled with Dry Ice and finally into a second trap containing a 2,4-dinitrophenylhydrazine solution. The reaction mixture was stirred and warmed gently and then finally heated under reflux for one hour.

TABLE III

TITRATION OF POLYALLOÖCIMENE WITH PERBENZOIC ACID

Solution	Amt. titrated, ml.	Time, hr.	Ml. 0.1 *N* $Na_2S_2O_3$	Moles perbenzoic acid per 1 mole of polymer units
Perbenzoic acid	10	0	27.51	..
	10	16	27.04	..
Perbenzoic acid + 1.3326 g. of polymer PA-2	10	16	2.95	2.45
Perbenzoic acid + 1.3732 g. of polymer PA-2	10	16	2.81	2.39
Perbenzoic acid	10	24	26.14	..
Perbenzoic acid + 1.3326 g. of polymer PA-2	10	24	2.67	2.40
Perbenzoic acid + 1.3732 g. of polymer PA-2	10	24	2.61	2.33

In the cold trap was collected 1.008 g. of a liquid which was identified as acetone by vapor phase chromatography and by conversion to a 2,4-dinitrophenylhydrazone melting at 124–125°. In the second trap 0.9 g. of crystalline 2,4-dinitrophenylhydrazone of acetone was obtained. The total calculated yield of acetone was thus 1.228 g. (57.5% of the theory based on the C_{10} recurring unit). The residue in the reaction flask after distillation of the acetone yielded 2.8 g. of a brown polymeric resin which was not further characterized.

In a second ozonization experiment 1 g. of polymer (PA-3) in 250 ml. of dry ethyl acetate was ozonized with a 4–5% ozone stream in oxygen at room temperature for four hours. The ozonide was cleaved at room temperature with hydrogen (20 atmospheres) in the presence of a palladium catalyst.[9]

The reduced mixture was slightly heated while a current of nitrogen was passed through it to carry volatile products into a 2,4-dinitrophenylhydrazine solution. From this solution was obtained a crystalline precipitate (m.p. 105–110°) which on recrystallization gave 0.82 g. of acetone 2,4-dinitrophenylhydrazone (m.p. 124–125°). No attempt was made to isolate all of the acetone in this run.

The ethyl acetate solution remaining after removal of the acetone was evaporated. The residue was taken up in a few ml. of methanol and this solution added to a 10% solution of 2,4-dinitrophenylhydrazine. The precipitate which formed was submitted to paper chromatography[10] and shown to be a mixture of a little acetone 2,4-dinitrophenylhydrazone, some unchanged reagent and glyoxal 2,4-dinitrophenylhydrazine with one unidentified compound of very low R_f. Recrystallization of the precipitate from pyridine and washing with methanol gave 0.174 g. of a crystalline solid, m.p. 292°. When this material was mixed with authentic glyoxal 2,4-dinitrophenylhydrazone the mixture melted at 288°. The yield of derivative corresponds to 22% of glyoxal based on the C_{10} polymer unit. Further recrystallization of this material raised the melting point to 312° and its mixture with the known glyoxal derivative melted at 307°. No other products were found.

A third ozonization experiment used 5 g. of polymer (PA-3) in 250 ml. of methylene chloride containing 1% of pyridine[11] at −10 to −15°. The ozonide solution was decomposed with zinc dust and acetic acid and the acetone distilled off through a condenser in a stream of nitrogen as before and collected in a 2,4-dinitrophenylhydrazone solution. From this operation 2.889 g. (44% based on oxidized

---

[9] M. Busch and H. Stöve, *Ber.*, **49**, 1064 (1916).

[10] W. J. Schmidt, E. J. Marconi and W. F. O'Connor, *Anal. Chem.*, **28**, 249 (1956).

[11] G. Slomp and J. L. Johnson, THIS JOURNAL, **80**, 915 (1958).

polymer) of acetone 2,4-dinitrophenylhydrazone was isolated.

The residual solution after removal of acetone was evaporated and taken up in ether. The ether solution was washed, dried and the solvent removed. The residual polymeric solid was only partially soluble in methanol. It was dissolved in benzene and the polymeric residue was precipitated by pouring this solution into methanol. About 1.2 g. of polymeric material was recovered. This had an infrared spectrum much like polyalloöcimene except there was a pronounced absorption at 1260 cm.$^{-1}$ (epoxide).

The methanolic solution was poured into water and a yellowish resin was precipitated. This was taken up in benzene and reprecipitated by pouring the benzene solution in heptane. After five solutions and reprecipitations the substance was freeze-dried to yield 0.87 g. of a white substance, m.p. 90–93°. This polymer gave a strong band in the infrared at 1725 cm.$^{-1}$ (aldehyde) and a medium band at 2720 cm.$^{-1}$. The yield of polymeric aldehyde was 37% based on the oxidized polymer; carbon methyl calcd. for 2 C–CH$_3$ per C$_5$ unit 35.7, found 34.8. The inherent viscosity (0.191 g. in 100 ml. of benzene at 25°) is 0.05.

Anal. Calcd. for $(C_5H_8O)n$: C, 71.4; H, 9.5. Found: C, 71.9; H, 9.1.

The water washings of the original ether solution and the water used to precipitate the polymer from methanol was treated with 2,4-dinitrophenylhydrazine and a derivative was obtained. Recrystallization from pyridine gave a product melting at 304° which showed a slight melting point depression when mixed with an authentic glyoxal derivative.

Aging Polyalloöcimene in Air.—A sample of polymer which was a white, fibrous solid melting at 128-145° and with an inherent viscosity of 1.0 was allowed to stand in a closed bottle in the laboratory for six weeks. It then was a yellow, sticky solid which showed some solubility in alcohol, whereas the original polymer was alcohol insoluble. The degraded polymer had an inherent viscosity of only 0.12 and it softened at 110° and seemed to decompose at 140°. The degraded polymer gave very little ultraviolet absorption at 245 (ϵ 3120) and had weak bands in the infrared at 1710 and 1670 cm.$^{-1}$ which were not present in the spectrum of the original polymer.

Another sample of polymer which stood for five months changed into a sticky, yellow solid. This product had a medium strong band in the infrared at 3415 cm.$^{-1}$ and a strong wide band at 1720–1715 cm.$^{-1}$ which were absent in the spectrum of the original polymer. The oxidized polymer showed a medium band at 905 cm.$^{-1}$ which is present in the original polymer, but all other bands below 1300 cm.$^{-1}$ in the original polymer seemed to have disappeared or to be obscured by broad absorption (Fig. 2).

Acknowledgments.—The microanalyses were performed by Mr. Jozsef Nemeth of the University of Illinois. Carbon methyl determinations were made by Clark Microanalytical Laboratory, Urbana, Ill. The infrared spectra were determined by Mr. Paul McMahon, University of Illinois, and Mr. J. Chiu determined the ultraviolet spectra.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Synthesis and Polymerization of Methyl Substituted Vinylcyclohexanes[1]

BY C. G. OVERBERGER AND J. E. MULVANEY[2]

RECEIVED MARCH 13, 1959

The synthesis of the *cis* or *trans* isomers of 2-methyl-, 3-methyl- and 4-methylvinylcyclohexanes are described. The latter two compounds were polymerized to linear crystalline high polymers using aluminum triisobutyl and titanium tetrachloride in heptane.

A number of crystalline α-olefin polymers have now been reported using Ziegler[3]–Natta[4] catalyst systems, and a comparison of their physical properties has been reported. In a series proceeding from polypropylene to polypentene-1, the melting point of the crystalline polymer decreases with increasing size of the side chain up to polyhexene-1 which is completely amorphous.[3] However, a six-carbon and even a seven-carbon α-olefin can be obtained crystalline if the side chain is branched as in the case of 3-methylhexene-1 and 4-methylpentene-1.[3] Another interesting aspect of the α-olefin polymers is that branched side chains usually result in higher melting points than their linear side-chain counterparts. Thus, for example, polypentene-1 melts at 80° whereas poly-3-methylbutene-1 melts at 245°.[3]

A crystalline polymer has also been prepared from a racemic monomer, 4-methylhexene-1. The polymer of this material is isotactic as far as the carbon atoms of the main chain are concerned. With respect to the asymmetric centers on the side chain, further cases of stereoisomerism are possible depending upon this order of steric regularity. Natta has suggested that the high solubility and the poor definition in X-ray photographs indicates a statistical distribution of the asymmetric side-chain molecules.[3]

X-ray diffraction data,[4,5] obtained on Natta's polypropylene, polybutene-1 and polystyrene, as well as the crystalline vinyl isobutyl ether prepared by Schildknecht,[6] showed a distinct identity period along the chain of 6.5-6.7 Å. Both Bunn[7] and Natta[4,5] concluded that this repeating unit for polypropylene involved three monomer units linked exclusively by head to tail orientation. Other α-olefin polymers give repeat distances of variable size. The polymer chain backbones exist in skew conformations which lead to helical chains in the isotactic configuration.[4,5,7]

It seemed that it would be of interest to compare the properties, *e.g.*, melting point, crystallinity, of some vinylcycloalkanes with the linear or branched-chain α-olefins. Early work in these laboratories has shown that vinylcyclohexane may be polymerized, using aluminum triisobutyl–titanium tetrachloride, to a high molecular weight crystalline polymer. It was decided, therefore, to prepare

---

(1) This is the 18th in a series of papers on new monomers and polymers. For the previous paper in this series see C. G. Overberger and P. V. Bonsignore, THIS JOURNAL, **80**, 5431 (1958).

(2) Abstracted in part from the Doctoral Thesis of J. E. Mulvaney, Polytechnic Institute of Brooklyn, June, 1959.

(3) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

(4) G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

(5) G. Natta, THIS JOURNAL, **77**, 1708 (1955).

(6) C. E. Schildknecht, *Ind. Eng. Chem.*, **40**, 2104 (1948).

(7) C. W. Bunn and E. R. Howells, *J. Polymer Sci.*, **16**, 307 (1955).