ampules and placed in the 100° thermostat. Samples were withdrawn periodically and the amount of decomposition and the composition of the remaining acid phthalate were determined as described above. The data for this experiment (Fig. 5, curve B) show that the composition of the acid phthalate mixture (65% *trans*, 35% *cis*) remained constant for the 55 hours that the reaction was observed.

Rearrangement of Fused *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate.—Carefully weighed samples (*ca.* 0.23 g.) of solid (−)I were sealed in ampules and immersed in the 100° bath. At measured time intervals samples were quantitatively transferred to 25.00-ml. volumetric flasks and diluted with chloroform to exactly 25 ml. at 25°. The rate of loss of optical activity was determined from the rotations of the chloroform solutions.

Samples of solid *dl*-I were used to study the decomposition and the isomerization. The acidity (decomposition) of the heated samples (*ca.* 0.3 g.) was determined by titration of aqueous acetone solutions to the phenolphthalein end-point. The increase in acidity (carboxyl groups) did not correspond to the formation of phthalic acid. For example, in 8 hours the number of carboxyl groups increased only 11.5%; however, a 28% yield of phthalic acid was isolated as follows. The contents of an ampule were extracted with chloroform and the insoluble phthalic acid collected on a filter and air-dried. This material was water insoluble and had a neutral equivalent of 78 (calcd. for phthalic acid 83).

Large samples (*ca.* 1 g.) of *dl*-I were used to study the rate of *cis–trans* isomerization. The remaining acid phthalate was separated from the phthalic acid and the composition of the binary mixture determined spectrophotometrically by the procedure described above for the rearrangement in acetonitrile. Typical data showing the change in composition with time are presented in Fig. 7.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Polymers. I. Synthesis of an All-*cis* Diene Polymer[1]

BY WILLIAM J. BAILEY[2] AND HAROLD R. GOLDEN[3]

RECEIVED APRIL 29, 1954

The cyclic diene, 1,2-dimethylenecyclohexane, was polymerized to a high molecular weight, all-1,4-, all-*cis* diene polymer. This polymer was a white crystalline solid, melting at 165° and possessing no rubber-like properties, even though it is very similar in structure to natural rubber.

Although much work has been published on the correlation of the structure and properties of condensation polymers,[4] no such comprehensive study has been reported for hydrocarbon polymers. Hydrocarbon polymers appeared to be an attractive field to study the effect of structure on properties since two complicating factors, hydrogen bonding and strong dipole interactions, are absent. Also, addition polymers of high molecular weight could be studied to eliminate further the additional complicating effect of molecular weight on the properties. With the number of variables thus reduced, it would appear much easier to develop a systematic correlation with hydrocarbon polymers than was possible with condensation polymers.

Natural rubber I appeared to be a logical starting point for this investigation, since its structure has been determined and found to be fairly simple. It is of further interest because natural rubber I is probably still the best available all-purpose rubber, even though many excellent special purpose elastomers have been developed. If other special purpose elastomers are to be discovered, knowledge of which structural features of natural rubber I are responsible for its excellent rubbery properties would be indeed helpful.

Natural rubber has been assigned a very regular structure composed of repeating isoprenoid units in which all the units are connected in a 1,4-, head-to-tail manner with the methyl groups always on the same side of the double bond.[5] All the double bonds have the *cis* structure; that is, the polymer chain enters and leaves from the same side of the double bond. Since there are relatively few structural features in this polymer, it should be possible to determine the relative importance of each in producing rubbery characteristics. The first clue to which feature was most important was available from a comparison of the structure of balata II (or gutta percha) with that of rubber. Balata II has been assigned a structure very similar to natural rubber, with the exception that the double bonds have the *trans* structure[6]; that is, the polymer chain enters and leaves from opposite sides of the double bond. Balata II is not a rubber at room temperature but is a hard, horny substance with a softening point at 60°,[6] while natural rubber maintains its rubbery properties to extremely low temperatures but will retain crystallites up to 25°.[5] This striking difference in the properties of these two polymers led to the widespread belief than any all-*cis* diene polymer would be a good rubber. It was considered of extreme importance, therefore, to synthesize an all-*cis* diene polymer in order to test this hypothesis.

Much energy has been spent in an effort to find experimental conditions that would permit simple dienes, such as 1,3-butadiene, to polymerize to an all-*cis* polymer or to a polymer with at least a high content of 1,4-*cis* units. However, the problem is extremely complex since butadiene can produce a polymer III consisting theoretically of a mixture of six structural units, as indicated in the diagram. Although experimental conditions will change the

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[1] Presented before the Division of Polymer Chemistry at the 117th National Meeting of the American Chemical Society, Detroit, Michigan, March, 1950; and the Elastomer Conference, Washington, D. C., May, 1949.

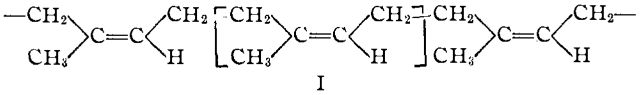
[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Atomic Energy Commission Fellow, 1949–1950.

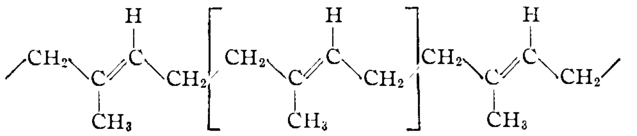
[4] (a) "High Polymers, Vol. I, Collected Papers of W. H. Carothers on High Polymeric Substances," Interscience Publishers, Inc., New York, N. Y., 1938; (b) R. Hill and E. E. Walker, *J. Polymer Sci.*, **3**, 609 (1948); (c) E. F. Izard, *ibid.*, **9**, 35 (1952).

[5] S. D. Gehman, *Chem. Revs.*, **26**, 203 (1940).

[6] K. H. Meyer, "High Polymers. IV. Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1950.



I



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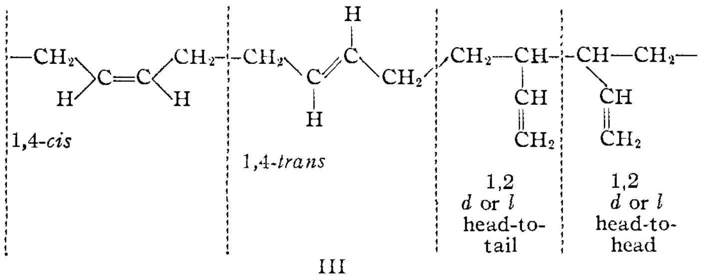
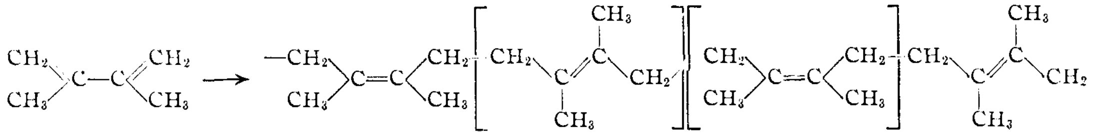
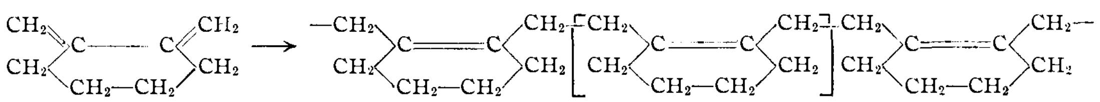


III



IV V

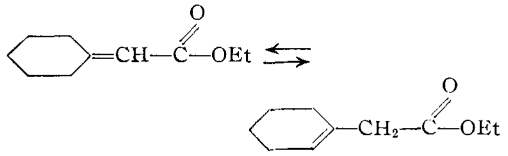


VI VII

relative amounts of these monomeric units, all known polybutadienes consist of a complex mixture of these units. Thus sodium polymerization will produce a polybutadiene rich in the 1,2-addition units[7] and polymerization at low temperature will increase the percentage of 1,4-*trans* units over that of a 50° emulsion polymerization.[7] Even though raising the temperature of an emulsion polymerization will increase the percentage of the 1,4-*cis* units in polyisoprene to as high as 30%,[8] it did not appear likely that experimental conditions for the formation an all-*cis* polymer from a simple diene could be found.

Since the introduction of substituents into butadiene also changes the proportion of these structural units, it seemed more probable that a diene could be designed that would produce an all-*cis* polymer. It has been shown, for instance, that chloroprene polymerizes to a polymer with a high proportion of 1,4-*trans* units[6] and 2,3-dimethylbutadiene (IV) produces a polymer V with less than 9% 1,2-addition.[9] IV appeared to be a promising model for a monomer to produce an all-*cis* polymer, since it is a hydrocarbon diene and produces a high molecular weight substance.

If some way could be found to produce a 2,3-disubstituted butadiene that would polymerize without the formation of the 1,4-*trans* unit, an all-*cis* polymer would be possible. Since a *trans* double bond is sterically impossible in a six-membered ring, the cyclic diene, 1,2-dimethylenecyclohexane (VI),[10] would not be expected to produce any 1,4-*trans* units when polymerized. Since VI is a 2,3-disubstituted butadiene related to IV, the polymer VII should be high molecular weight with very little 1,2-addition. In this case there is an additional driving force for 1,4-addition, since it has been shown that a double bond is considerably more stable *endo* rather than *exo* to a cyclohexane ring. Birch, Kon and Norris[11] showed that in the following pair of compounds



the equilibrium was far to the right, indicating that this double bond is more stable within the six-membered ring than even in conjugation with the carbonyl group. Thus, 1,2-dimethylenecyclohexane (VI) should produce a high molecular weight all-*cis* diene polymer with little or no 1,2-addition.

When 1,2-dimethylenecyclohexane (VI) was polymerized in a peroxide-catalyzed emulsion system, a high molecular weight polymer VII did result. Surprisingly enough, the polymer VII did not possess any rubbery properties but was a high-melting white crystalline solid. VII was almost completely insoluble and unswollen in cold or boiling benzene but was completely soluble in boiling toluene.

When the hot toluene solution of VII was cooled, the polymer crystallized out and could be filtered conveniently off. Thus it was possible to recrystallize polydimethylenecyclohexane (VII) by a procedure very similar to that used to recrystallize any simple organic solid. VII was not soluble enough in benzene at ordinary temperatures to determine its intrinsic viscosity. However, at 100° in decalin or chlorobenzene, VII has intrinsic viscosities of 0.38 to 0.59. Although no information was available in the literature concerning the relation of molecular weight of polymers and their intrinsic viscosities at 100°, it was found that a fractionated polystyrene sample with a molecular weight of 110,000[12] had an intrinsic viscosity of 0.48 in chlorobenzene at 100°. The poly-1,2-dimethylenecyclohexane (VII), there-

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[7] R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

[8] W. S. Richardson and A. Sacher, *J. Polymer Sci.*, **10**, 353 (1953).

[9] G. Salomon and C. Konigsberger, *ibid.*, **2**, 522 (1947).

[10] W. J. Bailey and H. R. Golden, THIS JOURNAL, **74**, 4780 (1953).

[11] S. F. Birch, G. A. R. Kon and W. S. G. P. Norris, *J. Chem. Soc.*, 1361 (1923).

[12] The authors are grateful to Dr. W. Heller for the sample of polystyrene which he had obtained from the Dow Chemical Co., Midland, Mich.

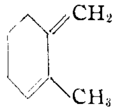
fore, probably possessed a molecular weight at least in the order of magnitude of 100,000.

When a melting point of poly-1,2-dimethylenecyclohexane was determined in a thin-walled capillary, the all-*cis* polymer underwent the transition from a white solid to a thin water-white liquid from 164.5 to 165.0°, although some shrinking was noted at 160°. That this melting point was a characteristic of the chemical structure of the polymer and not dependent on molecular weight was shown by the fact that samples of VII with intrinsic viscosities varying from 0.38 to 0.59 melted at the same temperature. The melting point was also independent of the method of polymerization, since a sample of VII, produced by the ionic polymerization of the cyclic diene VI, also had the same melting point.

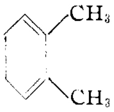
Infrared absorption[13] of VII showed no evidence of any terminal methylene groups formed by 1,2-addition. These physical data support the prediction that the polymer would be almost entirely composed of 1,4-addition units. Additional confirmatory evidence was obtained from the X-ray diffraction study on an oriented fiber. The X-ray diffraction pattern[14] showed that VII was a highly crystalline substance with a very regular structure. In order to explain this high crystallinity, the infrared spectrum, the low solubility in cold solvents, resistance to swelling, and the sharp, high melting point, it must be concluded that poly-1,2-dimethylenecyclohexane is a very regular polymer consisting only of repeating 1,4-*cis* units with no 1,4-*trans* units and little, if any, 1,2-addition. VII is then the first synthetic all-*cis* diene polymer.

Since the present work was originally reported,[1] a patent[15] has been issued which reported the polymerization of VI in a persulfate emulsion system but described the product only as "brittle resin" with no further characterization. In view of the highly unusual properties found in the present investigation, the description of the polymer in such general terms is indeed strange. The patent further reports the ionic polymerization of VI to produce an "oily polymer of value for use in drying oils, plasticizers and the like." Although low oily polymers can be prepared, this latter result is in sharp contrast to the high-melting crystalline solid obtained by the low temperature ionic polymerization reported in the present paper. The striking difference between the work of Wicklatz and Short and the present work can possibly be explained on the basis of the purity of the monomer used.

The fact that 1,2-dimethylenecyclohexane (VI) polymerizes to a high molecular weight product can be used not only as a confirmatory structure proof of the monomer VI, but also as an indication of its purity. The most likely impurities in VI produced by the pyrolysis of hexahydrophthalyl diacetate are the cyclic dienes VIII and IX. Neither of these two isomers of VI would be expected to polymerize to a high molecular weight product, since both monomers have hydrogens activated by a conjugated diene system. The propagating allylic free radical would exchange very frequently with the monomer in a chain-transfer reaction to produce only short chains. VIII and IX would be such efficient chain-transfer agents that even a small amount of either in a sample of VI would prevent the formation of a very high molecular weight polymer. Since VI did polymerize to a very high molecular weight, it may be concluded that the VI prepared by the pyrolysis of a diacetate is very pure. This is additional evidence that the pyrolysis of esters is an excellent method for the preparation of unsaturated compounds.



VIII



IX

The present work completely invalidates the hypothesis that any all-*cis* polymer would make a good rubber. Research is now in progress in this Laboratory to determine the reason for the striking difference between natural rubber (I) and poly-1,2-dimethylenecyclohexane (VII).

Experimental[16]

Emulsion Polymerization of 1,2-Dimethylenecyclohexane (VI).—In a 2-ounce screw-cap bottle were placed 10.0 g. of 1,2-dimethylenecyclohexane (VI), 0.50 g. of sodium stearate, 0.03 g. of potassium persulfate, 0.05 g. of lauryl mercaptan and 18.0 g. of water. The bottle was rotated end over end in a 55° water-bath for 24 hours, at which time the emulsion had broken. The mixture was acidified and the solid was filtered off, washed thoroughly and dried under vacuum to produce 8.5 g. (85% conversion) of the polymer VII. The 8.5 g. of polymer was dissolved in 1 liter of boiling toluene containing a trace of N-phenyl-β-naphthylamine and the solution was poured with rapid stirring into 3 liters of cold methanol to reprecipitate the polymer. The precipitate was filtered, washed with a solution of N-phenyl-β-naphthylamine and dried under vacuum to yield 7.5 g. of purified poly-1,2-dimethylenecyclohexane, m.p. 164.5–165.0°. Additional purification could be effected by dissolving the polymer in boiling toluene, filtering to remove any extraneous material, cooling to allow the polymer to crystallize out, filtering the precipitated polymer and treating as before. The melting point was determined by placing the polymer in a thin-walled capillary and heating the capillary in a melting point bath, in the same way that the melting point of any crystalline organic compound is determined. No visible change was noted below 160°, but at approximately this temperature shrinking occurred. Shrinking continued without any visible appearance of melting until the temperature reached 164.5°. At this temperature the polymer consisted of a solid white column with about half the original diameter but otherwise with very nearly the original appearance. Within a half of one degree the polymer passed from this white solid to a thin, water-white liquid which ran down the side of the capillary.

Ionic Polymerization of 1,2-Dimethylenecyclohexane (VI).—In a test-tube, 1.0 g. of 1,2-dimethylenecyclohexane (VI) was thoroughly mixed with approximately 5 g. of powdered Dry Ice and the mixture was cooled in additional Dry Ice. One drop of boron trifluoride etherate was added and the mixture was kept in the cold for 3 days before it was allowed to warm to room temperature over a 6-hour period. The solid polymer was filtered off and purified as described above to produce 0.1 g. of white, crystalline poly-1,2-dimethylenecyclohexane (VII), identical in all respects with the sample prepared above.

Addition of boron trifluoride gas to a sample of VI at room temperature produced a viscous oil.

Intrinsic Viscosity Determination.—Attempts to determine the inherent viscosity of VII at 25° in benzene failed because the polymer was almost completely insoluble under these conditions. Evaporation of 10 ml. of a saturated ben-

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(13) The authors are grateful to Dr. R. A. Spurr and Katheryn Gerdeman for the infrared absorption spectrum.

(14) The authors are grateful to Dr. H. N. Campbell, U. S. Rubber Co., Passaic, N. J., for the X-ray data on this polymer.

(15) J. E. Wicklatz and J. N. Short, U. S. Patent 2,600454 (1952).

(16) All melting points are corrected.

zene solution of VII produced less than 0.1 mg. of residue. Intrinsic viscosities were then determined by running the viscosities of chlorobenzene or decalin solutions of various concentrations of VII at 100°. For comparison, the intrinsic viscosity of a polystyrene sample[12] of 110,000 molecular weight was determined under identical conditions.

Sample	Intrinsic viscosity
A, emulsion VII	0.38
B, emulsion VII	.49
C, emulsion VII	.59
Standard polystyrene[12]	.48

X-Ray Diffraction Study.[14]—Oriented fibers were prepared by drawing out a melted sample of the polymer VII on a glass rod and gently stretching the fibers over a hotplate to 300 to 400% elongation. Examination of the X-ray diffraction pattern indicated that the poly-1,2-dimethylenecyclohexane (VII) was very highly crystalline. The unit cell was apparently monoclinic with the following constants: a = 11.75 Å.; b = 7.35 Å.; c = 10.38 Å.; β = 61°.

Infrared Absorption Spectrum.[13]—Attempts to prepare a transparent film of polydimethylenecyclohexane (VII) were not successful.[17] Since VII was not soluble in any common solvent at room temperature, infrared absorption spectrum was run on a mull of VII in mineral oil using a rock salt prism in a Perkin–Elmer model 12-C infrared spectrophotometer. No appreciable absorption was found in the 885–910 cm.$^{-1}$ region, which indicated little or no 1,2-addition.[18] Other interpretations of the absorption curve using model compounds will be reported later.

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[17] This failure to obtain a transparent film indicates that the second-order transition point of VII is below room temperature. An accurate determination of physical properties, including the second-order transition temperature for VII, is in progress and will be reported separately from another laboratory.

[18] W. S. Richardson and A. Sacher, *J. Polymer Sci.*, **10**, 353 (1953).

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. VIII. 1,2-Dimethylenecyclopentane[1]

BY WILLIAM J. BAILEY[2] AND WAYNE R. SORENSON[3]

RECEIVED FEBRUARY 3, 1954

By the use of a pyrolysis of a diacetate in the final step, 1,2-dimethylenecyclopentane (I) was synthesized in six steps, starting from malonic ester and trimethylene dibromide. The structure of this diene was proved by ultraviolet absorption and conversion through Diels–Alder reactions to solid derivatives.

Since the pyrolysis of esters gave excellent results in the synthesis of 1,2-dimethylenecyclohexane[4] and substituted 1,2-dimethylenecyclohexanes,[5] it was of interest to apply this method to the synthesis of other cyclic dienes. The synthesis of 1,2-dimethylenecyclopentane (I) was of special interest since the five-membered ring is fairly rigid and would produce an almost planar *cis*-diene. Poly-1,2-dimethylenecyclohexane,[6] even though it possessed an all-*cis* configuration very similar to natural rubber, was a high-melting crystalline solid. One possible reason for the difference in properties between these two all-*cis* polymers was the increase in steric hindrance to rotation due to the presence of the six-membered ring. Arnold and co-workers[7] showed that the steric requirement of a five-membered ring is considerably less than that of a six-membered ring. 1,2-Dimethylenecyclopentane (I), therefore, is of further interest because polymerization should produce an all-*cis* diene polymer with less steric hindrance than poly-1,2-dimethylenecyclohexane.

The cyclic diene I was synthesized in six steps from diethyl malonate and trimethylene dibromide (II). Perkin[8] prepared tetraethyl 1,1,5,5-pentanetetracarboxylate (IV) from diethyl malonate but did not report a yield. By following his directions, only a 25% yield of IV could be obtained under optimum conditions and decomposition of the unreacted halogen compounds during distillation was very troublesome. Cason and Allen[9] studied the reaction of diethyl malonate and II to form diethyl 1,1-cyclobutanedicarboxylate. Extrapolation of their results showed that if 12 moles of malonic ester reacted with 2 moles of sodium ethoxide and 1 mole of the dibromide II an 81% yield of the tetraester IV (based on II) could be obtained. Apparently the large excess of malonic ester suppressed the formation of the monoalkylated malonic ester anion III and therefore increased the concentration of enolate of malonic ester, giving a higher yield of the desired tetraester IV.

Perkin[10] converted the tetraester IV to the tetraethyl 1,1,2,2-cyclopentanetetracarboxylate (V) and subsequently[11] converted this tetraester to 1,2-cyclopentanedicarboxylic acid (VII). He did not report the yield of either reaction. When the Perkin method, which used iodine instead of bromine, was modified by not isolating the intermediate tetraester V, and distilling off the ethyl acetate formed by ester interchange through a distillation column, the *trans*-1,2-cyclopentanedicarboxylic acid (VII) was produced in an over-all yield of 70% in a very clean-cut reaction.

VII, which was only slightly soluble in ether, was reduced with lithium aluminum hydride by adding VII to the reaction flask by means of an exhaustive ether extractor. If care was taken to heat the reaction mixture for 14 hours after the addition was complete and to avoid strong acids in the hy-

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[1] Previous paper in this series, THIS JOURNAL, **76**, 3009 (1954).

[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Office of Naval Research Fellow, Wayne University, 1949–1951; University of Maryland, 1952–1953; Union Carbide Fellow, University of Maryland, 1951–1952.

[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[5] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

[6] W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

[7] R. T. Arnold, V. J. Webers and R. M. Dodson, *ibid.*, **74**, 368 (1952), and earlier papers.

[8] W. H. Perkin, Jr., *J. Chem. Soc.*, **51**, 242 (1882).

[9] J. Cason and C. F. H. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

[10] W. H. Perkin, Jr., *Ber.*, **18**, 3246 (1885).

[11] W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 587 (1894).