

sparingly soluble in water) obtained through sodium-carbonate extraction mentioned in the preceding paragraph was acidified with dilute hydrochloric acid to produce the free acid, X. This glistening white crystalline substance was recrystallized from 50% aqueous ethanol and dried in vacuo at room temperature, m.p. 198°. This keto-acid, X, has also been obtained by oxidizing the parent keto-aldehyde, IX, described in the preceding paragraph, with hydrogen peroxide in dilute acetic acid.

Anal. of X. (See Table II.)

In order to demonstrate that this acid, X, contains a keto group it was treated in the conventional manner³³ with hydroxylamine hydrochloride, and a white crystalline material was obtained with an m.p. 211–212°. Nitrogen analysis on this material corresponds to the derived ketoximino-hydroxamic acid.

Anal. Calcd. for C₂₀H₂₄N₂O₃: N, 8.23. Found: N, 8.32.

Condensation derivatives of p-(p-isopropyl- ω , ω -dimethylphenacyl)benzaldehyde (IX). The keto-aldehyde (IX) has by conventional methods³³ been converted into the dihydrazone derivative (XII), the dioxime (XIII), and the mono-2,4-

dinitrophenylhydrazone (XI). The melting points and the analyses for these derivatives are given in Table II.

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Some of the microanalyses reported in this paper were done at the Clark Microanalytical Laboratory, Urbana, Ill. Analyses reported in this paper of compounds containing relatively high N/C ratio have been performed in our own laboratories by Mr. Ratio Jones using a specially prepared combustion train, Huggins and Jones, *Unpublished results*; Ratio Jones, Master's thesis, Atlanta University, June 1954.

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Polymers II. Polydimethyleneacetylene^{1,2}

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Condensation of 1-chloro-4-bromo-2-butyne with magnesium produced a mixture of soluble and insoluble polymers. Extraction of this mixture produced a low yield of soluble polydimethyleneacetylene, m.p. above 400°, with a molecular weight of 1000 to 2000. The structure of the polymer was proved by analysis, oxidation to succinic acid, and hydrogenation to polymethylene. This result emphasizes the fact that symmetry greatly promotes crystallinity of polymers and strongly increases their melting points.

In order to determine the correlation between the chemical structure and the physical properties of hydrocarbon polymers the synthesis of a series of polymers of unusual but known chemical structure has been undertaken. Hydrocarbon polymers were chosen for this study since complicating factors, such as hydrogen bonding and strong dipole interactions, would be absent. In a previous paper the synthesis of an all-*cis* diene polymer, poly-1,2-dimethylenecyclohexane, related in structure to natural rubber, was reported. In contrast to natural rubber, the polydimethylenecyclohexane was a high melting crystalline solid. This result emphasized the fact that small changes in structure often have a very marked effect on the physical properties of polymers.

Since the phenomenon of *cis-trans* isomerism in diene polymers introduces several complications, it was of interest to study the effect of a symmetrical triple bond on the properties of a hydrocarbon

polymer, particularly a polymer in which the triple bond essentially replaces a double bond. The simplest case would be polydimethyleneacetylene (I), an analog of an all-1,4 polybutadiene. This polymer I was of special interest since it had been predicted to be a good low temperature rubber on the basis that the polymer chain would be free to rotate at low temperatures. One might expect that the acetylene group, which has no substituents and is symmetrical, would offer no steric hindrance to rotation about the adjacent single bonds. The acetylene polymer I was of further interest in that it might serve as a starting material for the synthesis of an all-*cis* or an all-*trans* polybutadiene.

The starting material for the preparation of polydimethyleneacetylene was 1-chloro-4-bromo-2-butyne (II).⁵ When the mixed dihalide II was vigorously stirred with a large excess of magnesium, a Grignard reagent easily formed. When it was allowed to stand, this Grignard coupled with itself to form an insoluble polymer mixture III. The untreated mixture contained a Grignard as an end group or some adsorbed Grignard reagent. When the polymerization was carried out in the usual

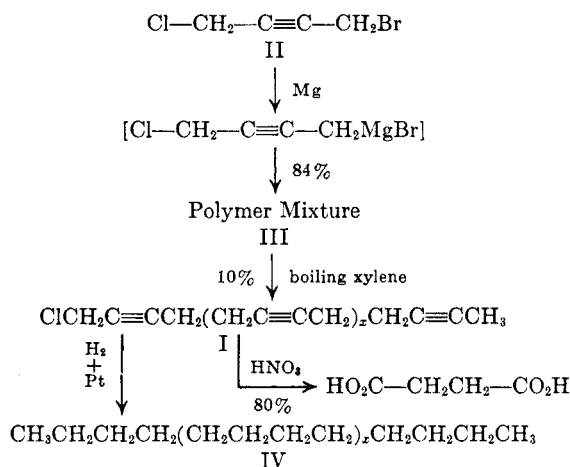
(1) Previous paper in this series, *J. Am. Chem. Soc.*, **76**, 5418 (1954).

(2) Presented before the Division of Polymer Chemistry at the 118th National Meeting of the American Chemical Society, Chicago, Ill., September 1950.

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(5) W. J. Bailey and E. J. Fujiwara, *J. Am. Chem. Soc.*, **77**, 165 (1955).



way, the formation of this insoluble precipitate began when about one third of the dihalide II had been added. The final products appeared to be identical, even if the addition of halide was stopped at this point. Titration of an aliquot of the reaction mixture indicated that, when all of the halide had been added, an 18% yield of soluble Grignard reagent was present. The powdery polymeric III was infusible and not completely soluble in any solvent tested, even at very high temperatures. The polymer was stable for indefinite periods when it was stored under nitrogen but it absorbed oxygen from the air quite rapidly.

In order to characterize the polymer mixture III, a separation was made into an insoluble fraction IIIa and a soluble fraction I. Thus when the polymer III was extracted with hot solvents, such as cumene, methylnaphthalene or biphenyl, approximately 10% of the polymer III dissolved. Boiling xylene, however, proved to be the most convenient solvent. When the hot solution was cooled, almost all of the dissolved polymer reprecipitated, but, for convenience in filtering, methanol was added to the cold solution. The product, soluble polydimethyleneacetylene (I), was a light-cream-colored powder. Although the polymer I was completely soluble in boiling xylene, 100 ml. of the hot solvent was required to dissolve 0.1 g. When a melting point determination was performed in a sealed tube in an atmosphere of carbon dioxide, no visible change occurred below 400° and the sample of I could be recovered unchanged. At temperatures above 400° the sample darkened somewhat but did not appear to soften or to melt even at 550°.

The structure of the soluble polydimethyleneacetylene (I) was indicated by a series of chemical and physical tests. If the chlorine atoms, which occur as end groups, are neglected, the polymer has the correct carbon-hydrogen analysis. Oxidation of the soluble I with nitric acid produced an 80% yield of succinic acid. (Oxidation with potassium permanganate gave only a 48% yield of succinic acid.) Catalytic hydrogenation in xylene at 200°

produced a linear polymethylene (IV). Although hydrogenation also occurred in biphenyl, the mechanical difficulties with this solvent were much greater. The structure of the polymethylene (IV) was indicated by the fact that it had the correct carbon-hydrogen analysis and softened at 65–90°. Viscosity measurements, followed by calculations according to Kemp and Peters⁶ for the normal hydrocarbons, indicated an approximate value of 1500 while cryoscopic measurements in camphor indicated a molecular weight of about 1300. In addition a polymethylene with a molecular weight of about 1500 might be expected to soften in the range of 65–90°.

A further check on the molecular weight of the original soluble polydimethyleneacetylene (I) was obtained from the chlorine end groups. If it is assumed that there is one chlorine atom at the end of each polymer chain, a molecular weight of approximately 2500 can be calculated. Because the polymer I underwent a smooth catalytic hydrogenation, one must conclude that the polymer formed a true solution and not an extremely fine dispersion of an insoluble polymer. In a cross-linked polymer some of the unsaturated groups could not be absorbed directly on the catalyst surface. It is also unlikely that any extensive degradation of the original polymer I took place during hydrogenation under a variety of experimental conditions.

The properties of the soluble polydimethyleneacetylene (I) can be rationalized by assuming that the triple bonds produce a rigid, symmetrical structure in which each dimethyleneacetylene unit is completely linear. The structure would look like a series of sticks joined at the ends. Such an arrangement would permit the polymer chains to align themselves very close together and to form strong crystallites in which the rigid nature of the molecules would make it very difficult for the molecules to move. Actually, the high degree of symmetry in this polymer would greatly enhance the crystallinity. The large effect of symmetry on the melting point of hydrocarbon polymers was emphasized by the high melting point and high crystallinity of poly-1,2-dimethylenecyclohexane.¹ The fact that this polydimethyleneacetylene (I) was crystalline was confirmed by an x-ray diffraction study⁷ on the powder. Unfortunately, the material could not be fused and drawn into a fiber for more exact structure determination.

The properties of the polydimethyleneacetylene (I) are quite similar to those reported by Jacobson⁸ and by Szwarc⁹ for poly-*p*-xylylene. Jacobson prepared his polymer by a Grignard coupling with

(6) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **35**, 1108 (1943).

(7) The authors are grateful to Dr. H. N. Campbell, General Laboratories, United States Rubber Co., Passaic, N. J., for the x-ray diffraction studies.

(8) R. A. Jacobson, *J. Am. Chem. Soc.*, **54**, 1514 (1932).

(9) M. Szwarc, *Discussions Faraday Soc.*, **46** (1947).

α,α' -dibromo-*p*-xylene. Szwarc, on the other hand, prepared his polymer by the pyrolysis of *p*-xylene, presumably through polymerization of the intermediate 3,6-dimethylene-1,4-cyclohexadiene. In both cases the products were high melting and relatively insoluble. One can assume that the benzene ring introduced rigidity and linearity into the polymer chain in the same way that the triple bond does in the present polymer.

Further evidence concerning the structure of the soluble polydimethyleneacetylene (I) was obtained from studies of its partial reduction. It was hoped that the acetylene polymer I would serve as a starting material for the syntheses of an all-*cis* and an all-*trans* polybutadiene. Previous workers have indicated that chemical reduction of a triple bond gives almost entirely the *trans* olefin,¹⁰ whereas catalytic hydrogenation gives primarily the *cis* isomer.¹¹ Preliminary chemical reductions of I were carried out with a variety of reducing agents, including sodium in liquid ammonia, sodium plus methyl or ethyl alcohol and disodiumnaphthalene. Because of the limited solubility of the polydimethyleneacetylene (I), only reductions with sodium plus a xylene solution of *n*-amyl alcohol were at all satisfactory. Results of several preliminary runs are listed in Table I. It is interesting that, as the percentage of triple bonds reduced to *trans* double bonds increases to about 50%, the softening point falls to 160–165° and the solubility in xylene increases markedly. That no other major transformation in the polymer structure occurred during this chemical reduction was indicated by the fact that complete hydrogenation of these partially reduced polymers produced a linear polymethylene identical with that obtained from the original soluble polydimethyleneacetylene (I). Since the properties of the partially reduced polymers do vary with the triple bond content, one may conclude that the decreased symmetry has a very large effect and that the properties of the original polymer I are not completely unexpected. Initial attempts at partial catalytic hydrogenation of the polymer I to produce an all-*cis* polymer were not successful because the products were invariably a mixture of starting material and the completely

reduced polymer. Apparently the polymer is adsorbed on the surface of the catalyst and is essentially completely reduced before it is desorbed.

The structure of the insoluble fraction (IIIa) of the original polymer mixture was not determined. Whether the insoluble polymer IIIa was cross linked or was just a high molecular weight polydimethyleneacetylene was not easy to establish. Oxidation of IIIa with nitric acid produced a 60% yield of succinic acid, but the lower yield may be due to the more vigorous conditions that were required for complete oxidation compared to those for the soluble I.

The mechanism of the polymerization of chlorobromobutyne may be quite complex. Johnson¹² found that the reaction of 1,4-dichloro- or 1,4-dibromo-2-butyne with ethyl- or methylmagnesium iodides gave good yields of the corresponding substituted acetylene. However, propargyl Grignard reagents have been shown to produce a mixture of products, including allenes,^{13a} when carbonated. However, alkylation reactions of these propargyl Grignard reagents have been reported to give the unrearranged product.^{13b,c}

One might speculate that an occasional allenic group could be formed during the polymerization and that these reactive groups could dimerize to form a cross-linked network as the main product. However, in view of the high melting point and relatively low molecular weight of the soluble polydimethyleneacetylene (I), it appears unlikely that it could contain any appreciable amount of allenes or branches resulting from their dimerization. It also is possible that some 1,2,3-butatriene could have been formed during the formation of the Grignard and subsequently polymerized to produce a complex structure.¹⁴ Actually, considerably more vigorous conditions are required for the preparation of butatriene from 1,4-dibromo-2-butyne than those used for the present condensation. Of course, a 1,4-addition of 1,2,3-butatriene would produce linear polydimethyleneacetylene identical with that produced by a coupling reaction.

EXPERIMENTAL¹⁵

Materials. Magnesium was freshly prepared by turning a bar of 99.9% pure magnesium on a lathe and storing the turnings under nitrogen. The 1-chloro-4-bromo-2-butyne (II),⁵ b.p. 45° (2 mm.), n_D^{25} 1.5470, was freshly distilled before use.

Polymerization of 1-chloro-4-bromo-2-butyne (II). Magnesium turnings (28.8 g.; 1.2 moles) and 800 ml. of anhydrous ether were placed in a 2-liter, three-necked creased flask equipped with an efficient stirrer. To this mixture was added 67 g. (0.4 mole) of 1-chloro-4-bromo-2-butyne

(12) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(13) (a) J. H. Wotiz, *J. Am. Chem. Soc.*, **72**, 1639 (1950); (b) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949); (c) T. Y. Lai, *Bull. soc. chim.*, **53**, 1543 (1933).

(14) W. M. Schubert, T. H. Liddicoet, and W. A. Lanks, *J. Am. Chem. Soc.*, **75**, 1929 (1954).

(15) The authors are indebted to Vivian Kapusinski for the microanalyses. All melting points are corrected.

TABLE I

Run	Sodium, G.	Reaction Temperature, °C.	Carbon-Hydrogen Ratio of Product	Softening Point, °C.	Solubility, Mg./100 Ml. of Benzene
1	1.2	90	1/1.12	215–220	20
2	2.4	120	1/1.18	180–190	80
3	4.8	140	1/1.25	160–165	310
4	6.0	140	1/1.25	160–165	300

(10) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).

(11) R. A. Raphael, *Acetylene Compounds in Organic Synthesis*, Academic Press, Inc., New York, N. Y., 1955.

(II) at a rate sufficient to maintain gentle reflux of the solvent. When approximately one third of the halide II had been added, a precipitate of a fine, light tan, flocculent powder formed in the reaction mixture and, as the addition and reaction progressed, the mixture became quite thick. After all of the halide II had been added, the reaction mixture was stirred for an additional hour until all evidence of reaction had subsided. (Since the chlorobromo compound II is an extremely potent vesicant and lachrymator, low concentrations can be detected by anyone who is sensitive to it.) Little or no unreacted dihalide remained after this period of stirring. The reaction mixture was diluted with anhydrous ether until the excess magnesium settled cleanly to the bottom. After the ether slurry of the polymeric precipitate was decanted from the magnesium, the slurry was centrifuged to collect the polymer. The precipitate was washed 3 times with ether and then suspended in a liter of 80% methanol containing 5% sulfuric acid and allowed to stand with frequent shaking for 10 hr. The polymer was removed by filtration, washed with water until free of acid, and then washed with acetone until all color was removed. The wet precipitate was treated with an acetone solution of an antioxidant (Neozone D) and dried in a vacuum desiccator at a pressure of 0.2 mm. to produce 17.5 g. (84%) of a light tan powdery polymer (III). When a sample of this powder was exposed to air for 2 days, it turned brown and increased in weight by 15%.

Isolation of a soluble fraction of polydimethyleneacetylene (I). A suspension of 17.5 g. of the light tan crude polydimethyleneacetylene (III) described above in 2 l. of anhydrous xylene was maintained under reflux for 48 hr. under an atmosphere of carbon dioxide. The hot solution was then quickly filtered through a fritted glass funnel of medium porosity, and the filtrate was concentrated under reduced pressure to about 200 ml. After the concentrate was added to approximately 600 ml. of methanol, the precipitated polymer was removed by means of a centrifuge. The solid was washed with acetone and dried under reduced pressure as described previously to yield 1.75 g. of light-cream-colored powder of soluble polydimethyleneacetylene (I).

Anal. Calcd. for C_2H_4 : C, 92.35; H, 7.65. Found: C, 91.30; H, 7.30; Cl, 1.19.

(When samples of this polymer I were analyzed in the usual way for carbon and hydrogen, they invariably ignited in an explosive manner; however, with proper wrapping of the sample with platinum foil satisfactory results were obtained.)

Oxidation of soluble polydimethyleneacetylene (I). To a mixture of 0.52 g. of soluble polydimethyleneacetylene (I) and 50 ml. of 10% nitric acid heated on a steam bath was added dropwise concentrated nitric acid until the oxidation became fairly vigorous. After the oxidation had subsided, the reaction mixture was evaporated to dryness on the steam bath. The thick pasty residue was mixed with 50 ml. of water and the mixture was exhaustively extracted with ether for 48 hr. The ether was removed from the extract by evaporation to produce 1.20 g. of crude succinic acid. This residue was dissolved in 5 ml. of boiling water and this solution was decolorized with charcoal. This solution was cooled and the resulting succinic acid was removed by filtration. The filtrate was concentrated to produce an additional quantity of acid and the process was repeated to produce a third crop of crystals. The total yield of succinic acid, m.p.

185–186° (reported¹⁶ m.p. 185°), was 0.95 g. (80%). A mixed melting point determination with an authentic sample of succinic acid showed no depression.

Catalytic reduction of soluble polydimethyleneacetylene (I). A mixture of 0.26 g. of soluble polydimethyleneacetylene (I), 200 ml. of xylene, and 0.05 g. of freshly prepared Adams catalyst (PtO_2) was hydrogenated at 200° and 90 atm. for 6 hr. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure to approximately 20 ml. This concentrated polymer solution was added dropwise to 100 ml. of methanol. The resulting precipitate was removed by filtration, washed with methanol, and dried under reduced pressure to produce 0.24 g. (85%) of a waxy linear polymethylene (IV), softening point 65–90°.

Anal. Calcd. for $(CH_2)_x$: C, 85.73; H, 14.27. Found: C, 85.50; H, 14.01.

Molecular weight determinations of the hydrogenated polydimethyleneacetylene (IV). Viscosity measurements at 25° of 1, 0.5, and 0.25% solutions of linear polymethylene (IV) in benzene indicated an intrinsic viscosity¹⁷ of 0.36. By the use of the equation of Kemp and Peters⁶ for normal hydrocarbons with a K_m of 2.4×10^{-4} a molecular weight in the range of 1500 is calculated.

A solution of 2.612 mg. of polymer IV in 39.175 mg. of camphor showed a melting point depression of 2.2°. Calculations¹⁸ with this cryoscopic data indicated a molecular weight of approximately 1300.

X-ray study of soluble polydimethyleneacetylene (I). Since this polymer I could not be drawn into a fiber, only a powder pattern was obtained. Crystallinity of the polymer was indicated by the powder pattern⁷ which possessed a very strong line corresponding to an interplanar spacing of 3.8 Å and a very weak line corresponding to a spacing of 4.2 Å.

Partial reduction of soluble polydimethyleneacetylene (I). To a solution of 52 mg. of soluble polydimethyleneacetylene (I) in 150 ml. of xylene was added 1.2 g. of sodium sand. While this mixture was vigorously stirred at 90°, 10 ml. of *n*-amyl alcohol was added dropwise over a period of 30 min. This reaction mixture was stirred at 90° until all the sodium had disappeared and the mixture was extracted with water until it was free of base. The xylene layer plus a small amount of a precipitate were dried by means of azeotropic distillation with a Dean-Stark trap under an atmosphere of carbon dioxide. The mixture was cooled to room temperature and the undesired precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to approximately 25 ml. and this concentrate was added dropwise to 125 ml. of methanol. The precipitate was removed by filtration and dried under partial vacuum to produce 0.43 mg. of partially hydrogenated polydimethyleneacetylene, softening point 215–220°. The results of several reductions under a variety of conditions are listed in Table I.

DETROIT 1, MICH.

(16) H. Marshall and A. T. Cameron, *J. Chem. Soc.*, 1522 (1907).

(17) A. Weissberger, *Physical Methods of Organic Chemistry*, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1950, p. 350.

(18) J. B. Niederl and V. Niederl, *Organic Quantitative Microanalyses*, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 217.