after which stirring was continued for three hours. The 3-bromo-1-iodo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 3-bromo-1-iodo-1-propyne was distilled under a nitrogen atmosphere to give 77 g. (31% yield); however, about one-third of the original solution was left in the distillation flask. The product had the following physical properties: b.p. 59.5–60.0° (2 mm.), $n^{20}\text{D}$ 1.6435, $n^{25}\text{D}$ 1.6405, $n^{30}\text{D}$ 1.6377, d^{20}_4 2.5663, d^{25}_4 2.5562, d^{30}_4 2.5473; *MR*(obsd.) 34.53, *MR*(sum) 34.62. The compound is unstable and turns dark brown on standing for a few minutes in the atmosphere.

Anal. Calcd. for C_3H_2BrI: Br, 32.6; I, 51.8. Found: Br, 32.8; I, 51.9.

3-Iodo-1-propyne–Iodopropadiene.—The procedure followed in the preparation of the mixture of 3-iodo-1-propyne and iodopropadiene was that of Jacobs and Brill.[6] The reaction between the 3-bromo-1-propyne and the sodium iodide was carried out in acetone as a solvent and in ethanol. Essentially the same mixture was obtained with either solvent and the 5.85 μ band was present in the infrared spectrum from the alcohol preparation as well as from the acetone preparation thus eliminating the possibility of carbonyl contamination causing the 5.85 μ absorption.

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The Copolymer of Allyl Alcohol and 1,3-Butadiene[1]

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Work in this Laboratory on the relation between polymer composition and the properties of the vulcanized rubber led us to believe that a butadiene–allyl alcohol copolymer might have both good oil resistance and good low temperature properties. Allyl acetate does not polymerize well alone[2] and allyl alcohol is an inhibitor for butadiene polymerization,[3] hence the direct preparation of a copolymer of suitable size did not seem to be feasible.

We have, however, been able to prepare the copolymer in an indirect manner by reducing a butadiene–methyl acrylate copolymer[4] in tetrahydrofuran solution with lithium aluminum hydride.[5] It has been well demonstrated that this reduction will not reduce double bonds which are not conjugated with carbonyl groups.[6] Infrared[7] and elemental[8] analyses of the reduced product indicated that the ester groups in the polymer were completely reduced to primary alcohol groups. This was confirmed by treating the polymer with *p*-nitrophenyl isocyanate to yield a urethan of the correct composition.

The butadiene–allyl alcohol copolymer thus obtained was soluble in tetrahydrofuran and could be precipitated by the addition of methanol. The product thus obtained could be dissolved in benzene while it was still wet with methanol. Once the polymer had been allowed to dry, it would not redissolve in benzene even though antioxidants were added to prevent oxidation.

A preliminary evaluation of the oil resistance and low temperature properties of the compounded and vulcanized copolymer was made by Mr. W. K. Taft and Mr. B. G. Labbe of the Government Laboratories at Akron. They found this copolymer to have the best balance between oil resistance at room temperature and low temperature properties that had been observed in this study. More extensive work on the preparation and evaluation of this material will be reported later.

Experimental

Butadiene–Methyl Acrylate Copolymer.—The butadiene–methyl acrylate copolymer was prepared according to the modified mutual GR-S recipe[9] which is listed below. The butadiene used was Phillips Special Purity Research grade. The methyl acrylate was obtained from Rohm and Haas Company and distilled just before use.

The modified mutual GR-S recipe consisted of: water, 34 g.; OSR soap, 1 g.; azo-bis-isobutyronitrile, 0.06 g.; HLM (commercial mixed primary mercaptans of which the main constituent is dodecyl mercaptan), 0.06 g.; methyl acrylate, 3.0 g.; and butadiene, 17.0 g.

In a standard four-ounce screw-cap bottle equipped with a self-sealing rubber gasket were placed 35 g. of soap solution followed by the other constituents in the order indicated. A slight excess of butadiene was added, and this allowed to boil down to the desired weight, sweeping the bottle free of air.

The bottle was then sealed and tumbled end-over-end for 12 hours in a 50° bath. The latices were coagulated with 25 ml. of sodium chloride coagulant using 10 ml. of a 10% solution of phenyl-β-naphthylamine as anti-oxidant. The coagulant was a 4% solution of sulfuric acid saturated with sodium chloride. After being washed with distilled water, the polymers were shredded and dried to constant weight in a vacuum desiccator at 1 mm. pressure.

Solubility determinations were made by covering 0.250 g. of dried polymer with 50.0 ml. of dry benzene for 48 hours in a sealed flask, filtering the mixture through a 200-mesh screen and determining the residual solids of an aliquot. Inherent viscosities were determined with the same solution using a modified Ostwald viscometer.

In 12 hours at 50° conversions from 68 to 72% were obtained. These polymers were soluble and had inherent viscosities of 2.5 to 2.8.

Anal. Found: C, 85.2; H, 10.6.

Butadiene–Allyl Alcohol Copolymers.—Five liters of tetrahydrofuran, which had been refluxed for 24 hours over calcium hydride, was distilled into a 12-l., three-necked, round-bottomed flask equipped with a Soxhlet extractor, a vibro-stirrer,[10] calcium chloride tubes on all openings, and a gas bubbler extended below the surface of the tetrahydrofuran. The flask was then swept out with nitrogen (purified by passing successively through Fieser's solution, concentrated sulfuric acid and finally sodium hydroxide pellets). The nitrogen was allowed to bubble slowly through the reaction during the remainder of the reduction.

A small piece of lithium aluminum hydride (about $^1/_2$ inch in diameter) was placed in the flask to take up any trace of moisture. Thirty grams of butadiene–methyl acrylate copolymer (reprecipitated once from benzene) was dissolved in the tetrahydrofuran with stirring (8–10 hours). Five grams of powdered lithium aluminum hydride was added to the Soxhlet thimble and the reaction mixture was heated

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[1] 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.

[2] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 816 (1941); P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

[3] H. W. Starkweather, P. O. Bare, A. S. Carter, F. B. Hill, V. R. Hurka, C. J. Mighton, P. S. Saunders, H. W. Walker and M. A. Youker, *Ind. Eng. Chem.*, **39**, 210 (1947); P. D. Bartlett and F. A. Tate, THIS JOURNAL, **75**, 91 (1953).

[4] A. M. Clifford and J. D. D'Ianni, private communication through the Office of Synthetic Rubber, Dec. 29, 1942.

[5] A. E. Finholt, A. C. Bond and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

[6] R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947); F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

[7] Anderson Physical Laboratory, Champaign, Illinois, carried out the infrared examination of this polymer.

[8] We are indebted to Mr. J. Nemeth and Mrs. L. Chang for the microanalyses.

[9] J. W. Wilson and E. S. Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948).

[10] Vibro-Mischer, Model E-1 made by A. G. Für Chemie-Apparatebau, Zurich, Switzerland. Ordinary stirring methods are not satisfactory.

(with a Glas-col heating mantle), with stirring, to reflux for 24 hours. The first extraction resulted in *vigorous* reaction and an efficient condenser was needed.

As the hydride reacted, the reaction mixture turned decidedly green in color. After several extractions the aluminum–polymer complex began to precipitate, finally covering the entire surface of the solution with a semi-transparent, gelatinous mass.

After 24 hours, the reaction mixture was allowed to cool to room temperature. The Soxhlet extractor was removed and 1 *N* sulfuric acid added cautiously until the reaction tested distinctly acid to congo red paper (*ca.* 350 ml.). The precipitate gradually redissolved (8–10 hours) leaving a small white, gelatinous residue. The polymer solution was then decanted, placed in a stoppered filter-flask and evaporated under vacuum to approximately one-half volume. Since the butadiene–allyl alcohol copolymer became insoluble when dried, it was customarily stored in this solution.

Viscosities were run on benzene solutions of this polymer which were obtained by precipitating the polymer from the tetrahydrofuran solution, pressing the methanol from the sample and immediately redissolving the polymer in dry benzene. Under these conditions the polymer was soluble and gave inherent viscosities of 1.8 to 2.4. Elemental analyses were run on these polymers.

Anal. Calcd. (on the basis of complete reduction): C, 86.81; H, 11.09. Found: C, 86.95; H, 11.19.

This analysis corresponds to a copolymer of butadiene and allyl alcohol which contained 7.87%, by weight, of allyl alcohol.

p-Nitrophenyl Isocyanate Derivative of the Copolymer.—A sample of 1.16 g. of butadiene–allyl alcohol copolymer, which had been reprecipitated from benzene, was dissolved in 50 ml. of dry benzene. Five grams of p-nitrophenyl isocyanate was added and the mixture refluxed for eight hours. The product was isolated by pouring the reaction mixture into a fourfold excess of methyl alcohol and purified by seven reprecipitations from benzene. The product was a pale yellow, rubbery solid.

Anal. Calcd. for N: 3.08. Found: N, 3.20.

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Creatine Ethyl Ether

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The preparation of esters of creatine was reported first by Dox and Yoder.[1] This was accomplished by passing dry hydrogen chloride into absolute alcoholic solutions of creatine at room temperature, a procedure which has been used successfully for the preparation of esters of amino acids. Analyses for nitrogen and chloride were in agreement with the expected values for creatine ester hydrochlorides, and recrystallization from another alcohol did not alter the analyses, indicating that the compounds were not solvates. Dox and Yoder also noted that upon melting, the esters decomposed with gas evolution, and the residue solidified to form a compound with properties similar to those of creatinine hydrochloride. Kapfhammer[2] repeated the preparation of several of these compounds and confirmed the findings of Dox and Yoder. He pointed out, however, that the behavior of these compounds in chemical reactions and toward colorimetric tests and precipitating agents was typical of creatinine and not of creatine. Since the conditions used for many of these reactions did not correspond to conditions favorable for the rapid conversion of creatine to creatinine, Kapfhammer concluded that these compounds were, in reality, derivatives of creatinine in which the alcohol was not bound as a solvate nor by an ester linkage but in "some uncertain manner." Hynd and MacFarlane[3] later showed that the behavior of creatine methyl ester hydrochloride toward nitrous acid was more consistent with that of a true derivative of creatine since 65% of its total nitrogen was evolved in the Van Slyke procedure compared to 68% for creatine, while only 39% of the total nitrogen of creatinine is liberated under similar conditions; however, when the chloride was removed by shaking creatine methyl ester hydrochloride with silver carbonate prior to the nitrous acid treatment, only 41% of the total nitrogen was evolved, suggesting that a conversion to creatinine may have occurred. Failey and Brand,[4] upon careful electrometric titration of creatine methyl ester hydrochloride with sodium hydroxide, noted an irreversible conversion during the titration, with the end-product giving a titration curve identical to creatinine.

In order to establish clearly whether these compounds are derivatives of creatine or of creatinine, it was felt that only the mildest conditions could be applied due to the extreme lability of these compounds. For this reason a spectrophotometric approach was investigated. Stuckey[5] has shown that compounds of the glycocyamidine or of the hydantoin type, with a hydrogen atom on the lactam nitrogen, have characteristic absorption maxima in the 220–240 mμ region when the spectra are observed in alkaline solution. Open chain structures such as creatine or hydantoic acid do not possess an absorption maximum in this region. Gaede and Grüttner[6] have shown that creatinine has a maximum at 234 mμ with a molecular extinction of 7420 when the spectrum is observed in an aqueous phosphate buffer solution at pH 7.38. Creatine under similar conditions was shown to absorb very little in the same region.

The preparation of the ethyl ester of creatine hydrochloride was found to be accomplished easily according to the directions of Dox and Yoder.[1] It was not found possible to prepare this compound by passage of dry hydrogen chloride into an anhydrous ethanol solution of creatinine,[7] indicating that the ester is not formed through the intermediate production of creatinine. At pH 7 the ethyl ester of creatine exhibited a rather strong absorption maximum at 235 mμ. However, the intensity of absorption was increasing at a very rapid rate and it approached a value equal to that for an equimolar amount of creatinine within about 30 minutes. A study of the absorption spectrum for creatinine in aqueous buffer solutions of pH less than 7 indicated that it was possible to observe the characteristic maximum at pH values as low as about 5, although at a somewhat diminished

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[1] A. W. Dox and L. Yoder, *J. Biol. Chem.*, **54**, 671 (1922).

[2] J. Kapfhammer, *Biochem. Z.*, **156**, 182 (1925); A. Hunter, "Creatine and Creatinine," Longmans, Green and Co., Ltd., London, 1928, pp. 38–39.

[3] A. Hynd and M. G. MacFarlane, *Biochem. J.*, **20**, 1264 (1927).

[4] C. F. Failey and E. Brand, *J. Biol. Chem.*, **102**, 767 (1933).

[5] R. E. Stuckey, *J. Chem. Soc.*, 331 (1947).

[6] K. Gaede and R. Grüttner, *Naturwissenschaften*, **39**, 63 (1952).

[7] These experiments were performed by Dr. John M. Ladino.