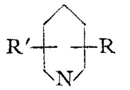
[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

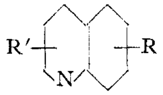
Monomers and Polymers. V. Vinylpyridines and Vinylquinolines[1,2]

BY G. BRYANT BACHMAN AND D. DONALD MICUCCI

The examination of synthetic rubbers prepared by the copolymerization of butadiene with various olefins has shown that the nature of the olefin exerts a considerable influence on the properties of the rubbers obtained. Relative to butadiene–styrene rubbers the butadiene–dichlorostyrene rubbers are more easily milled and processed and show better hot tensile strength. The butadiene–vinylpyridine rubbers are outstanding in tensile strength but are nervy and tough and mill poorly. It was hoped that, by combining the effects of halogen atoms and heterocyclic nuclei in the same molecule, monomers might be obtained which would give rubbers of outstanding value. The present paper reports the preparation of vinylpyridines and vinylquinolines, some of which contain nuclearly substituted halogen atoms, and describes preliminary experiments to determine the polymerizing and copolymerizing characteristics of each. The following compounds were studied.



I, R = 2-$C(CH_3)=CH_2$, R' = H
II, R = 3-$C(CH_3)=CH_2$, R' = H
III, R = 3-$C(CH_3)=CH_2$, R' = 5-Br
IV, R = 3-$CH=CH_2$, R' = 5-Br
V, R = 3-$C(CH_3)=CH_2$, R' = 5-Cl



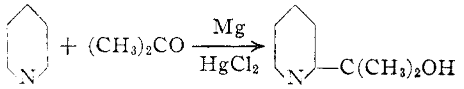
VI, R = 2-$CH=CH_2$, R' = H
VII, R = 2-$CH=CH_2$, R' = 6-Cl
VIII, R = 2-$C(CH_3)=CH_2$, R' = H
IX, R = 2-$C(CH_3)=CH_2$, R' = 6-Cl

Of these I,[3,4] II[5] and VI[6,7] have been prepared previously by others, but their polymerization characteristics are not reported. Compound VII was not obtained as a monomer since it polymerized very readily and attempts to prepare it by methods analogous to those used successfully for VI gave only a polymer.

In accord with our previous observations[2] the vinyl compounds of this series polymerized and copolymerized satisfactorily, while the alpha-methylvinyl compounds did not polymerize alone but did copolymerize with butadiene and other polymerizable vinyl compounds. The 2-alpha-methylvinyl derivatives of both pyridine and quinoline were however exceptional in that they did not copolymerize satisfactorily with butadiene, although they did form hard, black, brittle solids with maleic anhydride.

The introduction of halogen atoms seems to increase the rate of copolymerization of the vinyl heterocyclic monomers with butadiene and to soften the resulting rubbers somewhat but the effect is not as great as was hoped for. Our preliminary examination of these rubbers indicates that it would be desirable to introduce at least two halogen atoms per molecule of vinyl compound to obtain greater internal plasticization of the butadiene copolymers. This could probably be achieved more easily in the quinoline series than in the pyridine series since the number of positions available on the pyridine nucleus is limited. Furthermore, halogen atoms in 2, 4 and 6-positions of pyridine are readily hydrolyzed. This leaves only the 3- and 5-positions free for halogen atoms and the 2(6)- or 4-positions for the vinyl groups. It has been shown that alpha-methylvinyl groups in the 2(6)-position do not copolymerize, and the same may very well be true of such groups in the 4-position. Among quinoline compounds only the 2- and 4-positions hold readily hydrolyzable halogens. The 5, 6, 7 and 8 positions of the benzene ring and the 3-position of the pyridine ring offer suitable points of attachment of both halogen atoms and vinyl groups. The preparation of some of these compounds will be described at a later date.

The vinyl compounds studied were prepared by dehydrating corresponding alcohols. The $(CH_3)_2$-$C(OH)$– group in the 3-position of pyridine dehydrated more easily than the same group in the 2-position. Most of the alcohols were prepared from the corresponding acids by well-known methods, but the alcohols corresponding to I[3] and VI[8] were obtained by special methods. Emmert and Asendorf[3] have reported a little known but very interesting reaction for the preparation of 2-(2'-hydroxy-2'-propyl)-pyridine which involves a heterogeneous bimolecular reduction of acetone and pyridine in the presence of magnesium and mercuric chloride.



After improving the published procedure for this reaction we found it to be well suited for the synthesis of I.

Considerable time was spent studying syntheses for 5-chloro- and 5-bromonicotinic acids, intermediates for the preparation of III, IV and V. These acids are both known but the reported syntheses are difficult and give poor yields. We found that nicotinic acid chloride hydrochloride could be brominated directly to give the 5-substituted acid in excellent yields (87%) at 170°.

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[1] From the Ph.D. thesis of D. Donal Micucci, Purdue University, February, 1948.

[2] For previous papers in this series see THIS JOURNAL, **69**, 2022 (1947); **70**, 622, 2378 (1948).

[3] Emmert and Asendorf, *Ber.*, **72B**, 1188–1194 (1939); *C. A.*, **33**, 7300 (1939).

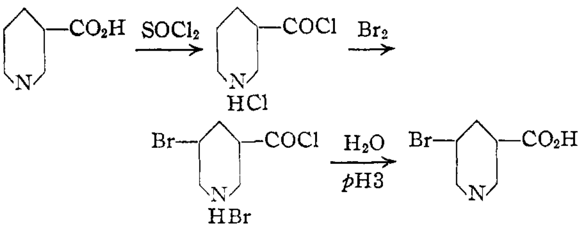
[4] Loffler and Grosse, *Ber.*, **40**, 1328 (1907).

[5] Oparina, *J. Russ. Phys.-Chem. Soc.*, **57**, 319–341 (1925); *C. A.*, **20**, 2499 (1926).

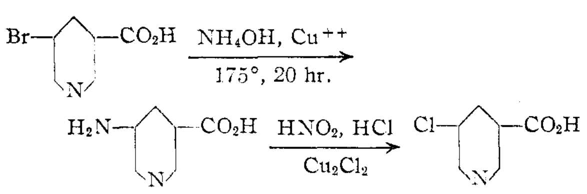
[6] Methner, *Ber.*, **27**, 2689 (1894).

[7] Einhorn and Lehnkering, *Ann.*, **246**, 172 (1888).

[8] Koenigs, *Ber.*, **32**, 224 (1899).



A similar reaction involving picolinic acid gave only tars. Many attempts were made to prepare 5-chloronicotinic acid by direct chlorination, but with only moderate success. On a small scale the desired product was obtained, but on a larger scale rapid sublimation, incomplete fusion of the acid chloride hydrochloride, and failure to form a perchloride complex interfered. Eventually the 5-chloro acid was prepared from the 5-bromo acid *via* the 5-amino acid.



A convenient new synthesis, suitable for laboratory scale preparations, was also developed for ethyl quinaldinate and its 6-chloro analog, intermediates for VIII and IX.

Acknowledgment.—The authors are indebted to the General Tire and Rubber Company for support in the form of a fellowship.

Experimental

2-Isopropenylpyridine

2-(2′-Hydroxy-2′-propyl)-pyridine.—A mixture of 24 g. (0.088 mole) of mercuric chloride, 24.3 g. (1.0 mole) of magnesium turnings and 200 g. (2.53 moles) of pyridine was warmed on the steam-bath until it acquired an opaque gray color. Then 200 g. (3.45 moles) of acetone was added dropwise with stirring during one and one-half hours. After an additional hour the magnesium had disappeared. The mixture was poured over ice and excess potassium carbonate solution, and the brown oil was separated and distilled. The fraction, b. p. 85–95° (12 mm.), was dissolved in dilute hydrochloric acid and steam distilled to remove volatile impurities. The product was recovered by treatment with bases and redistilled; yield 40 g. (29.3% based on the magnesium), b. p. 85–90° (10 mm.), m. p. 49–50° (from chloroform). These properties correspond with those previously reported by Sobecki[9] and by Emmert and Asendorf.[3]

2-Isopropenylpyridine.—The procedure of Emmert and Asendorf[3] gave a 67% yield of an oil b. p. 63–67° (10 mm.), $n^{25}\text{D}$ 1.5241, $d^{25}{}_{25}$ 0.9962 (reported[3] b. p. 172–176°).

3-Isopropenylpyridine

3-(2′-Hydroxy-2′-propyl)-pyridine.—This alcohol was prepared by Graf and Langer,[10] who gave no details of procedure. A solution of 137 g. (1.0 mole) of methyl nicotinate in 1000 ml. of anhydrous ether was added dropwise with stirring to a solution of 540 g. (3.25 mole) of methylmagnesium iodide in 900 ml. of ether. The yellow suspension was stirred and refluxed for three hours and then poured over chopped ice containing acetic acid. The solution was made just alkaline; the product was extracted with ether and distilled; yield 78 g. (57%), b. p. 130° (10 mm.); reported,[10] b. p. 130° (11 mm.), m. p. 53°.

3-Isopropenylpyridine.—Dehydration of the above alcohol with a mixture of sulfuric and acetic acids by the procedure of Oparina[5] gave 3-isopropenylpyridine in 79% yield, b. p. 75° (10 mm.), $n^{25}\text{D}$ 1.5381, $d^{25}{}_{25}$ 0.9775, methiodide, m. p. 103–104° (reported[5] b. p. 187–188°, $d^{20}{}_{20}$ 0.9771).

Dehydration by heating with half molar quantities of phosphorus pentoxide in benzene for several hours gave a 65% yield but only a 25% conversion to the same compound.

5-Bromo-3-isopropenylpyridine

5-Bromonicotinic Acid.—Nicotinic acid was converted to the acid chloride hydrochloride with thionyl chloride, heated ten hours at 150–170° (oil-bath temperature) with an equimolecular amount of bromine, and then cooled. Ice water was added, the *p*H was adjusted to 3 with base and the precipitated product was filtered and recrystallized (Norit) from ethanol; yield 87%, m. p. 183°.[11] Treatment with thionyl chloride and then dilute base gave the acid chloride, m. p. 75°,[11] in 86% yield.

5-Bromo-3-(2′-hydroxy-2′-propyl)-pyridine.—5-Bromonicotinyl chloride was treated with 3.5 moles of methylmagnesium iodide to obtain the desired tertiary alcohol, a colorless and very viscous oil, b. p. 135–140° (3 mm.), $n^{25}\text{D}$ 1.5615, $d^{25}{}_{25}$ 1.47; methiodide, m. p. 208–210°, dec.

Anal. Calcd. for $C_8H_{10}NOBr$: C, 44.47; H, 4.67. Found: C, 44.80; H, 4.70.

5-Bromo-3-isopropenylpyridine.—Dehydration of the above alcohol by heating with 20% sulfuric acid in acetic acid or by passing the vapors over alumina at 300° (50 mm.) gave 89 and 78% yields, respectively, of product, b. p. 85–87° (3 mm.), $n^{25}\text{D}$ 1.5820, $d^{25}{}_{25}$ 1.4204; methiodide, m. p. 228°, dec.

Anal. Calcd. for C_8H_8NBr: N, 7.07. Found: N, 6.91.

5-Bromo-3-vinylpyridine

Ethyl 5-Bromonicotinate.—A 95% yield of the desired ester, m. p. 38–39°, was obtained by adding excess absolute ethanol to 5-bromonicotinyl chloride, refluxing for thirty minutes, distilling off the excess alcohol, and making the residue alkaline. The crude material was recrystallized from petroleum ether (60–70°).

Anal. Calcd. for $C_8H_8NO_2Br$: N, 6.08. Found: N, 5.86.

3-Acetyl-5-bromopyridine.—This ketone was prepared by three different procedures: (A) from 5-bromonicotinyl chloride and methylmagnesium bromide, yield 18%; (B) from 5-bromonicotinyl chloride and dimethylcadmium. This procedure was more laborious, but gave a slightly better yield (25%). (C) From ethyl 5-bromonicotinate *via* ethyl 5-bromonicotinylacetate: a solution of 0.32 mole of anhydrous sodium ethoxide in 108 ml. of xylene was prepared and added to a mixture of 46 g. (0.2 mole) of ethyl 5-bromonicotinate, 33.4 g. (0.38 mole) of ethyl acetate, and 50 ml. of xylene. After being heated and stirred for six hours and standing overnight, the mixture was poured into 800 ml. of ice water, acidified with 40 ml. of concentrated hydrochloric acid, and hydrolyzed by heating on a steam-bath for five hours. The xylene was removed by distillation, the residue was made basic, and the solid ketone which precipitated was separated by filtration. Recrystallization from petroleum ether (60–70°) gave 30 g. (75% yield) of white plates, m. p. 90°.

Anal. Calcd. for C_7H_6NOBr: C, 42.03; H, 3.04. Found: C, 42.11; H, 3.04.

5-Bromo-3-(1′-hydroxyethyl)-pyridine.—Reduction of 20 g. (0.1 mole) of 5-bromo-3-acetylpyridine with 0.1 mole of aluminum isopropoxide by the standard procedure[12] and isolation by vacuum distillation gave 20 g. (85% yield) of

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(9) Sobecki, *Ber.*, **41**, 4103 (1908).

(10) Graf and Langer, *J. prakt. Chem.*, **146**, 103 (1937).

(11) Graf, *et al.*, *ibid.*, **138**, 244–258 (1933).

(12) Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1944, p. 203.

the desired alcohol as a viscous oil, b. p. 134–136° (3 mm.), $n^{25}\mathrm{D}$ 1.5728, d^{25}_{25} 1.5378.

Anal. Calcd. for C_7H_8NOBr: N, 6.93. Found: N, 7.00.

5-Bromo-3-vinylpyridine.—A 103-g. sample of 5-bromo-3-(1′-hydroxyethyl)-pyridine was dehydrated over alumina by the vapor phase method described previously. The 5-bromo-3-vinylpyridine fraction obtained amounted to 63 g. (67% yield), b. p. 74–75° (3 mm.), $n^{25}\mathrm{D}$ 1.5810, d^{25}_{25} 1.4823.

Anal. Calcd. for C_7H_6NBr: N, 7.61. Found: N, 7.46.

5-Chloro-3-isopropenylpyridine

5-Aminonicotinic Acid.—One mole, 202 g., of 5-bromonicotinic acid, 400 ml. of ammonium hydroxide solution (sp. gr. 0.9) and 50 g. of copper sulfate pentahydrate were heated to 170–180° for twenty hours in a glass-lined autoclave. The dark-colored solution was removed after cooling and treated with aqueous sodium sulfide to remove copper ions. The filtered solution was adjusted to *p*H 4–5 and the precipitated acid was filtered off, washed with water, and recrystallized from water (Norite). A yield of 96 g. (69%), m. p. 292–294°, was obtained. Graf[11] reports no yield and a m. p. of 288–290° for a product prepared similarly from 5-chloronicotinic acid.

5-Chloronicotinic Acid and Its Chloride.—A sample of 96 g. (0.7 mole) of 5-aminonicotinic acid dissolved in 400 ml. of concd. hydrochloric acid was cooled in an ice–salt-bath to 0° and diazotized with a cold solution of 50.4 g. (0.77 mole) of sodium nitrite in 145 ml. of water. The mixture was poured into a solution of 80 g. (0.7 mole) of cuprous chloride in 400 ml. of concentrated hydrochloric acid. After three hours of stirring the mixture was heated to 60° to complete the reaction, diluted with an equal volume of water, and treated with aqueous sodium sulfide to precipitate the copper ions. The filtered solution deposited the crude chloro acid at *p*H 3. Recrystallization from hot water (Norite) gave 20 g. (18% yield) of 5-chloronicotinic acid, m. p. 169–170°. Graf,[11] who obtained a 25–30% yield of this acid by long heating of nicotinic acid with excess thionyl chloride, eventually in a sealed tube, reports m. p. 170–171°. The acid chloride, m. p. 53°, was prepared in 90% yield with the aid of thionyl chloride by the procedure of Graf and Meyer,[13] who report the same m. p. but give no yield.

5-Chloro-3-(2′-hydroxy-2′-propyl)-pyridine.—Following the procedure for the corresponding 5-bromo compound but starting with 20 g. (0.12 mole) of 5-chloronicotinyl chloride gave 14.2 g. (73% yield) of the desired alcohol, b. p. 115° (3 mm.), $n^{25}\mathrm{D}$ 1.5377, d^{25}_{25} 1.199.

Anal. Calcd. for $C_8H_{10}NOCl$: N, 8.17. Found: N, 8.25.

5-Chloro-3-isopropenylpyridine.—Dehydration of 12 g. (0.7 mole) of the above alcohol by the procedure used for the 5-bromo analog gave 8.5 g. (79% yield) of the desired olefin, b. p. 70–73° (3 mm.), $n^{25}\mathrm{D}$ 1.5554, d^{25}_{25} 1.1520.

Anal. Calcd. for C_8H_6NCl: N, 9.12. Found: N, 9.15.

2-Vinylquinoline

2-(2′-Hydroxyethyl)-quinoline.—Condensation of quinaldine with formaldehyde by the procedure of Koenigs[8] gave a 30% yield of this alcohol.

2-Vinylquinoline.—A mixture of 10 g. of the above alcohol, 1.5 g. of powdered potassium hydroxide, and 0.1 g. of phenyl-β-naphthylamine was heated in an oil-bath at 140–150° under reduced pressure (5 mm.) until distillation stopped. The oily product was redistilled to obtain 4.2 g. (46.9% yield) of the vinyl compound.

2-Vinylquinoline was also prepared directly from a quinaldine–formaldehyde reaction mixture. Quinaldine, 200 g. (1.4 moles), formalin 180 g. (2.4 moles of formaldehyde), 100 ml. of ethanol and 100 ml. of water were heated twenty-four hours on a steam-bath. The solvents were distilled off, 5 g. of powdered sodium hydroxide and 1 g. of phenyl-β-naphthylamine were added, and the mixture was heated at 7 mm. pressure until distillation ceased. Redistillation gave 103 g. (49% yield) of product, b. p. 120–125° (7 mm.), $n^{20}\mathrm{D}$ 1.6439, d^{25}_{25} 1.0692.

Anal. Calcd. for $C_{11}H_9N$: N, 9.04. Found: N, 9.06.

2-Isopropenylquinoline

Ethyl Quinaldinate.—A solution of 111 g. (0.66 mole) of silver nitrate in 660 ml. of water was added carefully with stirring to a solution of 83 g. (0.22 mole) of 2-tribromoquinaldine in 800 ml. of ethanol. The mixture was refluxed for thirty minutes, filtered, acidified with 40 ml. of hydrochloric acid, and concentrated under vacuum to 300 ml. The solution was made strongly basic, the oily product was separated by decantation and ether extraction and was then purified by distillation; yield 25 g. (55%), b. p. 131–136° (1 mm.); reported,[14] b. p. 131–136° (0.3 mm.), $n^{20}\mathrm{D}$ 1.5973.

2-(2′-Hydroxy-2′-propyl)-quinoline.—Ethyl quinaldinate was treated with 3.3 moles of methylmagnesium bromide to obtain 16 g. (86%) of the alcohol, m. p. 67°.[15]

2-Isopropenylquinoline.—Dehydration of 17 g. of the above alcohol was accomplished by heating with 50 ml. of concentrated sulfuric acid in an oil-bath at 120–130° for three hours. The mixture was cooled, poured into cold water, made basic, and ether extracted. Distillation gave a pale yellow oil, 7.0 g. (45.5% yield), b. p. 119–120° (3 mm.), $n^{25}\mathrm{D}$ 1.6281, d^{25}_{25} 1.0600.

Anal. Calcd. for $C_{12}H_{11}N$: N, 8.28. Found: N, 8.05.

6-Chloro-2-isopropenylquinoline

6-Chloroquinaldine.—The following procedure gives over three times the yield reported previously.[16] A mixture of 80 g. (0.625 mole) of 4-chloroaniline, 500 ml. of absolute ethanol, 53 ml. of concentrated hydrochloric acid, 270 g. of ferric chloride hexahydrate and 10 g. of zinc chloride was heated to 60–65°. Crotonaldehyde, 35 g. (0.5 mole) was added dropwise in two hours. The mixture was refluxed two hours, let stand overnight, distilled under vacuum to remove the alcohol, and then made strongly basic and steam distilled. The distilled solid, after drying, weighed 70 g. (79% yield), m. p. 92–93° (reported,[16] m. p. 91°).

6-Chloro-2-tribromoquinaldine.—A solution of 227 g. (1.44 mole) of bromine in 61 ml. of glacial acetic acid was added in the course of one hour to a mixture of 245 g. (2.98 moles) of anhydrous sodium acetate, 85 g. (0.49 mole) of 6-chloroquinaldine, and 610 ml. of glacial acetic acid at 75–80°. After heating at 90–95° for one hour and standing overnight, the solid product was separated and recrystallized from petroleum ether (60–70°); yield 133 g. (67%), m. p. 59–60°.

Anal. Calcd. for $C_{10}H_5NBr_3Cl$: Br, 57.86; Cl, 8.56. Found: Br, 57.5, 57.6; Cl, 8.5, 8.5.

Ethyl 6-Chloroquinaldinate.—The procedure developed for the preparation of ethyl quinaldinate gave a 44% yield of the 6-chloro analog, m. p. 91–92°.

Anal. Calcd. for $C_{12}H_{10}NO_2Cl$: N, 5.94. Found: N, 5.94.

6-Chloro-2-isopropenylquinoline.—The reaction of 13 g. (0.055 mole) of ethyl 6-chloroquinaldinate with approximately 0.18 mole of methylmagnesium bromide in ether according to the procedure previously described using ethyl quinaldinate gave 7.5 g. of a viscous oil, chiefly 6-chloro-2-(2′-hydroxy-2′-propyl)-quinoline, which was not further characterized but was dehydrated directly with concd. sulfuric acid (20 ml.) at 120° for three hours. The olefin was a pale yellow oil which crystallized from an ethanol–water mixture; yield 4.3 g. (62.5%), m. p. 50°.

Anal. Calcd. for $C_{12}H_{11}NCl$: N, 6.84. Found: N, 6.67.

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[13] Graf and Meyer, *Ber.*, **61**, 2210 (1928).

[14] Campbell, *et al.*, THIS JOURNAL, **68**, 1841 (1946).

[15] Emmert and Pirot, *Ber.*, **74B**, 718 (1941).

[16] Bartow and McCollum, THIS JOURNAL, **26**, 703 (1904).

Polymerization Experiments

Compounds I, VIII and IX gave no polymers alone or copolymers with butadiene, styrene, or methyl methacrylate, in the presence of benzoyl peroxide. Of the remaining compounds II, III, and V gave no polymers alone but copolymerized readily with the above olefins. Compounds IV and VI polymerized readily alone and also copolymerized with the above olefins. Several attempts were made to prepare 6-chloro-2-vinylquinoline (VII) by procedures analogous to those used for 2-vinylquinoline (VI). In every case rapid polymerization interfered with isolation of the monomer. The bulk polymers were prepared by heating the monomers at 70° in stoppered test-tubes with 0.5% benzoyl peroxide catalyst. Equal weights of monomers were used for the copolymers. The emulsion polymers with butadiene were prepared in sealed tubes at 40° (thermostat) using the formula: butadiene 7.5 g., vinyl monomer 2.5 g., water 18 g., soap 0.5 g., potassium persulfate 0.03 g., lauryl mercaptan (OEI) 0.06 g.

Summary

A series of vinylpyridines and vinylquinolines, some containing nuclear halogens, have been prepared and a preliminary study made of their polymerizing and copolymerizing characteristics.

LAFAYETTE, INDIANA RECEIVED DECEMBER 23, 1947

[CONTRIBUTION NO. 145 FROM THE GOODYEAR TIRE AND RUBBER CO., RESEARCH LABORATORY]

Viscosity–Molecular Weight and Viscosity–Temperature Relationships for Polystyrene and Polyisobutylene[1,2]

BY THOMAS G FOX, JR., AND PAUL J. FLORY

The simple empirical relationship[3]

$$\log \eta = A + C\overline{M}_{\mathrm{w}}^{1/2} \tag{1}$$

where η is the viscosity, $\overline{M}_{\mathrm{w}}$ the weight average molecular weight and A and C are constants for a specified temperature, has been found to apply with remarkable accuracy to linear polyesters,[3,4] polyamides,[5] and to certain non-linear polymers as well.[5] Extension of this relationship to addition polymers of unsaturated compounds such as polyethylene[6] and polyisobutylene[7] and to polymeric dimethyl silicones[8] has been attempted recently with indications of success. However, either the molecular weights (weight average) were unreliably determined or the range was too limited for positive assurance that equation (1) may be applied to these polymers.

In the present investigation viscosities of two representative hydrocarbon polymers, polystyrene and polyisobutylene, of simple chain structure have been measured over wide ranges of molecular weight, molecular weight distribution and temperature. In addition to providing data with which to test the generality of equation (1), the present results demonstrate the nature of the dependence of the viscosity–temperature coefficient on molecular weight, molecular weight distribution and temperature. Apparent discrepancies which have appeared in the literature on viscosity–temperature coefficients for polystyrene have been accounted for. It is hoped that the results of this investigation will provide a basis for the better understanding of flow mechanisms in high polymers.

Experimental

Preparation and Fractionation.—Seven polymers of styrene varying in viscosity average molecular weight ($\overline{M}_{\mathrm{v}}$) from 7000 to 350,000 were prepared by bulk polymerization at 60°. An average molecular weight in the desired range was obtained in each case by using appropriate concentrations of benzoyl peroxide and dodecyl mercaptan as shown in Table I. The reactions were stopped at conversions of approximately 25%. The polymers were separated by precipitation in an excess of vigorously stirred methanol, and were dried *in vacuo* at 60°.

Four polyisobutylenes with molecular weights as listed in Table I were fractionated.[9] Thus, the polymer known commercially as "Vistanex-LMH" with a viscosity average molecular weight of 69,000, was separated into a series of polymer fractions identified as PB1F1, PB1F2, and so on. The polymer PB5 consisted of a mixture of two large coarse fractions separated from PB2 and PB3.

All polymers were fractionated by single precipitation methods carried out at 30.0°. Solvent–precipitant combinations employed were methyl ethyl ketone–methyl alcohol for polystyrene and benzene–acetone for polyisobutylene. In each case the precipitant was added slowly with stirring to a solution containing 1.3 to 2.5 g. of polymer per 100 ml. of solvent (Table I) until a condition of permanent turbidity was reached. After adding an appropriate excess of the precipitant, the solution was warmed until it became clear, then subjected to gentle stirring while cooling slowly to 30.0°. The insoluble gel which settled out on standing overnight at this temperature was separated from the clear solution by decantation, washed with the non-solvent, and dried first on a steam

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[1] The work presented in this paper comprises a program of fundamental research on rubber and plastics being carried out under a contract between the Office of Naval Research and the Goodyear Tire and Rubber Company.

[2] Presented before the High Polymer Forum at the Atlantic City Meeting of the American Chemical Society, April 15, 1947.

[3] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

[4] W. O. Baker, C. S. Fuller and J. H. Heiss, *ibid.*, **63**, 2142 (1941).

[5] J. R. Schaefgen and P. J. Flory, forthcoming publication.

[6] G. J. Dienes and H. F. Klemm, *J. Applied Phys.*, **17**, 458 (1946).

[7] R. L. Zapp and F. P. Baldwin, *Ind. Eng. Chem.*, **38**, 948 (1946).

[8] A. J. Barry, *J. Applied Phys.*, **17**, 1020 (1946).

[9] The polyisobutylene was supplied by the Standard Oil Co. of New Jersey. We are indebted to Mr. D. W. Young of the Esso Laboratories who made available to us PB7, a laboratory sample of low molecular weight.