7.95(w), 8.97(m), 9.16(m), 9.28(s), 9.54(s), 9.67(s), 10.68(m), 10.95(w), 11.28(m), 12.86–12.98(s), 13.25(s), and 14.20–14.33(s)μ.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.72; H, 5.01. Found: C, 59.85; H, 5.28.

The reaction of α-methylstyrene, bromoform, and potassium t-butoxide. (2,2-Dibromo-1-methylcyclopropyl)benzene (IId). α-Methylstyrene (177 g., 1.50 moles) was reacted with 63.2 g. (0.250 mole) of bromoform and potassium *t*-butoxide, from 10.0 g. (0.256 g. atom) of potassium, in the manner described for the reaction of α-methylstyrene and chloroform. The reaction product, (2,2-dibromo-1-methylcyclopropyl)benzene (IId) (58.9 g., 81%) was obtained as a colorless liquid, b.p 94–100° (2 mm.), n_D^{22} 1.5831–1.5848. A refractionation of the product through a 15-cm. Vigreux column yielded a middle fraction boiling at 91–92° (1 mm.), n_D^{22} 1.5842. The product solidified upon cooling, m.p. 35.5–36°. The infrared spectrum exhibits absorption maxima at 3.28(m), 3.31(m), 3.38(s), 3.43(m), 3.50(m), 6.24(m), 6.32(w), 6.69(s), 6.94(s), 7.00(s), 7.24(m), 7.57(w), 7.66(w), 7.98(w), 8.71(m), 8.99(m), 9.32(s), 9.42(s), 9.80(s), 10.73(m), 10.97(m), 11.59(m), 11.79(m), 13.10(s), and 14.30–14.41 (s)μ.

Anal. Calcd. for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48. Found: C, 41.55; H, 3.55.

The reduction of (2,2-Dichlorocyclopropyl)benzene with sodium and methanol. Cyclopropylbenzene (IIIa). The method described by Doering and Hoffmann[1] for the reduction of 7,7-dibromobicyclo[4.1.0] heptane was employed with only slight modification. Following the complete reaction of the sodium metal (46 g., 2.0 g. atoms) with the wet methanol (10 ml. of water to 300 ml. of methanol), 200 ml. of water was added, the layers were separated, and the aqueous layer was neutralized with hydrochloric acid before being extracted with ether. From 18.7 g. (0.100 mole) of (2,2-dichlorocyclopropyl)benzene (IIa) there was obtained 8.7 g. (74%) of cyclopropylbenzene as a colorless liquid, b.p. 64–70° (18 mm.). A redistillation of the product through a Todd Precise Fractionation Assembly yielded a middle fraction boiling at 69° (12 mm.), n_D^{22} 1.5316, d_4^{20} 0.936; M_D calcd. 38.8, M_D found 39.1 (lit., b.p. 60–63° (11 mm.), 7 n_D^{20} 1.5320,[7] d_D^{25} 0.9374[8]). Absorption maxima were observed in the infrared at 3.24(s), 6.22(s), 6.64(s), 6.80(s), 6.89(m), 6.97(m), 8.18(m), 8.49(w), 9.05(w), 9.22(s), 9.53(s), 9.74(s), 10.03(w), 11.11(s), 12.28(s), 13.26–13.37(s), and 14.30–14.39(s)μ.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.21; H, 8.51.

The reduction of (2,2-dibromomocyclopropyl)benzene with sodium and methanol. Cyclopropylbenzene (IIIa). (2,2-Dibromocyclopropyl)-benzene (IIb) (27.6 g., 0.100 mole) was reduced with 46 g. (2.0 g. atoms) of sodium and 300 ml. of wet methanol in the above manner. The product obtained (8.1 g., 69%) was identical with that obtained from the dichloro compound as evidenced by both boiling point (65° at 17 mm.) and refractive index (n_D^{22} 1.5315).

The reduction of (2,2-dichloro-1-methylcyclopropyl)benzene and (2,2-dibromo-1-methylcyclopropyl)benzene with sodium and methanol. (1-Methylcyclopropyl)benzene (IIIc). By the method described above, 10.1 g. (0.050 mole) of (2,2-dichloro-1-methylcyclopropyl)benzene (IIc) was reduced with 23 g. (1.0 g. atom) of sodium and 200 ml. of wet methanol to give 3.5 g. (54%) of colorless (1-methylcyclopropyl)-benzene (IIIc), b.p. 72–77° (22 mm.), n_D^{21} 1.5146–1.5150. Refractionation of the product through a 10-cm. Vigreux column yielded a middle fraction boiling at 69° (18 mm.), n_D^{21} 1.5151. The reduction of 21.8 g. (0.075 mole) of (2,2-dibromo-1-methylcyclopropyl)benzene (IId) by 32 g. (1.4 g. atoms) of sodium and 300 ml. of wet methanol yielded 4.0 g. (40%) of (1-methylcyclopropyl)benzene (IIIc), b.p. 70–74° (22 mm.), n_D^{21} 1.5152–1.5157. Redistillation of the product through a 10-cm. Vigreux column yielded a middle fraction boiling at 71° (20 mm.), n_D^{21} 1.5152. The infrared absorption spectrum of the product exhibits maxima at 3.22(s), 3.29(s), 3.35(s), 3.45(m), 6.22(s), 6.31(w), 6.66(s), 6.86(s), 6.92(s), 7.00 (m), 7.23(m), 7.42(w), 8.93(s), 9.24(w), 9.33(m), 9.71(s), 9.86(s), 10.72(m), 11.07(w), 11.61(w), 11.81(s), 12.73(w), 13.13–13.23(s), and 14.24–14.35(s)μ.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.04.

COLUMBIA, MO.

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

Preparation of Polymers Containing Pyridine Units from Polyvinyl Ketones

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Poly(methyl vinyl ketone) was converted to the polyoxime and this polymer, under the conditions of the Knoevenagel 1,5-dioxime ring closure, gave a copolymer of methyl vinyl ketone with some 2,6-dimethylpyridine units which consisted of 76.2 mole % of the latter. Similarly a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime containing 70.2 mole % ketoxime units was converted to a copolymer of phenyl vinyl ketone and 2,6-diphenylpyridine units which consisted of 50.3 mole % of the latter. Neither copolymer was thermally stable.

The marked thermal and chemical stability of the pyridine nucleus prompted an investigation of the heat resistance of polymers which incorporate a pyridine ring as a structural feature of the polymer chain. A promising approach to the desired polymers was suggested by the work of Marvel and Levesque[2] on the structure of low molecular weight poly(methyl vinyl ketone). During this

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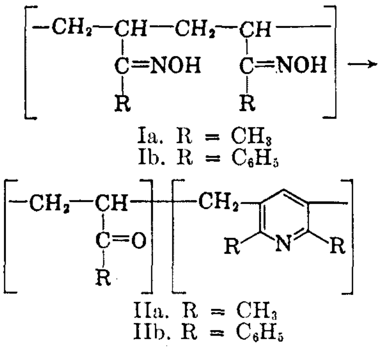
(2) (a) C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **60**, 280 (1938). (b) C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **61**, 3234 (1939).

study a material possessing the correct elemental composition for copolymer IIa was obtained by application of the Knoevenagel ring closure of 1,5-dioximes[3] to polymethyl vinyl ketoxime (Ia).



Ia. R = CH_3
Ib. R = C_6H_5

IIa. R = CH_3
IIb. R = C_6H_5

The limited information available on the copolymer necessitated a re-examination of this work to provide additional evidence as to the presence of a pyridine moiety in the polymer and to determine if such a copolymer were heat stable.

In order to insure the molecular weight and consequently the potential stability of the pyridine-containing copolymer, it was essential to polymerize the precursor vinyl ketone to the highest possible molecular weight polymer which still possessed the required solubility properties. To this end, a number of procedures for the polymerization of methyl vinyl ketone was examined. Bulk polymerization with benzoyl peroxide produced polyketones having an average inherent viscosity of 0.65. Standard emulsion polymerization techniques were found to be unsuccessful, but when the water solubility of the monomer was decreased by including varying amounts of sodium chloride in polymerization recipes employing solutions of potassium caproate, it was possible to prepare methyl vinyl ketone polymers having inherent viscosities in the range 0.83–1.45. A summary of the results obtained by use of this procedure is included in Table I. Considerably higher molecular weight polyketones were obtained with a modification of the potassium persulfate-silver nitrate aqueous solution procedure reported by Whitby and co-workers.[4]

TABLE I

POLYMERIZATION OF METHYL VINYL KETONE IN POTASSIUM CAPROATE–SODIUM CHLORIDE SOLUTION

No.	Time, Hr.	Temp.	Conversion, %	Salt Concentration, G.	Inherent Viscosity[a]
72	64	26	20	0.10	1.24
73	16	50	61	0.10	1.45
74	20	50	67	0.10	0.83
75	62	26	14	0.25	1.08
76	14	50	51	0.25	1.20
77	19	50	66	0.25	1.19
78	110	26	49	0.35	1.23
79	19	50	61	0.35	1.21
80	14	50	53	0.35	1.25

[a] Inherent viscosities were determined in methyl ethyl ketone.

With this technique poly(methyl vinyl ketones) possessing inherent viscosities of 1.27–2.60 (usual range 1.9–2.0) could be prepared at 5°, and polymers having inherent viscosities of 2.00–2.99 could be obtained at −15° (Table II). By comparison with the intrinsic viscosity–osmotic pressure molecular weight reported by Guillet and Norrish,[5] it can be estimated that methyl vinyl ketone polymers of inherent viscosity 2 to 3 should have molecular weights of the order of 3–4 × 10^5. Infrared analysis of the polyketone disclosed bands consistent with the expected vinyl polymer, but in addition, weak bands were found at 3620–3500 $cm.^{-1}$ and 3380 $cm.^{-1}$ which appeared to be due to strongy adsorbed water which was not removed by the drying procedure; this is in accord with the consistently low carbon analyses.

TABLE II

POLYMERIZATION OF METHYL VINYL KETONE

(Water Azeotrope Initiated by Potassium Persulfate-Silver Nitrate)

No.	Time, Hr.	Temp.	Conversion, %	Inherent Viscosity[a]
7	5	26	87	0.83
10	8	26	90	0.85
9	8	5	93	1.45
8	18	5	96	2.60
11	19	5	86	1.27
12	20	5	95	1.92
15	20	5	94	1.91
13	21	5	96	1.95
14	21	5	100	2.03
16	21	5	96	1.99
18	24	−15	82	2.00
19	36	−15	88	2.17
17	40	−15	100	2.45
20	42	−15	67	2.99
21[b]	24	−15	85	2.88
23	36	−15	69	2.55

[a] Inherent viscosities were determined in methyl ethyl ketone. [b] Runs 21 and 23 used one half the usual amount of potassium persulfate.

Conversion of the high molecular weight polymethyl vinyl ketone to polymethyl vinyl ketoxime (Ia) was effected by use of a modification of the procedure of Marvel and Levesque.[2a] Treatment of this material with an ethanolic hydrogen chloride solution produced a copolymer of methyl vinyl ketone and 2,6-dimethylpyridine units (IIa) containing 76.2 mole % of pyridine units. From poly-

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(3) (a) E. Knoevenagel and R. Weissberger, *Ber.*, **26**, 436 (1893). (b) E. Knoevenagel, *Ann.*, **281**, 25 (1894). (c) J. Wislicenus, *Ann.*, **302**, 235, 241 (1898). (d) E. E. Blaise and M. Montagne, *Compt. rend.*, **180**, 1760 (1925). (e) B. D. Shaw, *J. Chem. Soc.*, 300 (1937).

(4) G. S. Whitby, M. D. Gross, J. R. Miller, and A. J. Costanza, *J. Polymer Sci.*, **16**, 549 (1955).

(5) J. E. Guillet and R. Norrish, *Proc. Roy. Soc.*, **233A**, 153 (1955).

methyl vinyl ketoximes of inherent viscosity 3.2–3.6 in dimethyl sulfoxide, copolymers were obtained which possessed inherent viscosities in chloroform of 0.11–0.14. Infrared spectra of the copolymer in chloroform revealed pertinent absorption bands at 1708 (C=O), 1599, 1562 cm.$^{-1}$, and a weak shoulder at 1500 cm.$^{-1}$ (pyridine C=C and C=N bands). In addition a band of very weak intensity was noted at 3300–3160 cm.$^{-1}$ (—OH). The results of the elemental analysis eliminate the possibility of this absorption being due to the hydroxyl group of a residual oxime or an aldol condensation, and suggest the observed band was again due to residual water. This is consistent with the hygroscopic nature of the copolymer and the frequently low carbon analyses. The possibility of amide formation by rearrangement of the oxime functions under the conditions of the ring closure was excluded by treatment of the copolymer with 20% sulfuric acid at reflux temperature. The infrared spectrum of the material isolated from this reaction was identical at all significant points with the spectrum of the starting material. Comparison of the ultraviolet spectrum of the copolymer with spectra reported for a number of methyl substituted pyridines provided additional evidence for the presence of a recurring pyridine unit in the polymer. The general shapes of the curves were quite similar, a bathochromic shift being observed with increasing alkyl substitution. A summary of these data is presented in Table III. An average neutralization equivalent of 117.0 for the basic unit of the copolymer was obtained by titration of the polymer with perchloric acid in a nonaqueous system; this represents a 1.8% deviation from the theoretical value of 119.1.

TABLE III

COMPARISON OF ULTRAVIOLET ABSORPTION OF METHYLPYRIDINES WITH COPOLYMER IIa[a]

Compound	λ_{max} mμ)	ϵ
2,6-Dimethylpyridine	269–270	7,600
2,3,5-Trimethylpyridine	273–273.5	6,820
2,3,6-Trimethylpyridine	274.5–275	8,480
2,3,5,6-Tetramethylpyridine	279.5	10,060
Copolymer IIa	281.5	8,980

[a] Data used for comparison were taken from ref. 6; these values correspond to others reported in the lit.[7] Spectra were determined in 0.2N H_2SO_4.

Since the practicality of this route to a pyridine-containing polymer had been successfully demonstrated by the preparation of copolymer IIa, it was desirable to extend this series of reactions to the analogous aromatic system, poly(phenyl vinyl ketoxime). As a preliminary to this work, an examination of the ring closure reaction was carried out on a comparable monomeric system. It was found that 2,6-diphenylpyridine could be prepared from the dioxime of 1,3-dibenzoylpropane in a yield of 97.5%; therefore, it was evidently feasible to extend this reaction to poly(phenyl vinyl ketoxime).

The first point of attack in this phase of the work involved a series of experiments designed to uncover the optimum conditions for the preparation of high molecular weight poly(phenyl vinyl ketone). Solution polymerization of phenyl vinyl ketone initiated by benzoyl peroxide or azo-*bis*-isobutyronitrile produced polymers with inherent viscosities in the range 0.11–0.26 (Table IV). With a potassium persulfate system emulsified with Triton X-301, polymers of inherent viscosity 0.14–0.17 were obtained at temperatures of 5°–55°. The addition of silver nitrate to this system as an activator raised the inherent viscosity range to 0.21–0.30 for experiments carried out at 5°. Similar results were obtained with a potassium persulfate–ORR soap system containing 5% of emulsifier and 0.37% of initiator; polymers prepared by this procedure possessed viscosities of 0.16–0.31. Lowering the initiator concentration to 0.2% and raising the soap concentration to 7.5% changed the viscosity range to 0.41–0.65. A summary of these polymerizations is recorded in Table V.

TABLE IV

SOLUTION POLYMERIZATION OF PHENYL VINYL KETONE

No.	Procedure	Time, Hr.	Temp.	Conversion, %	Inherent Viscosity[a]
87	A	6	55	58	0.19
88	A	10	55	44	0.19
89	B	10	55	73	0.26
90	B	11	55	84	0.19
98	B	25	55	70	0.11

[a] Inherent viscosities of poly(phenyl vinyl ketone) were determined in benzene.

TABLE V

EMULSION POLYMERIZATION OF PHENYL VINYL KETONE

No.	Procedure	Time, Hr.	Temp.	Conversion, %	Inherent Viscosity
92	A	3	55	41	0.17
91	A	12	26	9	0.14
93	A	13	5	11	0.16
99	B	36	5	26	0.21
100	B	62.5	5	52	0.30
95	C	4	55	52	0.25
94	C	12	26	50	0.31
96	C	13	5	34	0.16
109	D	5	50	86	0.59
110	D	10	50	100	0.41
108	D	24	26	69	0.65

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(6) N. Ikekawa, M. Maruyama, and Y. Sato, *Pharm. Bull.* (*Japan*), **2**, 209 (1954).

(7) (a) R. J. L. Andon, J. D. Cox, and E. F. Herington, *Trans. Faraday Soc.*, **50**, 918 (1954). (b) J. I. Jones, *J. Chem. Soc. Ind.* (*London*), **69**, 99 (1950). (c) H. E. Podall, *Anal. Chem.*, **29**, 1423 (1957).

TABLE VI
ANIONIC POLYMERIZATION OF PHENYL VINYL KETONE

No.	Initiator	G.	Solvent	Temp.	Conversion, %	Inherent Viscosity
104	Sodium	0.01	Liquid ammonia	−78	66	0.09
113	Sodium	0.005	Liquid ammonia	−78	56	0.06
114	Lithium	0.005	Liquid ammonia	−78	68	0.03
105	Sodium ethoxide	0.03	Dimethylformamide	−78	10	Insoluble
106	Sodium ethoxide	0.03	Tetrahydrofuran	−78	100	0.03
115	Sodium cyanide	0.005	Dimethylformamide	−78	24	0.06
116	Sodium cyanide	0.01	Dimethylformamide	−78	20	0.08
118	Sodium cyanide	0.005	Dimethylsulfoxide	24	100	0.08
117	Potassium cyanide	0.005	Dimethylformamide	−78	28	0.10

Under anionic conditions, low molecular weight material was obtained with a number of initiator systems. Physically, these polymers varied from tacky semisolids to powders while the inherent viscosities ranged from 0.03–0.10. Comparison of the infrared spectra of the soluble polymers with spectra of authentic samples of poly(phenyl vinyl ketone) indicated the polymers were similarly constituted. Representative results of these polymerizations are summarized in Table VI.

A sample of the higher molecular weight poly(phenyl vinyl ketone) prepared under emulsion conditions was converted to a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime containing 70.2 mole per cent ketoxime units by oximation of the polyketone under very mild conditions. Infrared analysis was consistent with the proposed copolymer structure with pertinent bands at 3500–3260 cm.$^{-1}$ (—OH); 1665 cm.$^{-1}$ (ArC=O); 1635 cm.$^{-1}$ (C=N); 1600 cm.$^{-1}$, 1580 cm.$^{-1}$, and 1498 cm.$^{-1}$ (aromatic); 914 cm.$^{-1}$

When this copolymer was subjected to the conditions designed to effect ring closure of the 1,5-dioxime groups to a pyridine moiety, a polymer was obtained which dissolved slowly in dilute hydrochloric acid and was insoluble in sodium hydroxide solution. By contrast the precursor polyketone was completely insoluble in acid. On the basis of the elemental analysis it was possible to estimate that the "pyridine" copolymer consisted of 49.7 mole % phenyl vinyl ketone and 50.3 mole % 2,6-diphenylpyridine units (IIb). Infrared analysis indicated the absence of hydroxyl functions (no residual oxime) and showed a new absorption band at 1547–1545 cm.$^{-1}$ This absorption is somewhat lower than would be expected for a 2,6-diphenylpyridine nucleus but is in the general region for C=C, C=N aromatic absorption (*cf.* 2,6-diphenylpyridine: 1605, 1592, 1568, and 1497 cm.$^{-1}$; phenyl and pyridine C=C and C=N bands). Additional evidence consistent with the assignment of a 2,6-diphenylpyridine moiety to the copolymer was provided by a comparison of the ultraviolet spectrum of the polymer with the spectrum of 2,6-diphenylpyridine. In dioxane, absorption maxima for the monomeric pyridine occurred at 245 mμ (ϵ 28,200), 285 mμ (shoulder, ϵ 12,280) and 302 mμ (ϵ 11,200). In the same solvent, a similar spectrum was obtained for the copolymer containing 50.3 mole % 2,6-diphenylpyridine units. The maxima were found to have undergone a considerable hypsochromic shift with the long wave length bands compressed to a single maximum at 285 mμ (ϵ 11,200) and the main absorption shifted to 236 mμ (ϵ 20,900). Extinction coefficients for the pyridine units of the copolymer were calculated by subtracting the contribution expected from the phenyl vinyl ketone units at the wave lengths of the observed maxima; this contribution was determined from a spectrum of polyphenyl vinyl ketone in dioxane (λ 236, ϵ 7,760; λ285, ϵ 870).

Thermal stability tests on the pyridine-containing copolymers revealed that neither polymer was appreciably stable. At 225° the copolymer with 2,6-dimethylpyridine units (IIa) lost 3.2% of its weight in 12 hr. and the copolymer with 2,6-diphenylpyridine units (IIb) lost 2.7% of its weight in the same time. At 300° both polymers exhibited a steady weight loss; after 12 hr. polymer IIa had lost 21.6% of its original weight and IIb had lost 9.9%.

EXPERIMENTAL

Bulk polymerization of methyl vinyl ketone. Pure methyl vinyl ketone was obtained by treating the water azeotrope of methyl vinyl ketone (85% monomer) with an equal weight of acetic anhydride for 24 hr. at room temperature; the monomer was recovered by careful fractionation of this mixture under nitrogen at atmospheric pressure using a 30-cm. column packed with glass helices; b.p. 81–81.4°, $n_D^{20.7}$ 1.4096 (premature polymerization was prevented by collecting the distillate in Dry Ice-acetone). Polymerization was effected by adding 0.5% of benzoyl peroxide to 10 g. of freshly distilled monomer, flushing the system with nitrogen, and placing the samples in a constant temperature bath at 26° for 40 hr. The viscous, light yellow semisolid product was purified by successive reprecipitations from acetone into water. After drying at 50° for 48 hr., approximately 40% yields of a hard material soluble in acetone, methyl ethyl ketone, and dioxane were obtained. Inherent viscosities in methyl ethyl ketone averaged 0.65.

Polymerization of methyl vinyl ketone in potassium caproate-sodium chloride solution. Pure methyl vinyl ketone (10.0 g.), potassium caproate (20.0 g. of a 2.5% aqueous solution), sodium chloride (as indicated in Table I), Hooker's lauryl mercaptan (0.005 g.), and potassium persulfate (0.2 g.; 5 ml. of a solution containing 4 g. of potassium persulfate in 100 ml. of oxygen-free water) were added to 4-ounce screw-cap bottles equipped with self-sealing rubber gaskets. After bubbling nitrogen through the solutions, the bottles were capped and tumbled end-over-end in constant temperature baths. The polymers were recovered by slowly pouring the reaction mixtures into reagent grade methanol with rapid stirring followed by the addition of sufficient hydrochloric acid to adjust the solution pH to approximately 2. Purification was accomplished as previously described.

Polymerization of water azeotrope of methyl vinyl ketone initiated by potassium persulfate-silver nitrate. Methyl vinyl ketone was polymerized by the following modification of the procedure reported by Whitby *et al.*[4]

Into 4-ounce screw-cap bottles equipped with self-sealing rubber gaskets were placed 11.7 g. of methyl vinyl ketone water azeotrope (freshly distilled under nitrogen; approximately 10 g. of monomer) and 80 ml. of oxygen-free water. To this solution was added 0.2 g. of potassium persulfate (5 ml. of a solution containing 4 g. of potassium persulfate in 100 ml. of water). After bubbling nitrogen through the solutions, the bottles were capped and brought to the desired temperature. Silver nitrate (0.0105 g., 1 ml. of a solution containing 1.050 g. of silver nitrate in 100 ml. of water) was then added, the bottles swept out with nitrogen, recapped, and returned to constant temperature baths. Alternatively, the silver nitrate solution was injected with a hypodermic syringe through a puncture in the metal cap. For polymerizations at 26° or 5° the polymers were recovered by slowly pouring the white suspensions into reagent grade methanol. For polymerizations at −15° the polymers were isolated by allowing the samples to warm to room temperature, decanting the supernatant liquid and dissolving the solid in reagent grade acetone. Purification was effected as described above; samples for microanalysis were dried for three days over phosphorus pentoxide at 80° (0.75 mm.). Significant infrared bands (film): 3620–3500, 3380 (weak); 1710 ($C{=}O$), 1435, 1363 cm.$^{-1}$

Anal. Calcd. for $(C_4H_6O)n$: C, 68.54; H, 8.63. Found: C, 68.17, 68.09; H, 8.71, 8.33.

Polymethyl vinyl ketoxime. To a solution of 4.88 g. (0.070 mole) of hydroxylamine hydrochloride in 125 ml. of ethanol was added 5.82 g. (0.071 mole) of anhydrous sodium acetate in 190 ml. of ethanol. After 5 min. the precipitated sodium chloride was removed by filtration and the alcohol solution diluted with 80 ml. of redistilled dioxane. The solution was heated at reflux temperature with vigorous stirring while 2.46 g. (0.035 mole) of high molecular weight polymethyl vinyl ketone in 125 ml. of dioxane was added over a period of 45 min. The reaction mixture was stirred at this temperature for an additional 7 hr. during which time a large amount of the product precipitated. After allowing the mixture to stand at room temperature for 12 hr., the polymer was collected on a filter, washed thoroughly with water and methanol, and purified by reprecipitation from redistilled dimethyl sulfoxide into water; yield 2.6 g. (87%) of white powder; softening range 246–280°. Inherent viscosity in dimethyl sulfoxide: 3.59. Samples for microanalysis were dissolved in dimethyl sulfoxide, the solutions filtered, and the polymer recovered by pouring the solution into water (repeated three times). After washing with a large volume of water the samples were dried 4 days at 80° (0.1 mm.). Significant infrared bands (Nujol): 3400–3180 (—OH), 1658 ($C{=}N$), 955–935 cm.$^{-1}$ (characteristic of oximes[8]).

Anal. Calcd. for $(C_4H_7NO)n$: C, 56.45; H, 8.29; N, 16.46. Found. C, 56.24; H, 8.51; N, 15.86; residue, 0.88. Adjusted to account for residue. C, 56.86; H, 8.58; N, 16.00.

Copolymer of methyl vinyl ketone and "2,6-dimethylpyridine" (IIa). Poly(methyl vinyl ketoxime) (1.044 g., 0.0122 mole) was dissolved in 16 ml. of concentrated hydrochloric acid by adding the powdered oxime slowly to the well stirred acid. To this was added a solution of 44.4 g. (1.2 moles) of hydrogen chloride in 165 ml. of absolute ethanol. The resultant cloudy yellow solution was heated under reflux with stirring for 24 hr. At the end of this period the red-orange solution was concentrated under reduced pressure to 20 ml., diluted with water, and made basic with concentrated ammonium hydroxide. The precipitated polymer was collected on a filter and washed with 200 ml. of distilled water. Purification was effected as follows: The polymer was dissolved in dilute hydrochloric acid, insoluble material was removed by filtration, and the polymer recovered by reprecipitation with sodium carbonate solution (repeated four times). The material was then alternately suspended in distilled water and filtered until three complete washings gave negative chloride tests with silver nitrate. Following this, the solid was dried at 100° for 1 hr. Finally, the polymer was dissolved in reagent grade chloroform, insoluble material was removed by filtration, and the polymer recovered by slowly adding the chloroform solution to petroleum ether (b.p. 30–60°) (repeated four times). Yield: 0.65 g. (88%); decomp. 190°, partial melting 460°. Samples for analysis were dried at 100° (0.25 mm.) for 48 hr. Pertinent infrared bands (chloroform): 3400–3160, very weak (—OH); 1708 ($C{=}O$); 1599, 1562, and a weak shoulder at 1500 (pyridine $C{=}C$ and $C{=}N$ bands); 1445; 1365 cm.$^{-1}$ ($C{-}CH_3$). Ultraviolet maximum ($0.2N$ H_2SO_4): λ_{max} 281.5 mμ (ϵ 8980).

Anal. Calcd. for $(C_8H_9N)_{0.762}$-$(C_4H_6O)_{0.238}$: C, 78.74; H, 7.76; N, 9.93.[9] Found: C, 79.05; H, 8.01; N, 9.87.[10]

Neutralization equivalent of the basic moiety in the methyl vinyl ketone-"2,6-dimethylpyridine" copolymer (IIa). A sample of pure methyl vinyl ketone-"2,6-dimethylpyridine" copolymer was dried at 100° (0.25 mm.) for 2 days. Immediately upon removal of the material from the drying apparatus, a 47.519-mg. sample was placed in a 25-ml. volumetric flask and diluted to volume with reagent grade chloroform. From this solution, 2-ml. aliquots were removed, diluted with 30 ml. of glacial acetic acid, and titrated with $0.00288N$ perchloric acid (in acetic acid; standardized with potassium acid phthalate to a crystal violet end point). When crystal violet was used to determine the end point of the polymer titration, 9.40 ml. (average value) of standard acid was required; with methyl violet as the indicator, 9.65 ml. (average value) was required. These values correspond to equivalent weights of 118.5 and 115.5, respectively (theoretical: 119.1). For the calculation of the equivalent weight, it was assumed the polymer was 84.46 gram per cent C_8H_9N; this is the result of the hydrolysis of 13.53% of the ketoxime groups during the ring closure.[9]

Dioxime of 1,3-dibenzoylpropane. (a) *Glutaryl chloride.* Glutaric acid (30 g., 0.23 mole) was mixed with phosphorus pentachloride (94.4 g., 0.46 mole). After the reaction had started, the mixture was heated on the steam bath for 1 hr. The phosphorus oxychloride was then removed by distillation at atmospheric pressure and the residue fractionated under reduced pressure; b.p. 105–106° (18 mm.), [lit., 107–108° (16 mm.)[12]]. The yield was 34.5 g. (90%).

(b) *1,3-Dibenzoylpropane.* A mixture of 59.6 g. (0.448 mole) of anhydrous aluminum chloride in 300 ml. of dried, distilled benzene was cooled in an ice bath and 34.5 g. (0.204 mole) of freshly distilled glutaryl chloride was added dropwise with stirring over a period of 15 min. When all the acid chloride had been added, the ice bath was removed and the

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(8) A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954).

(9) The percentage composition of this polymer was calculated on the basis of the assumed hydrolysis of 13.53% of the ketoxime groups during the reaction *i.e.* for 0.4324 mole C_8H_9N and 0.1353 mole of C_4H_6O.[2b,11]

(10) The hygroscopic nature of the polymer necessitated drying the sample to a constant weight prior to analysis.

(11) P. J. Flory, *J. Am. Chem. Soc.*, **61**, 1518 (1939).

(12) K. v. Auwers and M. Schmidt, *Ber.*, **46**, 457 (1913).

reaction stirred at room temperature for 2 hr. The solution was then poured slowly onto a mixture of cracked ice and 40 ml. of concentrated hydrochloric acid; 400 ml. of benzene was added and the organic layer separated. After washing with an equal volume of sodium bicarbonate solution and then with water, the benzene was evaporated under reduced pressure leaving a heavy oil which solidified on cooling. Upon recrystallization from ethanol-petroleum ether (b.p. 30–60°), 38.1 g. (74%) of pure 1,3-dibenzoylpropane was obtained; m.p. 65–66° [lit., 62–63°,[13a] 67.5°[13b]]. Infrared analysis (chloroform): 1683 (ArC=O); 1601, 1584, 1495–1490 (aromatic); 1453; 685 cm.$^{-1}$ (monosubstituted phenyl). Ultraviolet maximum (absolute ethanol): λ_{max} 243 mμ (ε 25,200).

(c) *Dioxime of 1,3-dibenzoylpropane.* To 25.4 g. (0.31 mole) of anhydrous sodium acetate in 425 ml. of ethanol were added at equivalent rates a solution of 1,3-dibenzoylpropane (25.2 g., 0.10 mole) in 350 ml. of ethanol and a solution of 20.9 g. (0.30 mole) of hydroxylamine hydrochloride in 300 ml. of ethanol. After the reaction had been heated at reflux temperature for 4 hr., the hot mixture was filtered, and the filtrate concentrated to one half its original volume and diluted with water to precipitate 27.6 g. of crude product (98%). Two recrystallizations from ethanol-water yielded 22.3 g. (79%) of 1,3-dibenzoylpropane dioxime; m.p. 163–164° [lit., 165–166° (dec.)[14]]. Infrared analysis (Nujol): 3100 (—OH); 1625–1620 (C=N); 1600 (shoulder), 1575, 1499 (aromatic); 938 (oxime); 770–765, and 700 cm.$^{-1}$ (monosubstituted phenyl).

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found. C, 72.32; H, 6.33; N, 9.71.

2,6-Diphenylpyridine. A solution of 100 g. of hydrogen chloride in 400 ml. of absolute ethanol was added to 2.82 g. (0.01 mole) of the dioxime of 1,3-dibenzoylpropane in 40 ml. of absolute ethanol and the resulting solution heated at reflux for 19 hr. The light pink reaction mixture was then concentrated to 30 ml., cooled, and neutralized with ammonium hydroxide. An additional 100 ml. of water was added to the mixture, the precipitate collected on a filter, washed well with water, and dried; crude yield: 2.25 g. (97.5%); m.p. 80–81.6°. After treatment with Darco in absolute ethanol, the yield of pure 2,6-diphenylpyridine was 1.68 g. (73%); m.p. 81.5–82° [lit., 81–82°[15]]. Infrared analysis (chloroform): 3035; 1605 (shoulder), 1592, 1568, and 1497 (pyridine and phenyl, C=C and C=N); 1457; 1444; 1268; and in Nujol: 826; 778, 758, 742; and 697 cm.$^{-1}$ Ultraviolet maxima (absolute ethanol): λ_{max} 245 mμ (ε 28,200), λ_{max} 285 mμ (ε 12,280), λ_{max} 302 mμ (ε 11,200).

Anal. Calcd. for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.34; H, 5.60; N, 5.92.

Phenyl vinyl ketone. (a) *β-Chloropropiophenone.* β-Chloropropiophenone was prepared by a modification of the procedures used by Allen and Barker[16] and Hale and Britton.[17] With this procedure 60–74% yields of pure β-chloropropiophenone were obtained if the reaction was carried out on $^1/_2$ molar amounts or less, but when the reaction scale was increased the product was found to be contaminated with 30–38% of β-phenylpropiophenone. Higher yields of pure product were obtained with the following procedure.

Anhydrous aluminum chloride (83 g., 0.62 mole) was cooled in an ice bath and 69.9 g. (0.55 mole) of β-chloropropionyl chloride in 140 ml. of reagent grade carbon disulfide was added with stirring. With continued cooling, 42.9 g. (0.55 mole) of dry distilled benzene in 100 ml. of carbon disulfide was added over a period of 10 min.; at this point a large amount of solid was present in the reaction flask. The reaction was stirred at 0° for 1 hr. and then heated to reflux for $^1/_2$ hr. at which time the clear solution was poured onto cracked ice. Chloroform was added, and the two phases separated. The aqueous layer was extracted with two 50-ml. portions of chloroform which were combined with the original organic layer. The combined organic phases were then washed with four 200-ml. portions of water and finally with 100 ml. of a saturated sodium chloride solution. After drying the yellow chloroform solution over sodium sulfate, the solvent was removed under reduced pressure, never allowing the solution to become warm. The resulting solid was pulverized and dried in air; crude yield: 89.4 g. (96%). One recrystallization from petroleum ether (b.p. 30–60°) produced 78.5 g. (85%) of β-chloropropiophenone; m.p. 49–50° [lit., 49–50°[18]].

Anal. Calcd. for C_9H_9OCl: C, 64.11; H, 5.38. Found: C, 64.22; H, 5.39.

(b) *Phenyl vinyl ketone.* Phenyl vinyl ketone was prepared in 69% yield according to the procedure of Allen *et al.*[19] by the dehydrohalogenation of β-chloropropiophenone; b.p. 37–38° (0.05 mm.); n_D^{20} 1.5588; phenylhydrazine derivative (1,3-diphenyl-Δ^2-pyrazoline) m.p. 152.5–153° [lit., 152–153°[20]]. Phenyl vinyl ketone can be stored at Dry Ice temperature for at least 3 weeks without change in the refractive index of the material.

Solution polymerization of phenyl vinyl ketone. Polymerizations were carried out in 21 × 70 mm. screw-cap vials fitted with rubber gaskets. The reagents were added in the order listed, the vials swept out with nitrogen, capped, and placed in constant temperature baths for the indicated times. The polymers were recovered by evaporating the solvent and triturating the residue with methanol. Purification was effected by dissolving the polymers in benzene and reprecipitating into petroleum ether (b.p. 30–60°).

Procedure A: Phenyl vinyl ketone, 2.0 g.; benzoyl peroxide, 0.0125 g. (10-ml. aliquot of a solution containing 0.125 g. of benzoyl peroxide in 100 ml. of benzene).

Procedure B: Phenyl vinyl ketone, 2.0 g.; azo-*bis*-isobutyronitrile, 0.0125 g. (10-ml. aliquot of a solution containing 0.125 g. of AIBN in 100 ml. of benzene). Table IV lists the results of these polymerizations.

Emulsion polymerization of phenyl vinyl ketone. The polymerization samples were prepared in the same manner as in the solution polymerizations described above, and then tumbled in constant temperature baths for the indicated periods. The polymers were recovered by pouring the emulsions into methanol with stirring. Purification was accomplished by dissolving the solid in benzene, removing any insoluble material by filtration, recovering the polymers by slowly adding the benzene solutions to low boiling petroleum ether, and finally freeze-drying the polymers from benzene.

Procedure A: Phenyl vinyl ketone, 2.0 g.; Triton X-301, 0.1 g.; potassium persulfate, 0.0075 g. (0.37%; 3-ml. aliquot of a solution containing 0.250 g. of potassium persulfate in 100 ml. of oxygen-free water).

Procedure B: Phenyl vinyl ketone, 2.0 g.; Triton X-301, 0.1 g.; potassium persulfate, 0.0125 g. (0.62%; 5-ml. aliquot of a solution containing 0.250 g. of potassium persulfate in 100 ml. of oxygen-free water); silver nitrate, 0.0005 g.

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(15) (a) M. Scholtz, *Ber.*, **28**, 1726 (1895). (b) O. Döbner and P. Kuntz, *Ann.*, **252**, 349 (1889). (c) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Am. Chem. Soc.*, **79**, 6430 (1957).

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(20) (a) F. Ramirez and A. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953). (b) T. Matsumoto and K. Hata, *J. Am. Chem. Soc.*, **79**, 5506 (1957).

(0.03%; 1-ml. aliquot of a solution containing 0.050 g. of silver nitrate in 100 ml. of oxygen-free water).

Procedure C: Phenyl vinyl ketone, 2.0 g.; ORR soap, 3.6 g. (2.8% solution, 5%); potassium persulfate, 0.0075 g. (as in procedure A above).

Procedure D: Phenyl vinyl ketone, 2.0 g.; ORR soap, 5.4 g. (2.8% solution, 7.5%); potassium persulfate, 0.004 g. (0.2%; 3-ml. aliquot of a solution containing 0.133 g. of potassium persulfate in 100 ml. of oxygen-free water).

Pertinent infrared bands (chloroform): 3000; 2905; 1677 (ArC=O); 1600, 1585 (aromatic); 1454; 1263; 1225; 1005; 976; 695 cm.$^{-1}$

Anal. Calcd. for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: 81.81, 81.83; H, 6.28, 6.24.

Representative results of these polymerizations are recorded in Table V.

Anionic polymerization of phenyl vinyl ketone. All anionic polymerizations were performed as follows: A mixture of 25 ml. of the solvent and the initiator was placed in a 50-ml. flask and brought to the desired polymerization temperature. To this mixture, 2.0 g. of monomer was added at once and the reaction mixtures allowed to warm to room temperature. In runs using dimethylformamide, solution of the monomer did not occur until the solvent melted as it warmed to room temperature. The polymers were isolated from the indicated solvents by use of the following techniques: (a) Liquid ammonia: ammonia allowed to evaporate and residue dissolved in benzene; (b) Tetrahydrofuran: reaction mixture precipitated by pouring into water; (c) Dimethylformamide: reaction mixture precipitated by pouring into isopropyl alcohol; (d) Dimethylsulfoxide: reaction mixture precipitated by pouring into isopropyl alcohol. Purification was accomplished as previously described. The results of these polymerizations are recorded in Table VI.

Copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime. Polyphenyl vinyl ketone (0.39 g., 0.003 mole) in 50 ml. of dioxane, hydroxylamine hydrochloride (2.09 g., 0.030 mole) in 30 ml. of dioxane to 50 ml. of ethanol, and anhydrous sodium acetate (2.46 g., 0.030 mole) in 20 ml. of dioxane to 50 ml. of ethanol were mixed and allowed to stand at room temperature for 52 days. The inorganic precipitate was removed by filtration and the filtrate added slowly to water to precipitate the polymer. The product was collected on a filter, washed well with water, dried briefly in air, and dissolved in pure tetrahydrofuran. Purification was accomplished by reprecipitating the polymer from tetrahydrofuran into low boiling petroleum ether (repeated 4 times); yield of copolymer: 0.405 g. Significant infrared bands (Nujol): 3500–3260 (—OH); 1665 (ArC=O); 1635 (C=N); 1600, 1580, 1498 (aromatic); 914; 765, 694 cm.$^{-1}$ (monosubstituted phenyl).

Anal. Calcd. for $(C_9H_8O)_{0.298}$—$(C_9H_9NO)_{0.702}$: C, 75.75; H, 6.14; N, 6.89. Found: C, 75.69; H, 6.03; N, 6.89.

On the basis of the analytical results it was concluded that this polymer was 70.2 mole per cent phenyl vinyl ketoxime.

Copolymer of phenyl vinyl ketone and "2,6-diphenylpyridine" (IIb). A solution of 35 g. of hydrogen chloride in 100 ml. of ethanol was gradually added to 10 ml. of pure tetrahydrofuran containing 0.3023 g. of a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime which consisted of 70.2 mole per cent ketoxime units. After the reaction had been stirred at reflux temperature for 48 hr., the red solution was concentrated to 20 ml. and a sodium carbonate solution was added dropwise until the *p*H reached 8–9. The mixture was diluted with water and extracted with two 50-ml. portions of chloroform. Traces of insoluble material were removed from the chloroform by filtration, the solution was concentrated to 20 ml. and then added slowly to low boiling petroleum ether to precipitate the product. The polymer was purified by reprecipitation from chloroform into low boiling petroleum ether (five times); yield: 0.1089 g.; softening range: 200–235°. Significant infrared bands (chloroform): 3040 (shoulder); 2950; 1673 (ArC=O); 1593, 1577, 1547–1545, 1492 (aromatic C=C and C=N); 1440; 1072; 1016; 693 cm.$^{-1}$ Ultraviolet maxima (dioxane): λ_{max} 236 mμ (ϵ 20,900), λ_{max} 285 mμ (ϵ 11,200).

Anal. Calcd. for $(C_9H_8O)_{0.497}$—$(C_{18}H_{13}N)_{0.503}$: C, 86.39; H, 5.64; N, 3.75. Found: C, 86.09; H, 5.60; N, 4.03.

Thermal stability of copolymers IIa *and* IIb. Previously dried samples of the two polymers were heated in air in aluminum cups and the weight loss was determined at given intervals during the heating period; the results of these tests have been described above.

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Reaction of Hydrazine Hydrate and Phenylhydrazine with Malononitrile

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The condensation products from hydrazine hydrate and phenylhydrazine with malononitrile were examined and are believed to be derivatives of 3-amino-4-cyano-5-(cyanomethyl)pyrazole rather than of 3,5-diaminopyrazole as reported by Rothenberg. Evidence is given for the proposed structures, and the chemical properties are described.

Rothenberg reported that the reaction of malononitrile with hydrazine and phenylhydrazine yielded oily substances which were assumed to be diaminopyrazole derivatives Ia and Ib, on the basis of the elementary analyses of their derivatives.[1]

As a result of repeating his procedure in our laboratory, however, the reaction seemed to proceed not in the way assumed by him and detailed study on the reaction products under various experimental conditions indicated a different process for the reaction. The reaction was studied under

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[1] R. v. Rothenberg, *J. prakt. Chem.*, **52**, 45 (1895).