Anal. Calcd. for $C_{16}H_{30}N_4O_4$: C, 56.10; H, 8.77; N, 16.37. Found: C, 56.06; H, 8.77; N, 16.06.

N,N'-Bis[(1-nitrocyclohexyl)methyl]hexamethylenediamine. Using hexamethylenediamine in a manner similar to that used with ethylenediamine, a 32% yield of product was obtained which after recrystallization from a mixture of ethyl ether and 30–60° petroleum ether melted at 51–52°.

Anal. Calcd. for $C_{20}H_{38}N_4O_4$: C, 60.30; H, 9.55; N, 14.07; neut. equiv., 199.0. Found: C, 61.09; H, 9.40; N, 14.25; neut. equiv., 199.5.

Bis(1-nitrocyclohexylmethyl)amine. To a stirred solution of 258 g. (2 moles) of nitrocyclohexane and 270 g. (2.75 moles) of concd. ammonium hydroxide (28%) in 500 ml. of 95% ethanol was added 180 g. (2.2 moles) of 37% formaldehyde dropwise over a period of 1 hr. When the addition of formaldehyde was complete, the reaction mixture was refluxed for 4 hr. and then allowed to cool to room temperature. The mixture was poured into a liter of 1/1 solution of concentrated hydrochloric acid and water. The hydrochloride salt which precipitated was removed by filtration, washed in ethanol, and dried. The hydrochloride was neutralized with aqueous sodium hydroxide solution, and the free amine was recrystallized from 95% ethanol. The yield of white crystalline product, m.p. 57–58°, was 176 g. or 59%.

Anal. Calcd. for $C_{14}H_{24}N_3O_4 \cdot HCl$: C, 50.07; H, 7.74; N, 12.51. Found: C, 50.24; H, 7.66; N, 12.58.

The infrared spectra of all of the dinitro compounds showed a high nitro group absorption at 6.50–6.52, typical of tertiary nitro compounds.[5]

Reduction of dinitro amines to polyamines. All of the Mannich condensation products were reduced to the corresponding polyamines with hydrogen in a Parr hydrogenator by using 2 g. of Raney nickel[6] for 0.1 mole of dinitro compound in 175 ml. of 95% ethanol. The heavy-walled reaction bottle was shaken until the hydrogen required for the reduction of the nitro groups was absorbed. Then the catalyst was filtered off and the ethanol solvent removed under reduced pressure. The liquid products were purified by distillation *in vacuo*. The piperazine derivative was recrystallized from acetone, while the 2,5-dimethylpiperazine compound was recrystallized from 90–120° petroleum ether at −15°. Table I lists the properties of these compounds.

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(5) N. Kornblum, H. E. Ungnade, and R. A. Smiley, *J. Org. Chem.*, 21, 377 (1956); J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(6) E. C. Horning, *Org. Syntheses*, **Coll. Vol. III**, p. 176 (1955).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PLASTICS DIVISION, MONSANTO CHEMICAL CO.]

Synthesis of Polyfunctional Polymers[1]

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Received December 12, 1957

Polyfunctional polymers were synthesized by chemical modification of hydrocarbon and nitrile polymers and by copolymerization of selected monomers. Reactions included aromatic nitration, chloromethylation and acylation, reduction of nitro, oximino, carbonyl and nitrile groups and other carbonyl reactions. Polymers utilized included polystyrene, polyacrylonitrile, and copolymers of methyl vinyl ketone with acrylonitrile and styrene.

Chemical modification of high polymers has been studied extensively. In this study polystyrene was chosen as a base polymer for modification because of the ready reactivity of the benzene ring to well defined products of definite structure for a number of reactions. Nitropolystyrene was prepared as a precursor of a variety of substituted polystyrenes such as aminopolystyrene and the products of reaction of diazotized aminopolystyrene. The nitrated polymer has been previously prepared[2–5] under conditions resulting in varying degrees of polymer degradation because of the vigor of the nitrating techniques (use of concentrated sulfuric and nitric acid mixtures at elevated temperatures). Acetylnitrate is an efficient nitrating agent at moderate temperatures, however, and should effect nitration of polystyrene without simultaneous polymer degradation. To increase the solubility of polystyrene in nitrating media, several polystyrenes of low molecular weight were prepared by polymerization in the presence of bromotrichloromethane (1–6%) as a chain transfer agent (Table I).

Nitropolystyrene was obtained when acetylnitrate was used as the nitrating agent and elemental analysis showed this material to contain less than one nitro group per benzene ring (0.6). Varying the conditions of reaction with acetyl nitrate did not yield a $-NO_2$ to C_6H_5 ratio greater than .6 (Table II).

Concentrated nitric acid did not dissolve polystyrene and, as would be expected, nitration was negligible. Fuming nitric acid reacted with polystyrene at 0° to yield a viscous sirup and considerable nitration occurred. Elemental analysis on the product corresponded to 1.2 nitro groups per benzene ring. Chemical and catalytic hydrogenations were carried out on the low molecular weight nitropolystyrenes. Chemical reduction was ineffectual. Products from catalytic hydrogenation (palladium-on-carbon catalyst) appeared to be aminopolystyrene[7–9] with infrared bands at 1600

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(1) This paper was presented at the November 1957 Meeting in Miniature of the Connecticut Valley Section of the American Chemical Society, Hartford, Conn.

(2) G. Komppa, *Ber.*, **26**, 677 (1893).

(3) H. Zenftman, *J. Chem. Soc.*, 982 (1950).

(4) A. Langhans, *Explosivstoffe*, **516**, 68 (1953); *Chem. Abstr.*, **48**, 373 (1954).

(5) K. Bjotveit (Norsk Hydro-Elektrick), Nor. Patent **83,373** (Mar. 22, 1954); *Chem. Abstr.*, **48**, 8585 (1954).

(6) Q. A. Trementozzi, *J. Phys. Colloid Chem.*, **54**, 1227 (1950).

(7) W. E. Bachmann, *J. Org. Chem.*, **12**, 108 (1947).

(8) H. P. Gregor, C. G. Overberger, *J. Am. Chem. Soc.*, **77**, 3675 (1955).

TABLE I

Low Molecular Weight Polystyrene

Sample	% Chain Transfer Agent	% Yield of Polymer	[η]	M_v[a]	% Cl in Polymer
1	1	70	.078	10,000	2.07
2	2	55	.058	7,000	2.98
3	4	45	.045	5,000	4.05
4	6	20		Below 5,000	5.24

[a] $[\eta] = 5.74 \times 10^{-5} M^{0.78}$ (Ref. 6).

TABLE II

Nitration of Polystyrene

Polystyrene	Nitration Method	Temp. °C.	Time, Hr.	% Yield	NO_2/C_6H_5[a]	% N in Polymer[b]
Sample 3	Acetyl nitrate	40	1	90	.6	5.26
Sample 4	Acetyl nitrate	40	1	98	.6	5.98
Sample 4	Acetyl nitrate	40	4.5	100	.6	5.77
Sample 4	Acetyl nitrate	75	4.5	95	.6	5.45
Mw 67,000	Acetyl nitrate	75	4.5	98	.2	2.30
Mw 67,000	Conc. HNO_3	100	12	98	.2	1.78
Mw 67,000	Fuming HNO_3	0	8			
		25	24	96	1.2	10.98

[a] From elemental analytical data. [b] Theoretical value for mononitrated polystyrene; N = 9.39%.

and 3350 cm.$^{-1}$ but were insoluble in organic solvents and aqueous acids and may be crosslinked. The nitropolystyrene showed strong bands at 1350 and 1550 cm.$^{-1}$ (Fig. 1).

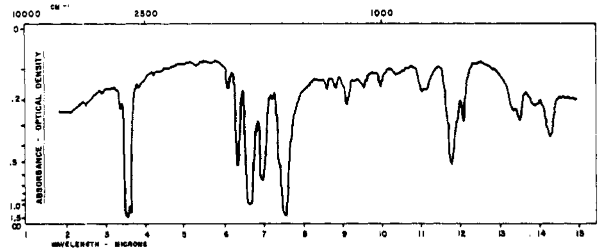

Fig. 1. *p*-Nitropolystyrene infrared curve

Polystyrene was acetylated[10,11] by a Friedel-Crafts reaction[12–14] with acetyl chloride. The elemental analysis and infrared data corresponded to quantitative monoacetylation. The butyryl and stearoyl homologs were prepared and, as expected, the products became less soluble (*i.e.* benzene, methyl ethyl ketone) as the aliphatic carbon chain was lengthened. Softening points (*cf.* EXPERIMENTAL) decreased[15] as the aliphatic chain was lengthened (Table III).

TABLE III

Softening Points

Compound	Softening Point
Polystyrene (base polymer)	140–145
Acetylpolystyrene	130–135
Butyrylpolystyrene	95–100
Stearoylpolystyrene	50– 55
p-(α-Hydroxyethyl)polystyrene	120–125
Oxime of acetylpolystyrene	170–175
p-(α-Aminoethyl)polystyrene	170–175
Styrene–methyl vinyl ketone copolymer	100–105
Reduced styrene–methyl vinyl ketone copolymer	135–140
Oxime of styrene–methyl vinyl ketone copolymer	145–150
p-[2-(Cinchoninic acid)]polystyrene	–240
Nitropolystyrene	210–215
Chloromethylpolystyrene[a]	135–145
Stearoylpolystyrene[a]	50– 55

[a] Softening point of polystyrene (base polymer) 100–105°.

Stearoylpolystyrene, in particular, was insoluble in most organic solvents (slightly soluble in polyhalogenated aromatic solvents and soluble in nujol). This material resembled a wax in its physical appearance and behavior. An interesting experimental observation was that the acetyl and butyryl reaction mixtures became heterogeneous early in the reaction; whereas the stearoyl-aluminum chloride complex remained in solution. In the latter reaction, the viscosity increased and gelation occurred toward the end of the reaction. The greater solubility of the stearoyl-aluminum chloride complex than either that of the butyryl or acetyl complexes is probably the consequence of the higher percentage of carbon disulfide compatible aliphatic chain

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(9) H. Brandenberger, *J. Polymer Sci.*, **20**, 215 (1956).

(10) W. O. Kenyon, G. P. Waugh, C. C. Unruh (Eastman Kodak Co.), U.S. Patent **2,713,570** (July 19, 1955).

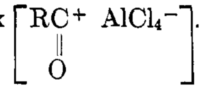
(11) A. W. Ralston, R. J. Vander Wal (Armour and Co.), U.S. Patent **2,197,709** (Apr. 16, 1940).

(12) D. T. Mowry, M. Renoll, W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

(13) P. W. Sherwood, *Petrol. Processing*, **8**, 724 (1953).

(14) P. Teyssie, G. Smets, *J. Polymer Sci.*, **20**, 351 (1956).

(15) L. L. Ferstandig, J. C. Butler, A. E. Strauss, *J. Am. Chem. Soc.*, **76**, 5779 (1954).

in the R group of the ionic complex  $\left[\overset{\displaystyle \text{O}}{\underset{\|}{}}\text{RC}^{+}\ \text{AlCl}_4^{-}\right]$.

The reaction of phthalic and succinic anhydrides with polystyrene to yield keto acids, another more soluble polyfunctional polystyrene, was not successful. The anhydrides were insoluble in any polystyrene solvent suitable for the reaction.

To introduce amino groups on polystyrene in positions other than on the backbone of the molecule, acetylpolystyrene was converted to the oxime[16] which was then reduced with lithium aluminum hydride[17] to the corresponding primary amine. A Beckman rearrangement on the oxime[18] gave an insoluble resin which could not be identified. Lithium aluminum hydride reduction of the acetylpolystyrene yielded the corresponding secondary alcohol. The number of hydroxyl or amino groups in the polymer was varied from 0 to 1 per benzene ring by controlling the degree of acylation. *p*-Carboxypolystyrene, 1700 and 2500–3000 cm.$^{-1}$ (Fig. 2), was obtained by the oxidation of acetylpolystyrene, 1670 cm.$^{-1}$, with sodium hypochlorite. The sodium salt of the product was completely soluble in water and the solution exhibited detergent properties. The free acid resembled a fatty acid in physical appearance rather than a polymeric material.

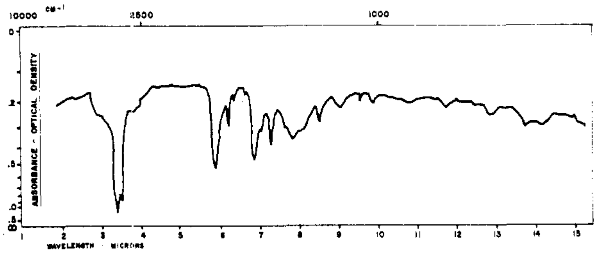
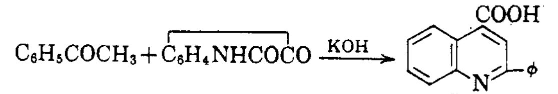


Fig. 2. *p*-Carboxypolystyrene infrared curve

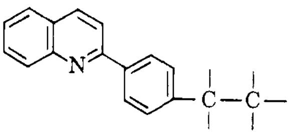
The chloromethylation[19–21] of polystyrene was attempted and numerous runs were made varying reaction conditions and ratios of reactants. In many of these runs no chloromethylation took place and when a chloromethylated product was isolated it was very insoluble. Using low molecular weight polystyrene, a chloromethylated product was isolated which was partially soluble in several solvents but attempts to replace the halogen with hydroxyl and nitrile groups were unsuccessful.

The reaction of isatin with aryl methyl ketones, known as the "Pfitzinger Reaction",[22]



I

has lead to 4-carboxy-2-aryl substituted quinolines (derivatives of cinchoninic acid). Reports in the literature[23–26] suggest possible physiological or pharmacological activity for these compounds. Atophan, (I) has been used in treating gout and rheumatism. Further, it has been shown that if the aryl group of the ketone is alkyl-substituted the activity is enhanced. The condensation of acetylpolystyrene with isatinic acid gave a resin (II)



II

which contained the expected structure as confirmed by infrared comparison with the spectrum of a model compound (I), Fig. 3 and 4. This resin can be considered a styrene-quinoline copolymer.

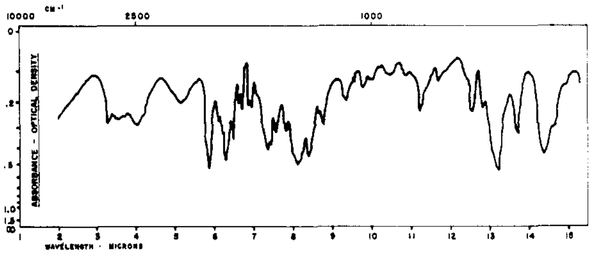


Fig. 3. 4-Carboxy-2-phenyl quinoline infrared curve

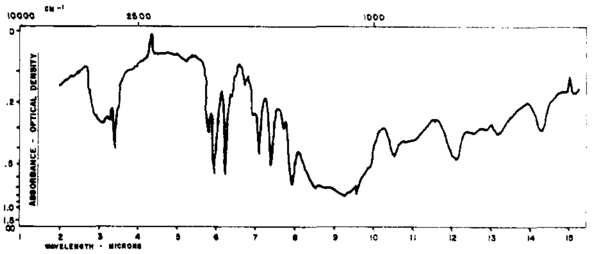


Fig. 4. *p*-(2-[Quinoline-4-carboxylic acid])polystyrene infrared curve

A styrene–methyl vinyl ketone copolymer[27,28] was made as a prototype polymer with a high percentage of carbonyl groups. In this material the

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(16) W. E. Bachmann, *J. Am. Chem. Soc.*, **58**, 2097 (1936).

(17) R. E. Lyle, H. J. Troscianiec, *J. Org. Chem.*, **20**, 1757 (1955).

(18) A. Schaffler, *Ber.*, **88**, 767 (1955).

(19) C. H. McBurney, U.S. Patent **2,629,710** (Feb. 24, 1953).

(20) Dow Chemical Co., Brit. Patent **677,350** (Aug. 13, 1952); *Chem. Abstr.*, **47**, 8943 (1953).

(21) G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686 (1952).

(22) Pfitzinger, *J. prakt. Chem.* **33**, 100 (1886).

(23) J. A. Knight, H. K. Porter, P. K. Calaway, *J. Am. Chem. Soc.*, **66**, 1893 (1944).

(24) N. P. Buu-Hoï, P. Cagniant, *Bull. soc. chim.*, **11**, 343 (1944).

(25) N. P. Buu-Hoï, R. Royer, *Rec. trav. chim.*, **66**, 300 (1947).

(26) M. Colonna, *Gazz. chim. ital.*, **78**, 502 (1948); *Chem. Abstr.*, **43**, 2210 (1949).

(27) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, W. J. Wenisch, *J. Am. Chem. Soc.*, **70**, 1527 (1948).

(28) H. J. Hagemeyer, *J. Am. Chem. Soc.*, **71**, 1119 (1949).

carbonyls are on the chain rather than on the benzene rings. The copolymer was converted to the oxime and reduced to a primary amine. Reduction of the carbonyl groups with lithium aluminum hydride gave the corresponding secondary alcohol. The infrared carbonyl band at 1690 cm.$^{-1}$ was changed to hydroxyl at 3600 cm.$^{-1}$, Fig. 5 and 6.

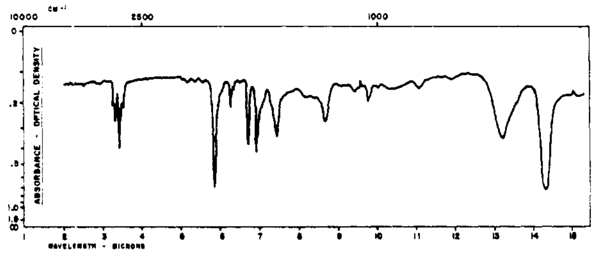

Fig. 5. Styrene-methyl vinyl ketone copolymer infrared curve

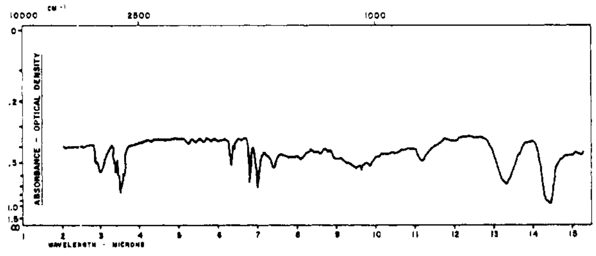

Fig. 6. Reduced styrene-methyl vinyl ketone copolymer infrared curve

An approximately 60/40 methyl vinyl ketone–acrylonitrile copolymer[29,30] was prepared by mass polymerization in sealed tubes. The copolymer was isolated and purified by solution followed by precipitation and then catalytically hydrogenated over Raney nickel in tetrahydrofuran. Infrared analysis showed strong amine and hydroxyl absorption and some nitrile indicating considerable but incomplete reduction. Using similar experimental conditions with polyacrylonitrile[30] in dimethylformamide, a discolored insoluble material was obtained.

It is evident that chemical reactions on polymeric materials are, in many instances, not as easily facilitated as the same reactions with simple organic compounds. Limited solubility, side reactions, and crosslinking are among the more persistent problems. The chemical properties of the modified polymers are quite different from those of the parent compounds (Table III, softening points; solubilities in EXPERIMENTAL section). These chemical compositions lend themselves to further chemical modification and reaction.

EXPERIMENTAL

Low molecular weight polystyrene. Four samples of polystyrene were prepared by mass polymerization in sealed tubes. Bromotrichloromethane was used as a chain transfer agent in 1, 2, 4, and 6% by weight of styrene monomer. Di-tertiary butyl peroxide was the catalyst at .02%. The polymerizations were carried out at 90° for 12 hr. and then brought to 190° for 5 hr. These low viscosity materials were dissolved in methyl ethyl ketone and precipitated from methanol as solids, Table I.

Nitration of polystyrene. Ten grams of polystyrene sample 3 (Table I) was dissolved in 100 ml. of carbon tetrachloride. Fifteen ml. of acetic anhydride was slowly added followed by the cautious addition of 5 ml. of concentrated nitric acid keeping the temperature below 40°. The solution was poured into 300 ml. of methanol with stirring and then filtered. The pale yellow solid was reprecipitated from carbon tetrachloride with methanol. Several runs were made by this procedure and the results are given in Table II.

A sample of polystyrene, prepared without chain transfer agent (M_v 67,000), was nitrated with fuming nitric acid. Twenty grams of polystyrene was added slowly to 160 ml. of fuming nitric acid while keeping the temperature at 0°. After 8 hr. the temperature was allowed to come to room temperature and stand for 24 hr. The thick sirup was poured carefully into water and the yellow solid removed by filtration, washed several times with water, and dried. The molecular weight of the product was 58,000. The molecular weights of the polystyrene $[\eta] = 0.343$ and of nitropolystyrene $[\eta] = 0.290$ were calculated from the relationship[6] $[\eta] = 5.74 \times 10^{-5} M^{0.78}$ (toluene at 25°; g./100 ml.). The value for nitropolystyrene is an approximation as used by Zenftman.[3] The nitrated polystyrenes were soluble in dimethylformamide and tetrahydrofuran, and slightly soluble in benzene and toluene.

Reduction of nitropolystyrene. A series of chemical and catalytic reduction experiments was unsuccessful for the reduction of nitropolystyrene. Unreacted nitropolystyrene was recovered along with up to 10% insoluble material in some runs. Palladium-on-carbon gave an aminopolystyrene.

Method of Reduction	Conditions	Result
$LiAlH_4$	THF, reflux 1 hr.	No reduction
Sn, HCl (gaseous)	THF, reflux	No reduction 90%; material insoluble in all common solvents 10%
Raney nickel	60°, 900 lb./sq. in. 4 hr.	No reduction
Raney nickel	100°, 1400 lb./sq. in. 4 hr.	No reduction

Palladium-on-carbon powder. Fifteen grams (.1*M*) of nitropolystyrene (degree of nitration 1.2) was dissolved in 135 ml. of purified dimethylformamide to which 3 g. of 5% palladium-on-carbon was added. This was charged to a Parr low pressure hydrogenator at 50 lb./sq. in. and 50° for 12 hr. The reaction consumed the theoretical amount of hydrogen. The yellow product, isolated as previously described, was almost completely reduced as shown by infrared analysis, but was insoluble in HCl and all solvents.

Acylation of polystyrene. p-acetylpolystyrene (polyvinylacetophenone). In a 2-liter three-necked flask, fitted with a mechanical stirrer, dropping funnel, and a reflux condenser were placed 67 g. (.5 mole) of Eastman grade aluminum chloride and 250 ml. of carbon disulfide. Stirring was begun and 30 g. (.37 mole) of practical acetyl chloride was added. While maintaining vigorous stirring, a dope of 26 g. (.25 mole) of polystyrene, sample 1, in 200 ml. of carbon disulfide was added gradually over a period of about 20 min. The mixture became yellow, a soft bulky precipitate was formed, the carbon disulfide refluxed gently, and hydrogen chloride was evolved. After the addition of polystyrene was complete, the mixture was refluxed for 1.5 hr. until the evolution of hy-

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(29) W. E. Elwell, R. L. Meier (California Research Co.), U. S. Patent **2,451,435** (Oct. 12, 1948).

(30) N. H. Shearer, H. W. Coover (Eastman Kodak Co.), U. S. Patent **2,719,144** (Sept. 27, 1955).

drogen chloride ceased. Stirring was maintained during this period. The reflux condenser was replaced by a tube leading to a distilling condenser, stirring was stopped, and about 70% of the carbon disulfide was removed leaving a damp yellow mass which was poured into water containing ice and 100 ml. of HCl. This was then steamed to remove the remainder of the CS_2 and the acidic water was decanted from the solid which adhered to the walls of the container. Cold water was added and the solid hardened on contact and was removed by filtration. The product was dissolved in 800 ml. of acetone and precipitated by 3 l. of water to yield a pale yellow solid in 92% yield.

Anal. Calcd.: C, 82.20; H, 6.90. Found: C, 82.10; H, 6.78. The material was soluble in acetone, ethylene chloride, acetophenone, dioxane/alcohol, dioxane/methanol, and tetrahydrofuran.

When stannic chloride was used no acetylation occurred. With acetic anhydride and aluminum chloride, 25% acetylation (1 CH_3CO/4 benzene rings) was the most obtained.

Butyrylpolystyrene. This compound was prepared by the same method with *n*-butyryl chloride. The purification was more difficult due to decreased solubility and the recovery was 50%.

Anal. Calcd.: C, 82.75; H, 8.05. Found: C, 82.06; H, 8.41. The material exhibited limited solubility in methyl ethyl ketone, xylene, and dichlorobenzene.

Stearoylpolystyrene. This compound was prepared by the same method (using freshly distilled stearoyl chloride) in 80% yield as a white, very waxy solid, with limited solubility in methyl ethyl ketone, xylene, and dichlorobenzene and soluble in hot nujol.

Anal. Calcd.: C, 84.32; H, 11.35. Found: C, 83.78; H, 11.25.

Phthalic and succinic anhydrides could not be used since they are insoluble in all Friedel-Crafts type solvents which will dissolve polystyrene. A run was made using nitrobenzene as solvent but no reaction occurred.

Derivatives of p-acetylpolystyrene. p-(α-Hydroxyethyl)polystyrene. Five grams (.034 mole) of acetylpolystyrene was dissolved in 50 ml. of tetrahydrofuran. Five grams (0.14 mole) of lithium aluminum hydride was suspended in 50 ml. of tetrahydrofuran. The tetrahydrofuran was distilled from calcium hydride and then from lithium aluminum hydride. The polymer solution was added slowly to the lithium aluminum hydride suspension in a 200-ml. flask fitted with a reflux condenser, stirrer, and dropping funnel. The solution became warm during the addition and began to reflux and the viscosity of the mixture increased. After refluxing for 2 hr. the mixture was cooled and excess $LiAlH_4$ was decomposed with ethanol followed by water and HCl to dissolve the aluminum hydroxide. The polymer was removed by filtration, dissolved in methyl ethyl ketone, and reprecipitated from water. The yield was 4.5 g. (90%) and infrared confirmed conversion of carbonyl to hydroxyl.

Anal. Calcd.: C, 81.06; H, 6.99. Found: C, 80.68; H, 7.06.

Oxime of acetylpolystyrene. Seven and one half grams (0.047 mole) of acetylpolystyrene and 6 g. (.085 mole) of hydroxylamine hydrochloride were dissolved in a mixture of 30 ml. of absolute ethanol and 45 ml. of dry pyridine. The mixture was refluxed for 48 hr. and then poured into cold water. The white solid amounted to 7.2 g. (88%). The oxime was purified by dissolving in acetone and reprecipitating from water. It was soluble in acetone and pyridine, slightly soluble in ethanol and benzene, and insoluble in water. The infrared spectrum showed essentially complete conversion of carbonyl to oxime.

Anal. Calcd.: N, 8.70. Found: N, 8.05.

An attempted Beckman rearrangement of the oxime gave a completely insoluble mass.

p-(α-Aminoethyl)polystyrene. Five grams (0.31 mole) of the oxime was dissolved in 50 ml. of purified tetrahydrofuran and added to a slurry of 5 g. (0.14 mole) of lithium aluminum hydride. A vigorous reaction occurred and a gel formed. After 1 hr. of reflux the mixture was carefully decomposed with ethanol and then poured into water. The *p*H was adjusted to 8–10 and the gummy precipitate was removed by filtration, dissolved in methyl ethyl ketone, and reprecipitated from water. The yield of fine yellow powder was 3.7 g. (80%).

Anal. Calcd.: C, 81.60; H, 9.50; N, 8.90. Found: C, 81.00; H, 9.40; N, 8.55.

p-Carboxypolystyrene. Six grams of acetylpolystyrene was added to an aqueous solution of sodium hypochlorite (Merchlor) and the suspension refluxed for 12 hr. during which time the odor of chloroform was observed. At the end of this time the polymer was all in solution and the clear liquid was acidified. An excessive amount of foam was observed at this point. The white solid was removed by filtration (75%). The infrared spectrum showed complete conversion of carbonyl to carboxyl. The material was soluble in methanol, ethanol, and in water as the sodium or ammonium salt, and insoluble in other common organic solvents. Dilute aqueous solutions of the sodium salts exhibited heavy foaming characteristics.

Anal. Calcd.: C, 72.98; H, 5.40. Found: C, 72.83; H, 5.41.

Chloromethylation of polystyrene. In a 1-l. four-necked flask equipped with condenser, stirrer, thermometer, dropping funnel, and drying tubes was added 25 g. (0.25 mole) of polystyrene dissolved in 200 ml. of carbon disulfide. Stirring was started and the solution was cooled to about 0° with an ice-salt bath. Fifty-five g. (0.69 mole) of chloromethyl ether was then added to the cold solution followed by the dropwise addition of 13 ml. (0.11 mole) of $SnCl_2$. The temperature rose a few degrees, the solution slowly darkened until about 15 min. after the first addition of catalyst when the mixture became a dark red gel. The mixture was allowed to stand for 1 hr. after which methanol was added. The color disappeared leaving an off-white solid which was washed repeatedly with methanol and dried. The material was insoluble in dioxane, methyl ethyl ketone, tetrahydrofuran, carbon disulfide, and chloroform.

A second run was made adding the polymer solution and $SnCl_2$ simultaneously to the chloromethyl ether and quenching immediately after the last addition to prevent excessive cross-linking. The product was again insoluble. Using this procedure with the low molecular weight polystyrene (sample 2) a product was obtained which was soluble in CS_2 and partially soluble in dioxane, methyl ethyl ketone, and tetrahydrofuran. Sodium fusion showed the presence of chlorine and the infrared curve deviated from that of the starting material. Softening point of polystyrene used was 100–105°; for the product 135–140°.

Attempts to replace the halogen of the above chloromethylated polystyrene with nitrile and hydroxyl groups were unsuccessful.

Styrene–methyl vinyl ketone copolymer. This copolymer was prepared by mass polymerization in sealed tubes. Seventy g. (0.67 mole) of purified styrene, 35 g. (0.5 mole) of methyl vinyl ketone and .02% di-*tert*-butyl peroxide were placed in tubes, flushed with nitrogen, and sealed. The tubes were placed in an oven at 95° for 8 hr. and brought to 190° for 15 hr. The pale yellow sticky mass was dissolved in methyl ethyl ketone and precipitated from methanol (81% conversion).

Anal. Found: C, 85.31; H, 8.37 which corresponds to about 65% styrene, 35% methyl vinyl ketone.

Derivatives of styrene–methyl vinyl ketone copolymer. Reduced styrene–methyl vinyl ketone copolymer. Twenty grams (0.11 mole) of dry styrene–methyl vinyl ketone copolymer (65/35) was dissolved in 150 ml. of dry tetrahydrofuran. Fifteen grams (0.39 mole) of lithium aluminum hydride was suspended in 150 ml. of tetrahydrofuran. The tetrahydrofuran was previously distilled from calcium hydride and then from lithium aluminum hydride. The polymer solution was slowly added to the lithium aluminum hydride suspension in a 2-l. three-necked flask fitted with a reflux condenser, stirrer, and dropping funnel. The solution became warm during the addition and began to reflux. After about one half of the polymer solution was added, the mixture became gelatinous and broke up into small lumps. After the addition of the polymer solution was complete (about 45 min.), stirring and refluxing was continued for 2 hr. The mixture was cooled and ethanol was cautiously added after which it was poured into 150 ml. of cold 20% HCl. The polymer was removed by filtration, dissolved in methyl ethyl ketone, and reprecipitated from water. The yield was 20 g., 98%. The infrared spectrum showed complete conversion of carbonyl to hydroxyl. Analysis for hydroxyl content gave 5.86% hydroxyl. Calculated hydroxyl for 33% methyl vinyl ketone composition is 6.01%.

Oxime of styrene–methyl vinyl ketone copolymer. Five g. (.03 mole) of styrene–methyl vinyl ketone copolymer and 5 g. (.071 mole) of hydroxylamine hydrochloride were dissolved in a mixture of 30 ml. of absolute ethanol and 30 ml. of dry pyridine. The mixture was refluxed for 48 hr. and then poured into cold water. The clean white solid amounted to 5.5 g. (96%). The infrared spectrum showed complete conversion of carbonyl to oxime.

Anal. Calcd.: N, 4.77. Found: N, 5.01.

The semicarbazone was prepared by an analogous procedure.

p-[2-(Quinoline-4-carboxylic acid)]polystyrene (II). Five g. (.034 mole) of acetylated polystyrene and 5 g. of isatin (.034 mole) were dissolved in 100 ml. of pyridine and 50 ml. of 30% aqueous potassium hydroxide was added. The dark red solution was refluxed for 3 days after which time it was poured into 250 ml. of methanol. The small amount of insoluble material was removed by filtration leaving a clear, deep red solution. The methanol solution was acidified whereupon a reddish-brown solid precipitated and was removed from the yellow solution by filtration. The solid was dissolved in tetrahydrofuran and reprecipitated from water. There was obtained 7.5 g., 80% yield, of a pale pink solid. A model compound was prepared from isatin and acetophenone. The infrared spectrum showed that these two materials were of similar composition.

Acrylonitrile–methyl vinyl ketone. This copolymer, prepared by mass copolymerization of equimolar quantities of these monomers, was precipitated from methyl ethyl ketone solution in methanol. This was a clear, brittle, glassy material with exceptional adhesive properties.

Reduction of methyl vinyl ketone–acrylonitrile copolymer. The methyl vinyl ketone–acrylonitrile copolymer was reduced in the low pressure hydrogenator with Raney nickel catalyst in tetrahydrofuran solution. The pale yellow solid which was isolated showed hydroxyl, nitrile, and amine groups by infrared. A similar reduction on polyacrylonitrile in dimethylformamide yielded a black, insoluble, amorphous mass.

Softening points. This data was taken on the Fisher-Johns apparatus and reported in Table III. The softening point (range) was measured from initial softening to complete flow of the sample.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY SECTION MIDWEST RESEARCH INSTITUTE]

An Application of Statistical Design to Organic Synthesis. The Reductive Alkylation of *t*-Butylamine (Leuckart Reaction)

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A series of experiments was designed to simultaneously determine by statistical analysis the effect of five experimental conditions on the yield of *t*-butylmethylamine and *t*-butyldimethylamine in the reductive methylation of *t*-butylamine by the Leuckart procedure. Optimum conditions were determined for the preparation of both amines.

Although tertiary amines are the usual products in the Leuckart reaction of formaldehyde with primary amines in the presence of formic acid,[1] we have observed that *t*-butylamine, treated in this manner, yields significant amounts of the secondary amine, *t*-butylmethylamine. Since we had need of a large amount of this product and there is no satisfactory synthesis reported,[2] we considered it of interest to determine the optimum conditions for its preparation by this method. After consideration of some excellent reviews on the mechanism of the Leuckart reaction,[3] we chose to study the effects of several experimental variables. In a previous study in our laboratories,[4] application of the method of experimental design[5] provided outstanding results in determining ideal conditions for a synthesis problem involving the variation of several experi-

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[1] M. L. Moore, *Org. Reactions*, **V**, 307 (1949).

[2] *t*-Butylmethylamine was prepared in unspecified yield (along with neopentylamine) by the hydrogenation of *t*-butylcarbylamine [P. Sabatier and A. Mailhe, *Compt. rend.*, **144**, 957 (1907)]. This compound was also formed in about 6 per cent yield by the alkylation of *t*-butylamine with methyl iodine [N. Bortnick, *et al.*, *J. Am. Chem. Soc.*, **78**, 4039 (1956)]. Hurwitz [U. S. Patent **2,582,128** (1952)] suggests the possibility of hydrogenating the Schiff base (aldimine) formed on treatment of *t*-butylamine with formaldehyde.

[3] See, for example, (a) E. R. Alexander and R. B. Wildman, *J. Am. Chem. Soc.*, **70**, 1187 (1948); (b) V. J. Webers and W. F. Bruce, *J. Am. Chem. Soc.*, **70**, 1422 (1948); (c) P. A. S. Smith and A. J. MacDonald, *J. Am. Chem. Soc.*, **72**, 1037 (1950); (d) D. S. Noyce and F. W. Bachelor, *J. Am. Chem. Soc.*, **74**, 4577 (1952); (e) E. Staple and E. C. Wagner, *J. Org. Chem.* **14**, 559 (1949); (f) C. B. Pollard and D. C. Young, Jr., *J. Org. Chem.*, **16**, 661 (1951).

[4] Results to be published later.

[5] For a general reference to the method of experimental design, see C. A. Bennett and N. L. Franklin, *Statistical Analyses in Chemistry and the Chemical Industry*, John Wiley & Sons, Inc., New York, (1954).