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Summary

1. 5,6-Diaminoquinoline was prepared from 6-nitroquinoline through several improved steps.

2. Pyrido(3,2-f)quinoxaline and 2,3-dimethylpyrido(3,2-f)quinoxaline were synthesized. The former yielded a tri-N-oxide whereas the latter formed only a di-N-oxide when heated with a solution of hydrogen peroxide in acetic acid.

3. Tricyclic systems could not be obtained from 7,8-diaminoquinoline with glyoxal or diacetyl. The condensation stopped at the iminoaldehyde and iminoketone, respectively. Both condensation products were identified.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Polymerization of *p*-Chlorostyrene in the Presence of Polymethylacrylate

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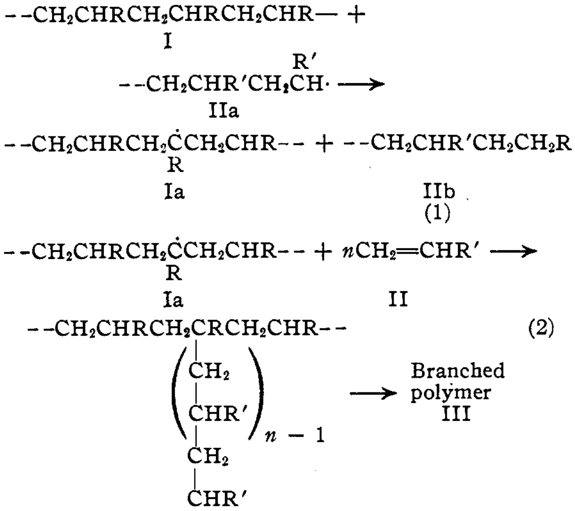
The first indication that a polymer molecule, in the presence of growing polymer chains, may be capable of increasing its molecular size was provided by the experiments of Houtz and Adkins.[1] Their viscosity measurements led them to conclude that new styrene units may attach themselves to polystyrene molecules when the latter are subjected to the action of polymerizing monomer. Flory[2] suggested that branched vinyl polymers could result from chain transfer reactions involving polymer molecules (I) and growing polymer chains (IIa)



$$\underset{\mathrm{I}}{\text{--}CH_2CHRCH_2CHRCH_2CHR\text{—}} + \underset{\mathrm{IIa}}{\text{--}CH_2CHR'CH_2\overset{R'}{C}H\cdot} \longrightarrow \underset{\mathrm{Ia}}{\text{--}CH_2CHRCH_2\underset{R}{\dot{C}}CH_2CHR\text{--}} + \underset{\mathrm{IIb}}{\text{--}CH_2CHR'CH_2CH_2R'} \quad (1)$$

$$\underset{\mathrm{Ia}}{\text{--}CH_2CHRCH_2\underset{R}{\dot{C}}CH_2CHR\text{--}} + \underset{\mathrm{II}}{nCH_2{=}CHR'} \longrightarrow \text{--}CH_2CHRCH_2CRCH_2CHR\text{--} \ (-CH_2-CHR'-)_{n-1}-CH_2-\dot{C}HR' \longrightarrow \text{Branched polymer III} \quad (2)$$

It is apparent that Flory's mechanism could account for the results reported by Houtz and Adkins. Mayo[3] presented experimental evidence that growing polymer chains engage in chain transfer reactions with solvent molecules; and a comparison of the activities of various solvents in the chain transfer reaction prompted Mayo to propose that growing polymer chains could also undergo chain transfer reactions with polymer molecules as Flory had suggested. It appeared likely that growing polymer chains could undergo chain transfer not only with polymer molecules composed of the same monomer units (equations 1 and 2, $R = R'$) but also with polymer molecules composed of different monomer units ($R \neq R'$). If such is the case, then branched chains (III) should be formed in which the principal chain is composed of units of one kind and the branch of units of another kind. If the polymer (I) and the monomer (II) which is to form the growing chains (IIa) are selected in such a way that polymers I and IIb have widely differing solubility characteristics, then it should be possible to separate completely one or the other of the polymers from the branched molecules (III). If, further, either R or R′ contains a group which can be detected by analytical methods, then the presence of III can be established after I or IIb has been separated from the polymer mixture. This paper reports a preliminary investigation of the polymerization of *p*-chlorostyrene (II, $R' = pC_6H_4Cl$) in the presence of polymethylacrylate (I, $R = COOCH_3$). The polymer mixture which presumably contained I, IIb and III was saponified in order to convert polyacrylate chains into polyacrylic acid chains (I and III, $R = COOH$), and the product was extracted with benzene, in which IIb is soluble, and I ($R = COOH$) insoluble. It was anticipated that the branched polymer, if present, (III, $R = COOH$, $R' = C_6H_4Cl$) would be substantially insoluble in benzene so that its presence could be detected by analysis of the insoluble material for chlorine.

In order that a maximum number of chain transfer reactions of the type represented by equation 1 could occur in the polymerizing mixture, experimental conditions were so chosen that other types of chain transfer reactions were minimized. Since solvents have been shown to serve as chain transfer agents,[3] the polymerizations were carried out in bulk. Inasmuch as growing chains presumably may be terminated by coupling or disproportionation reactions, both of

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[1] Houtz and Adkins, THIS JOURNAL, **55**, 1609 (1933).

[2] Flory, *ibid.*, **59**, 241 (1937).

[3] Mayo *ibid.*, **65**, 2324 (1943).

which are undoubtedly second order with respect to the concentration of free radicals, and since the chain transfer reaction is apparently first order with respect to the same quantity, it was considered advisable to keep the free radical concentration as low as possible—in other words, to use no catalyst. Indeed, Cohen[4] concluded that in the benzoyl peroxide catalyzed polymerizations of styrene which he studied, most of the growing chains were terminated by reactions involving the interaction of two growing chains. It also appeared likely that most of the branched polymer (III, R = COOH; R′ = *p*-C_6H_4Cl) would be formed during the early part of the reaction, when the concentration of poly-*p*-chlorostyrene (IIb) was very low. As the reaction proceeded, of course, the concentration of IIb would increase, and the probability that growing chains (IIa) could undergo chain transfer with IIb, rather than with I, would increase in proportion. The product of this reaction would be a branched poly-*p*-chlorostyrene (III, R = R′ = *p*-C_6H_4Cl), which would be expected to be inseparable on the basis of benzene solubility from linear poly-*p*-chlorostyrene (IIb).

Experimental

p-Chlorostyrene was prepared by the dehydration[5] of *p*-chlorophenylmethylcarbinol.[6] The preparation was carried out immediately before the monomer was to be used, in order to avoid the use of an inhibitor. It was found that inhibitors, once added, were quantitatively removed only with great difficulty; and *p*-chlorostyrene which had once been treated with an inhibitor always showed an appreciable induction period when polymerized in the absence of catalysts. A poly-*p*-chlorostyrene sample, prepared in the absence of catalysts at 50° had a reduced viscosity (η_{sp}/c) in 1,4-dioxane solution (1%) of 0.945.

Polymethylacrylate.—Methyl acrylate (Eastman Kodak Co.) was purified by distillation and then polymerized by heating it to the boiling point in the presence of 1% of benzoyl peroxide. The polymer was precipitated into methanol from its solution in ethyl acetate, washed with methanol, and dried in a vacuum desiccator. The reduced viscosity of a typical sample, determined in 1,4-dioxane solution (1%), was 1.66.

Polymerization of *p*-Chlorostyrene Solutions of Polymethylacrylate.—A weighed sample of polymethylacrylate was stirred into a weighed amount of *p*-chlorostyrene for twenty-four hours at room temperature, in an atmosphere of purified nitrogen. The concentrations of polymethylacrylate in the solutions were made to stay within the limits 20–23%. Samples of the solution were weighed into glass tubes, which were sealed and placed in a furnace, where the temperature was maintained at 50°. Since the results of the experiments were to be interpreted only in a semi-quantitative way, no exact temperature control was necessary; nevertheless, variations in temperature during any run did not exceed 5°. Tubes were withdrawn at appropriate times during the experiment, opened, and the weight of *p*-chlorostyrene which had polymerized was determined gravimetrically. The polymer was precipitated by pouring a 1,4-dioxane solution of the reaction mixture into methanol. It was washed with methanol and dried to constant weight in a vacuum desiccator at room temperature. The difference between the weight of polymethylacrylate introduced into the sample and the weight of the precipitated polymer was taken to be the weight of *p*-chlorostyrene which had polymerized.

Saponification and Extraction of the Polymer.—The procedure given by Staudinger and Trommsdorff[7] for the saponification of polymethylacrylate was followed. After saponification, the supernatant liquid was decanted from the insoluble polymer, and the latter was stirred with water until the lumps disappeared and a milky suspension was formed. This suspension was treated with hydrochloric acid in order to convert sodium acrylate units into the free acid units and then dialyzed through a cellophane membrane until no test for chloride ion could be obtained either from the liquid inside or outside the membrane. The mixture within the membrane was evaporated to dryness under reduced pressure. The powdery polymer was transferred to a Soxhlet cup which was then placed in a Soxhlet extractor, and the polymer was extracted with benzene until the extracts showed no cloudiness when poured into excess methanol and the chlorine content of the insoluble polymer had become constant.

Control experiments established that the procedure just described sufficed to separate all but a comparatively small amount of chlorine-containing material from mixtures of pure poly-*p*-chlorostyrene and polymethylacrylate. Weighed amounts of *p*-chlorostyrene were sealed into glass tubes and allowed to polymerize in a furnace at 50°. Tubes were withdrawn after appropriate periods of time and the contents dissolved in dioxane. These solutions were combined with solutions prepared by dissolving polymethylacrylate, in amounts comprising 20–23% of the weight of the *p*-chlorostyrene–poly-*p*-chlorostyrene mixture, in dioxane. The combined dioxane solutions were then subjected to the same procedures which were applied to the dioxane solutions of the mixtures obtained by polymerizing *p*-chlorostyrene in the presence of polymethylacrylate.

Chlorine analyses were carried out by the Parr bomb method, using 100–125 mg. samples. A blank experiment showed that inappreciable amounts of chlorine were introduced by the reagents.

Results and Discussion

The following tables summarize the results obtained from samples prepared by polymerizing *p*-chlorostyrene in the presence of polymethylacrylate at 50° and from the control samples.

TABLE I

POLYMERIZATION OF *p*-CHLOROSTYRENE IN THE PRESENCE OF POLYMETHYLACRYLATE AT 50°

Time of pzn., hr.	Monomer pzd., %	Cl content after extraction, %[a]	
33	2.0	1.7, 1.6	1.7, 2.2
43	1.2	2.3, 1.6	1.5, 2.2
81.5	9.4	2.2, 2.3	2.3
115	12.3	3.5, 3.4	3.5, 3.3
139	17.2	4.6, 4.7	4.9

[a] When duplicate analyses were carried out, both results are given and appear separated by commas. The results reported for the same run in the right column were obtained from samples which were subjected to benzene extraction for at least twenty-four hours longer thant hose whose analyses are given in the left column.

TABLE II

CONTROL EXPERIMENTS

Time of pzn., hr.	Per cent. monomer pzd.	Cl content after extraction, %[a]	
35	8.7	0.86	0.73
45	11.9	.65	.51
60	13.8	.63	.67
73	18.3	.82	.65

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(4) Cohen, *ibid.*, **67**, 17 (1945).

(5) Brooks, *ibid.*, **66**, 1295 (1944).

(6) Marvel and Schertz, *ibid.*, **65**, 2054 (1943).

(7) Staudinger and Trommsdorff, *Ann.*, **502**, 201 (1933).

Although the polymerization reactions were not carried out under sufficiently carefully controlled conditions to permit the results given in the tables to be interpreted quantitatively, certain trends are apparent, and some conclusions can be drawn. First, the results make it apparent that *p*-chlorostyrene units do become bound chemically to polymethylacrylate during the course of the polymerization of the former in the presence of the latter under the conditions used in these experiments. The constancy of the chlorine contents of the control samples suggests that chlorine from a foreign source may have been introduced during the separation procedure. If the presence of small amounts of chlorine in these polymers were to be attributed to the physical entanglement of a few poly-*p*-chlorostyrene chains with the polyacrylic acid molecules or to a chemical combination occurring during saponification and extraction, then it might be expected that the chlorine content would increase with increasing amounts of poly-*p*-chlorostyrene in the mixtures.

The data given in Table I indicate an increase in the chlorine content of the saponified, extracted polymer with increasing conversion of *p*-chlorostyrene to its polymer. If it is assumed that the structure of the branched polymer molecules does not change greatly during the course of the polymerization, then the relative amount of branched polymer soluble in benzene should be nearly constant, and the increasing chlorine content with monomer conversion simply indicates an increasing number of branched polymer molecules formed. The data also support the prediction that the rate of formation of mixed branched polymer should be at a maximum during the early part of the reaction if the mechanism represented by equations 1 and 2 is correct. If the chlorine blank is taken to be constant at 0.7%, and if this value is subtracted from the averages of the chlorine content values obtained from each of the samples indicated in Table I, the resulting "net chlorine content" of each sample may be considered to be a measure of the chlorine present in that sample as a result of chemical interaction between *p*-chlorostyrene and polymethylacrylate. These "net chlorine contents," 1.1, 1.2, 1.6, 2.7 and 4.0%, respectively, indicate a distinct trend toward lower rate of formation of branched polymer molecules with increasing monomer conversion.

Throughout this discussion, polymers which were found to contain both *p*-chlorostyrene and acrylic acid units have been termed "branched polymers," and no mechanism for the interaction of *p*-chlorostyrene and polymethylacrylate other than that represented by equations 1 and 2 has been considered. Actually, other mechanisms may also be employed to account for the observed interaction. Evidence recently presented[8] indicates that mixtures of styrene and polystyrene, in the presence of light, air and catalysts, undergo simultaneous polymerization and depolymerization. If these reactions occurred under the conditions employed in the experiments described in this report, a copolymer comprising methyl acrylate and *p*-chlorostyrene units would have been formed. The formation of such a copolymer could account for the results which are summarized in Tables I and II. A comparison of the experimental conditions used by Mesrobian and Tobolsky with those described in this communication, however, discloses that the rate of the depolymerization-repolymerization process would probably be much too slow, under the conditions imposed, to account for the values given in the tables. Several mechanisms which account for the formation of a mixed, branched polymer, other than that represented by equations 1 and 2, may be written; but considerations of concentration and of activation energy render them less probable than that of chain transfer.

The results of the preliminary experiments which form the subject of this report suggests studies, such as the effect of temperature and concentration on the number of branched molecules produced and the examination of the benzene extracts for polyacrylic acid units, as the subjects for future work. These investigations are now in progress.

Summary

Evidence is presented to show that the thermal polymerization of *p*-chlorostyrene in the presence of polymethylacrylate at 50° produces some polymer molecules which contain units of both kinds. In the light of available evidence, a chain transfer mechanism appears to offer the best explanation of the results, although other mechanisms cannot be excluded.

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[8] Mesrobian and Tobolsky, THIS JOURNAL, **67**, 785 (1945); Taylor and Tobolsky, *ibid.*, **67**, 2063 (1945).