

## The Mechanism of Chain Initiation and Chain Transfer in the Polymerization of Vinylpyridine\*

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### I. INTRODUCTION

If the steps of chain initiation and chain transfer in the polymerization of 2-vinylpyridine involve benzene derivatives, the resultant polymers might contain structures of the benzylpyridine type. The oxidation of such polymers should yield fragments which could prove the position of the benzene nuclei in the polymer and consequently disclose the mechanism of polymerization. The isolation of such fragments has been attempted in the present work. A study of the oxidation of simple benzylpyridine derivatives necessarily preceded a study of polymers of this type.

Alpha benzylpyridine has been reported by Tschitschibabin<sup>1</sup> to yield benzoic acid and no picolinic acid when oxidized with potassium permanganate in neutral solution. In acid solution the pyridine ring was converted to the more stable salt and permanganate oxidation gave picolinic acid and no benzoic acid.

Inasmuch as deactivating substituents such as halogen or carboxyl groups generally render benzene nuclei more resistant to oxidation, chlorobenzylpyridine and similar molecules might be expected to produce appreciable quantities of substituted benzoic acids when oxidized with potassium permanganate in 25% sulfuric acid solution. As such experiments have not been reported, it was decided to prepare  $\alpha$ -(*p*-bromobenzyl)- and  $\alpha$ -(*p*-chlorobenzyl)pyridine and oxidize them under these fixed conditions. It was also decided to prepare  $\alpha$ -(*p*-methylbenzyl)pyridine and oxidize it with permanganate in dilute acid solution for chain transfer with the nucleus of a toluene derivative might produce a molecule of this type.

Upon completion of the preliminary experiments, these oxidation techniques were applied to 2-vinylpyridine polymers in which benzene nuclei were incorporated in the steps of chain initiation or chain transfer.

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## II. EXPERIMENTAL

(a) **Preparation and oxidation of benzylpyridines.** Since the completion of this unit of work, the preparation of  $\alpha$ -(*p*-methylbenzyl)-pyridine and  $\alpha$ -(*p*-chlorobenzyl)pyridine has been reported.<sup>2</sup> However, as no derivatives of value for identification were reported, the physical properties of these compounds are included in the present paper. The method of Crook<sup>3</sup> was used to prepare  $\alpha$ -(*p*-bromobenzyl)pyridine (b.p. 125–130° at 1 mm.) in 16% yield. This crude amine was converted to the corresponding picrate which was recrystallized from alcohol to constant melting point of 170–171°. The recrystallized picrate was converted to the free amine by means of aqueous alkali. Identical procedures produced  $\alpha$ -(*p*-chlorobenzyl)- and  $\alpha$ -(*p*-methylbenzyl)pyridine. Pertinent data are listed in Table I.

TABLE I  
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF SUBSTITUTED  
BENZYLPIRIDINES AND THEIR PICRATES

Property determined	$\alpha$ -( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )-C <sub>5</sub> H <sub>4</sub> N	$\alpha$ -( <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )-C <sub>5</sub> H <sub>4</sub> N	$\alpha$ -( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )-C <sub>5</sub> H <sub>4</sub> N
Percentage yield	32	16	35.4
Index refraction at 25°	1.5838	1.5855	1.5698
% N calc.	6.87	—	7.65
% N found	6.80	—	7.58
% halogen calc.	17.40	32.2	—
% halogen found	17.34	31.8	—
M.p. of picrate	169–170.5	170–171	148.5–149.5
% N calc. for picrate	12.9	11.9	13.6
% N found for picrate	12.95	11.8	13.3

*Oxidation of  $\alpha$ -(p-chlorobenzyl)pyridine.* To a solution of 10.12 g. of  $\alpha$ -(*p*-chlorobenzyl)pyridine in 800 ml. of 40% sulfuric acid, kept at 55°, was slowly added 40 g. of potassium permanganate dissolved in 400 ml. of water. After the addition was complete, the temperature was raised to 70° and held at this point for 36 hours. After extraction of the mixture with 25 ml. of ether, an additional 83 ml. of concentrated sulfuric acid and 210 ml. of an aqueous solution of 60 g. of potassium permanganate were slowly added to the raffinate. The temperature was again maintained at 70° for 15 hours. The reaction mixture was again extracted with ether and the combined ether extracts evaporated to give 1.16 g. of a crude residue with m.p. 233° and neutralization equivalent 167 (m.p. of *p*-chlorobenzoic acid 242°; neutralization equivalent 157). Purification of this crude material by dissolving in alkali and reprecipitating with hydrochloric acid gave *p*-chlorobenzoic acid, m.p. 240–241°. Assuming that the impurities were neutral in character, the yield of *p*-chlorobenzoic acid was 14% of the theoretical value.

The acid reaction mixture remaining after the final ether extraction was neutralized with solid potassium hydroxide to the Congo red end point. The precipitate which formed, principally potassium sulfate, was removed by filtration and extracted with alcohol. The alcohol extract was evaporated to dryness and the residue recrystallized from hot water to give white crystals, m.p. 133–135° (m.p. of  $\alpha$ -picolinic acid 137°). This proved the alpha orientation of the parent amine.

*Oxidation of  $\alpha$ -(*p*-bromobenzyl)pyridine.* By a procedure identical with that described above, 3.03 g. of the amine was found to produce 0.39 g. (16.2%) of *p*-bromobenzoic acid, m.p. 249–250°.

*Oxidation of  $\alpha$ -(*p*-methylbenzyl)pyridine in dilute acid solution.* Three grams of the amine was dissolved in 30 cc. of 2% sulfuric acid, heated to 80°, and 9.5 g. of potassium permanganate and 5.5 cc. concentrated sulfuric acid added in small portions. After heating for three days at 80°, the acid reaction mixture was filtered. The precipitate was extracted with 20 ml. of 10% sodium hydroxide to remove the organic acids (0.937 g.). This mixture had a neutralization equivalent of 194 and contained 5.23% N. A mixture containing 9.7% terephthalic acid and 90.3% 2-(4-carboxybenzoyl)pyridine would have a neutralization equivalent of 194 and would contain 5.55% N. Recrystallization of a portion of the mixture from alcohol gave 2-(4-carboxybenzoyl)pyridine, m.p. 229.5–231°, neutralization equivalent 220 (literature<sup>4</sup> m.p. 229.3–230.5°; neutralization equivalent 227). Portions of the residue from the alcohol recrystallization of the mixture of acids were converted to the *p*-phenacyl ester, m.p. 189–190° (literature<sup>5</sup> m.p. of *p*-phenacyl terephthalate, 192°) and the methyl ester, m.p. 139.5–140° (literature<sup>6</sup> m.p. of dimethyl terephthalate, 140°).

(b) **Chain transfer with *p*-chlorotoluene.** Preparation of polymer. Over a period of 12 days, 20.2 g. (0.05 mole) of lauroyl peroxide (Lucidol Corp. Alperox C precipitated from benzene by addition of methanol) was added to a solution of 96.0 g. (0.913 mole) of 2-vinylpyridine (Reilly Tar and Chemical Co., redistilled) in 873.6 g. (6.90 moles) of *p*-chlorotoluene. A reaction temperature of 75° was maintained. At the end of 12 days, the solvent and unreacted monomer were removed by distillation at 25 mm. pressure. The dark brown residue (79 g.) was dissolved in 300 ml. of 20% sulfuric acid, and the acid solution was filtered and washed with ether to remove any traces of unreacted *p*-chlorotoluene. Neutralization with aqueous sodium hydroxide precipitated the polymer. Unreacted monomer and low molecular products were apparently removed in this process for three successive treatments with acid, etc., as described above, ultimately yielded a fairly hard and brittle product. The purified polymer was finally boiled with water to remove any sodium sulfate and then dried to constant weight (38.3 g.) by heating at 55° under reduced pressure. Analysis of the polymer by the Carius method showed the per cent chlorine to be 0.34, 0.36%. As the chlorine content was very low (only 3 mg. of silver chloride was obtained in the analysis), to correspond to the limited accuracy of the determination, the value should be properly expressed as 0.35  $\pm$

0.04%. The halogen content of the monomer, determined by another method of analysis,<sup>7</sup> has been shown to be less than the magnitude of error and has been disregarded.

To a solution of 30.0 g. of this polymer (0.286 mole on the basis of vinylpyridine) in 500 cc. of 2% sulfuric acid was added 166.6 g. (1.05 mole) of potassium permanganate in small portions. A temperature of 80° was maintained. After reduction of each portion of permanganate, the calculated amount of sulfuric acid was added to re-establish the acidity at the original level. After the addition was complete (30 hours), the solution was kept at 80° for an additional 15 hours. Sulfur dioxide was then passed into the mixture to reduce the manganese dioxide. The crystalline precipitate which formed was removed by filtration and the filtrate extracted with ether. The crystalline precipitate was treated with aqueous sodium hydroxide, and this alkaline solution acidified with hydrochloric acid and extracted with ether. The ether extracts from both sources were combined and the ether evaporated. The residue was dissolved in aqueous sodium hydroxide and the resultant solution filtered to remove neutral impurities. The clarified alkaline solution was then neutralized with sulfuric acid and extracted with ether. Evaporation of the ether extract left a mixture of fatty acids (catalyst fragments) and *p*-chlorobenzoic acid.

The mixture of acids was heated with 5 ml. of hot water. After filtering from the residual acids, the aqueous solution was chilled to yield a small quantity of crystalline material. These crystals were collected by filtration and the mother liquor was used again for extraction of the residual acid mixture. This process was repeated until extraction no longer produced crystals. The crystalline material had a m.p. of 243–244° and a neutralization equivalent of 153 (*p*-chlorobenzoic acid m.p. 243°,<sup>8</sup> neutralization equivalent 157). The 0.166 g. of *p*-chlorobenzoic acid isolated represented 35.7% of theoretical yield.

A second sample of polymer was prepared by the procedure previously described and analyzed for chlorine content (% Cl, 0.65 and 0.71). The variation in halogen content from the polymer previously prepared may be due to addition of the catalyst less rapidly or in different-sized portions. The yield of purified polymer was also somewhat lower (26 g. from 88 g. of monomer).

The oxidation of this polymer was accomplished in 25% sulfuric acid. To 21.0 g. of the polymer dissolved in 40 ml. of concentrated sulfuric acid and 45 ml. of water were added 195 ml. of concentrated sulfuric acid and a solution of 163.5 g. (1.04 moles) of potassium permanganate in 670 ml. of water. The permanganate solution was added in three equal portions and quantities of the sulfuric acid were added at proper intervals of time to maintain an acid concentration of 25 to 40%. After complete reduction of each portion of permanganate (one to nine days for complete decolorization), the reaction mixture was cooled and extracted with ether. A fourth portion of potassium permanganate was added but, as subsequent extraction with ether produced no organic acids, this fourth treatment with oxidizing agent was unnecessary.

After completion of the oxidation, the combined ether extracts were evaporated and *p*-chlorobenzoic acid isolated from the residue by the procedure described in the preceding experiment. The yield of acid, m.p. 237–239°, was 172 mg., or 27.3% of the theoretical yield. The neutralization equivalent was 160 (calc. 157).

(c) **Chain initiation with the bromophenyl radical.** One hundred and thirty grams (1.24 moles) of freshly distilled 2-vinylpyridine (Reilly Tar and Chemical Co.) was polymerized at 65–80° using 12.3 g. (0.05 mole) of *N*-nitroso-*p*-bromoacetanilide<sup>9</sup> as catalyst. The polymer was purified by the method previously described. Carius analysis of the purified polymer (63 g.) gave Br 3.66, 3.40, 3.45; average 3.55%.

*Oxidation, procedure A.* Thirty grams of polymer was dissolved in 300 cc. of 6 *N* sulfuric acid, and a hot solution of 50 grams (0.32 mole) of potassium permanganate in 200 cc. of water was slowly added. After 2.5 hours, the reaction mixture was extracted with ether to give 0.482 gram of *p*-bromobenzoic acid, which melted at 251–252° (literature m.p. 251–253°), neutralization equivalent 199 (calc. 201). The reaction mixture was made alkaline with dilute sodium hydroxide to precipitate partially oxidized polymer. Thirteen grams of partially oxidized polymer was recovered and when subjected to a Carius analysis gave: Br 2.14, 1.93; average 2.04. Therefore, correcting for the bromine in the partially oxidized polymer, a 24% yield of *p*-bromobenzoic acid was obtained.

The partially oxidized polymer was then subjected to further oxidation. The 13 g. of polymer were dissolved in 130 cc. of 6 *N* sulfuric acid, and 20 g. (0.13 mole) of potassium permanganate dissolved in 100 cc. of hot water was added. After 2.5 hours, the reaction mixture was extracted with ether to give 0.294 g. of *p*-bromobenzoic acid (m.p. 250.5–252°). When the reaction mixture was made alkaline, 0.8 g. of polymer was recovered (Br 1.07%). The yield of *p*-bromobenzoic acid from oxidation of the 13 grams of polymer was 46% (corrected for recovered polymer). The over-all yield of *p*-bromobenzoic acid from the 30 grams of original polymer was 30%.

*Oxidation, procedure B.* To a solution of 15.31 g. of polymer in 100 cc. of water and 82 g. of sulfuric acid was added 147 g. of potassium permanganate in saturated aqueous solution. The permanganate was added in eleven successive portions, each portion being reduced completely to the manganous state before addition of more permanganate. Sulfuric acid was added with each batch of permanganate to maintain a minimum acidity of 25% (6 *N*) by compensating for acid consumption as well as dilution effects. A total of 755 g. of sulfuric acid was necessary, as 2000 cc. of water was used to dissolve the potassium permanganate. During the entire course of the oxidation, the reaction mixture was subjected to continuous ether extraction. The ether extract was evaporated to dryness, and the product was purified by dissolving in dilute sodium hydroxide, filtering the alkaline solution, washing the alkaline solution with ether, and finally precipitating with aqueous acid to give 0.441 g. of a crude prod-

uct, m.p. 245–248°. This corresponds to a 32.5% yield of *p*-bromobenzoic acid.

(d) **Chain transfer with bromobenzene.** To a solution of 83.2 g. of freshly distilled 2-vinylpyridine (Reilly Tar and Chemical Co.) dissolved in 1860 g. of bromobenzene kept at 70 to 80° was added 10.2 g. of lauroyl peroxide (Novadel-Agene Corporation, recrystallized from benzene-methanol) in 2-g. quantities over a period of seven days. Unreacted monomer and solvent were then removed by distillation to give 24.8 g. of crude polymer. To the mixture of bromobenzene and monomer recovered from the first polymerization was added an additional 89 g. of 2-vinylpyridine, and polymerization at  $75 \pm 5^\circ$  was obtained by addition of 13.8 grams of lauroyl peroxide over a period of eight days. Unreacted monomer and solvent were again removed by distillation. The two polymer residues were combined and purified by the method previously described. The purified polymer (76 g.) when subjected to a Carius analysis gave Br 0.41%.

To a solution of 30.8 g. of the polymer dissolved in 370 ml. of 25% aqueous sulfuric acid was added 241 g. of potassium permanganate dissolved in water. The potassium permanganate was added in nine successive portions, each portion being reduced completely to the manganous state before addition of more permanganate. Sulfuric acid was added with each batch of permanganate to maintain a minimum acidity of 25% (6 *N*). A total of 588 g. of sulfuric acid was necessary, as 880 cc. of water was used to dissolve the potassium permanganate. The reaction mixture was extracted with ether just before each addition of permanganate. After the combined ether extracts were evaporated to dryness, the residue was dissolved in aqueous alkali and the alkaline solution was extracted with ether to remove impurities. Acidification of the alkaline solution and extraction with ether gave 1.137 g. of a mixture of *p*-bromobenzoic acid and fatty acids. This mixture of acids was subjected to a Carius analysis to give Br 1.64, 1.75; average 1.70%. Assuming that all the bromine was present as *p*-bromobenzoic acid, the yield of *p*-bromobenzoic acid from the original polymer was 6.4%. The presence of *p*-bromobenzoic acid was proved by extracting the fatty acids from the mixture with ligroin and filtering. The yield of *p*-bromobenzoic acid melting at 247–249° (literature 251°) was 6.7 mg. from 478 mg. of the mixture. This corresponds to a yield of 4.7%.

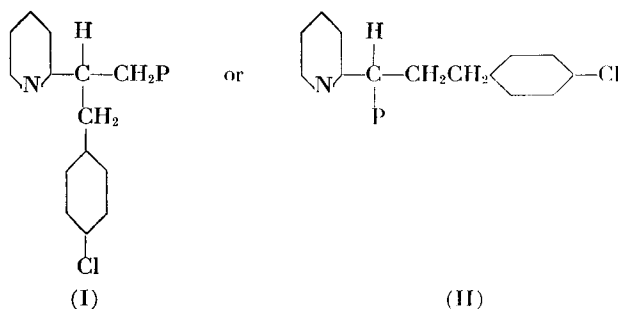
### III. DISCUSSION

(a) **Chain transfer with *p*-chlorotoluene.** Alkylbenzenes are unique among most ring compounds in that, when they serve as chain transfer agents in vinyl polymerization, reaction might occur with the substituent instead of the nucleus. Side chain attack has been proposed to explain the molecular weights of the polymers obtained by the free radical polymerization of styrene in a series of alkylbenzenes.<sup>10</sup> Inasmuch as other typical homolytic reagents such as acetyl peroxide<sup>11</sup> and *tert*-butyl peroxide<sup>12</sup> have been found to react with the side chains of alkylbenzenes,

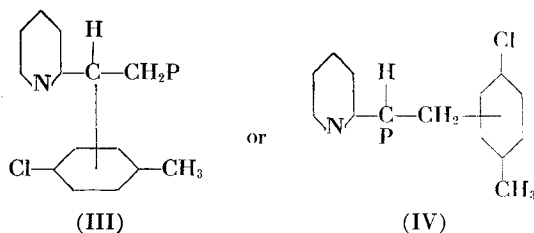
the interpretation seems reasonable. Since benzoyl peroxide, however, reacts with the nucleus as well as the side chain of such hydrocarbons,<sup>13</sup> proof of the site of reaction in chain transfer with alkylbenzenes is desirable.

The attack of a poly-2-vinylpyridyl radical upon either the nucleus or the side chain of the chain transfer agent *p*-chlorotoluene could occur by several mechanisms. Ultimately, however, any mechanism which results in incorporation of fragments of the chain transfer agent into the polymer must:

(a) by side chain attack give:



(b) by nuclear attack give:



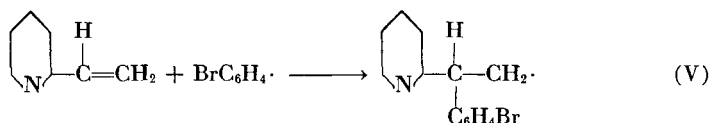
(The orientation might be ortho or meta to the chlorine substituent. "P" represents the rest of the polymer molecule.)

Structures III and IV contain  $\alpha$ -(methylbenzyl)pyridine-type structures. Since  $\alpha$ -(*p*-methylbenzyl)pyridine itself was found to produce terephthalic acid in 3.3% yield when oxidized with potassium permanganate in dilute sulfuric acid, III and IV should give appreciable quantities of a chlorophthalic acid under these conditions. Structures I and II in contrast should yield *p*-chlorobenzoic acid upon oxidation. Since a 36% yield of *p*-chlorobenzoic acid (and no chlorophthalic acid) was actually isolated from such a polymer by this method of oxidation, evidence is presented supporting chain transfer by reaction of the polymer radical with the side chain of *p*-chlorotoluene. No stronger statement may be made, for it is obvious that mechanisms other than chain transfer may be responsible for the incorporation of chlorophenyl groups in the polymer. For example, reaction of the lauroyl peroxide with *p*-chlorotoluene could produce a chlorobenzyl radical which could act as a chain initiator.

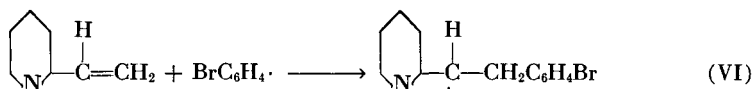
Of greater significance was the fact that this particular sample of polyvinylpyridine was now known to contain chlorophenyl and pyridyl groups separated by a chain of two or more carbon atoms. The oxidation of this polymer with potassium permanganate in 25% sulfuric acid produced a 27% yield of *p*-chlorobenzoic acid. This represents the maximum yield of halobenzoic acid which may be obtained by oxidation under these stringent conditions of a polyvinylpyridine containing trace quantities of halobenzene and pyridine rings separated by a chain of two or more carbon atoms.

(b) **Chain initiation with the *p*-bromophenyl radical.** The step of chain initiation in the polymerization of a compound such as 2-vinylpyridine could proceed by attachment of a free radical (*e.g.*, the bromophenyl radical) to either the alpha or beta carbon atom of a monomer molecule.

Alpha carbon atom reaction:



Beta carbon atom reaction:



Beta carbon atom reaction seems more reasonable from resonance considerations, but direct experimental confirmation has not been obtained. The orientation of addition of homolytic reagents to olefins to form telomers<sup>14</sup> does not provide rigid proof of this point for it is difficult to determine which fragment is added first to the double bond in such chain reactions.

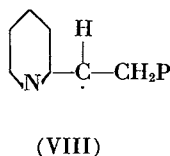
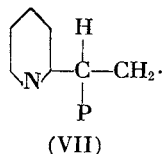
Structure V contains a bromobenzylpyridine structure.  $\alpha$ -(*p*-Bromobenzyl)- and  $\alpha$ -(*p*-chlorobenzyl)pyridine have been shown to give the corresponding halobenzoic acids in essentially the same yields (16 and 14%, respectively) when oxidized with potassium permanganate in 25% sulfuric acid solution. Structure V would certainly be expected to give no more than 16% yield of *p*-bromobenzoic acid when oxidized under these conditions and a polymeric structure of this complexity would probably give even lower yields of halobenzoic acid than bromobenzylpyridine itself. Structure VI, on the other hand, contains pyridine and benzene nuclei separated by a chain of two carbon atoms and should (based upon the experiments already discussed) give a yield of about 27% bromobenzoic acid.

The oxidation in 25% sulfuric acid of a polyvinylpyridine prepared using *N*-nitroso-*p*-bromoacetanilide as the catalyst gave a 31% (average) yield of *p*-bromobenzoic acid. Since this corresponds within the limits of experimental error to the yield expected from V, chain initiation must occur by addition of the bromophenyl radical to the beta carbon of 2-vinylpyridine.

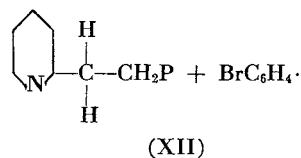
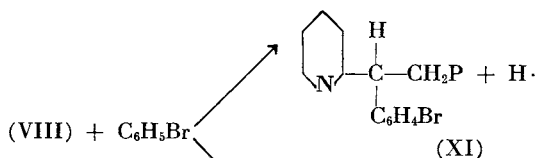
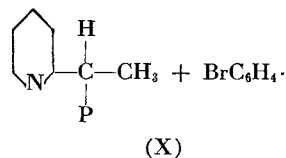
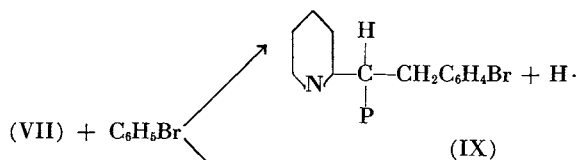
(c) **Chain transfer with bromobenzene.** In the chain transfer step



of the polymerization of 2-vinylpyridine, the polymer radical theoretically might have either of the following two structures, depending on whether addition occurred to the alpha or beta carbon atom of a monomer unit in the last step of chain growth.



If the polymer radical undergoes a substitution reaction with an aromatic nucleus as other free radicals do,<sup>16</sup> both VII and VIII have the possibility of reacting in two ways with bromobenzene as a chain transfer agent: either to unite with a bromophenyl group and release a hydrogen atom, or to unite with the hydrogen atom and release a bromophenyl radical:



The hydrogen atom or bromophenyl radical released would initiate a new polymer chain.

Structure IX and the polymer molecules initiated by the bromophenyl radicals released in the formation of X and XII should yield *p*-bromobenzoic acid in 27–31% yield (see previous experiments) upon oxidation with permanganate in 25% sulfuric acid. Only structure XI contains a benzylpyridine structure and would be expected to produce a smaller yield (16% or less) of *p*-bromobenzoic acid.

The oxidation of a polymer prepared in bromobenzene solution gave a yield of *p*-bromobenzoic acid not exceeding 6.5% of the theoretical value. This is in agreement with the reaction of a 2-pyridylmethyl type of polymer radical (VIII) with the ring of the bromobenzene molecule with subsequent release of a hydrogen atom. This would also indicate that in the step of chain growth preceding chain transfer, a normal head-to-tail addition occurred.

Since  $\alpha$ -(*p*-bromobenzyl)pyridine has been shown to yield 16% *p*-bromobenzoic acid under these conditions of oxidation, the 6.5% yield obtained from the polymer in the present experiment most probably is obtained from XI, but the existence of a maximum of 20% of structures IX, X, and XII would not be excluded. This figure of 20% is obtained by dividing the 6.5% yield by the 31% yield obtained from polymers known to contain benzene and pyridine nuclei separated by two or more carbon atoms.

The existence of the hydrogen atom as an entity in this step of chain transfer is debatable, but does not affect the results presented. The polymer radical may unite with the bromobenzene molecule to form a new radical which then transfers a hydrogen atom to a monomer unit. At the moment of transfer to the monomer, the hydrogen atom would have a transient existence reminiscent of that of carbonium ions and carbanions in many ionic reactions.

Determination of structure from relative yields is not a desirable procedure and is dictated only by the complexity of the molecules studied. The conclusions just reached are dependent upon reaction of the polymer radical with bromobenzene to give substitution. Stockmayer<sup>15</sup> has offered evidence that, instead of substitution, addition occurs. Since nonbenzenoid nuclei would not yield bromobenzoic acid upon oxidation, the addition reaction supported by Stockmayer cannot occur exclusively. However, the low yield (6%) of bromobenzoic acid could alternatively be attributed to a major incorporation of bromobenzene nuclei by an addition reaction.

Mayo<sup>16</sup> has found that the polymerization of styrene in bromobenzene solution involves participation of the solvent in the chain transfer process without incorporation of appreciable quantities of bromine in the polymer. Since the present work is related only to bound bromine, it is applicable to only one of several possible competing chain transfer processes.

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### Synopsis

(1) Polymerization of 2-vinylpyridine in *p*-chlorotoluene solution produced a polymer which, when oxidized with potassium permanganate in dilute sulfuric acid, gave no chlorophthalic acid, but a 35.7% yield of *p*-chlorobenzoic acid (based upon the halogen content of the polymer). Therefore, incorporation of the aromatic groups in the polymer, probably in the step of chain transfer, occurred by reaction with the side chain and not the nucleus of the *p*-chlorotoluene. The absence of chlorophthalic acid was significant, for a similar oxidation of  $\alpha$ -(*p*-methylbenzyl)pyridine gave a 3% yield of terephthalic acid as well as a 23% yield of 2-(4-carboxybenzoyl)pyridine. (2) Permanganate oxidation of this same polymer in 25% sulfuric acid gave a 27% yield of *p*-chlorobenzoic acid. This represents the maximum yield of halobenzoic acid to be expected from a polyvinylpyridine containing trace quantities of halophenyl and pyridine nuclei separated by a chain of two or more carbon atoms. In contrast, similar oxidations in 25% sulfuric acid of  $\alpha$ -(*p*-bromobenzyl)- and  $\alpha$ -(*p*-chlorobenzyl)pyridine gave much smaller yields (16 and 14%, respectively) of the corresponding halobenzoic acids. In concentrated acid, the heterocyclic rings form stable salts and oxidation of the benzylpyridine type structures leads to preferential cleavage of the benzene nucleus. (3) Initiation of the polymerization of 2-vinylpyridine with *N*-nitroso-*p*-bromoacetanilide formed a polymer which, upon oxidation with potassium permanganate in 25% sulfuric acid, gave a 31% (average) yield of *p*-bromobenzoic acid. Since this yield is that expected from a polymer in which pyridine and bromobenzene rings are separated by a chain of two or more carbon atoms, beta carbon atom addition in chain initiation by a bromophenyl radical is substantiated. (4) Polymerization of 2-vinylpyridine in bromobenzene solution provided a polymer which, upon oxidation with permanganate in 25% sulfuric acid, gave only a 6% yield of bromobenzoic acid, corresponding to a bromobenzylpyridine structure in the polymer. Reasons are given why this data supports but does not prove the hypothesis that chain transfer consists of substitution in the bromobenzene nucleus by a polymer radical possessing a 2-pyridylmethyl structure.

### Résumé

(1) La polymérisation de la 2-vinylpyridine en solution para-chlorotoluénique produit un polymère, dont l'oxydation au permanganate en solution sulfurique diluée ne fournit pas d'acide chlorophthalique; par contre on obtient 35.7% d'acide para-chlorobenzoïque (calcul basé sur la teneur en halogène). On en conclut à l'incorporation de groupes aromatiques dans le polymère, vraisemblablement au cours de réactions de transfert de chaîne avec le groupe méthyle du dérivé toluénique et non avec le noyau aromatique. L'absence d'acide chlorophthalique était également significative car une oxydation similaire de alpha-(para-méthylbenzyl)pyridine fournit 3% d'acide téréphthalique et 23% de 2-(4-carboxybenzoyl)pyridine. (2) L'oxydation permanganique de ce même polymère dans l'acide sulfurique à 25% donne 27% d'acide para-chlorobenzoïque. Ceci représente le rendement maximum d'acide benzoïque halogéné que l'on peut obtenir aux dépens de polyvinylpyridine contenant de très faibles quantités de noyaux phényles halogénés et des noyaux pyridiniques séparés par une chaîne de deux ou plus d'atomes de carbone. Par contre, des oxydations similaires dans l'acide sulfurique à 25% de

alpha-(para-bromobenzyl)pyridine et de alpha-(para-chlorobenzyl)pyridine fournissent des rendements beaucoup plus faibles (16 et 14% respectivement) en acides benzoïques halogénés correspondants. Dans l'acide concentré, les hétérocycles forment des sels stables et l'oxydation de structures du type benzylpyridine entraîne une rupture préférentielle du noyau benzénique. (3) L'initiation de la polymérisation de la 2-vinylpyridine avec le *N*-nitroso-para-bromoacétanilide produit un polymère, dont l'oxydation au permanganate dans l'acide sulfurique à 25% donne en moyenne 31% d'acide para-bromobenzoïque. Comme ce rendement correspond à celui que l'on attendrait aux dépens d'un polymère dans lequel les noyaux pyridiniques et bromobenzéniques sont séparés par une chaîne de deux ou plusieurs atomes de carbone, on admet une addition à l'atome de carbone en bêta au cours de l'initiation par un radical bromophénylé. (4) La polymérisation de la 2-vinylpyridine en solution bromobenzénique fournit un polymère dont l'oxydation permanganique en solution sulfurique à 25% produit seulement 6% d'acide bromobenzoïque, ce qui correspond à une structure bromobenzylpyridinique du polymère. Des motifs sont donnés à titre explicatifs, sans avoir de valeur probante définitive; ils consistent à admettre un transfert de chaîne par substitution du noyau bromobenzénique par l'attaque d'un radical polymérique possédant une structure 2-pyridyl-méthylque.

### Zusammenfassung

(1) Polymerisation von 2-Vinylpyridin in *p*-Chlorotoluollösung ergab ein Polymer, welches bei Oxydation mit Kaliumpermanganat in verdünnter Schwefelsäure keine Chlorophthalsäure ergab, sondern eine 35,7%ige Ausbeute an *p*-Chlorobenzoessäure (auf den Halogengehalt des Polymers gestützt). Deshalb trat Eingliederung der aromatischen Gruppen in das Polymer, wahrscheinlich während der Stufe der Kettenübertragung, durch Reaktion mit der Seitenkette und nicht mit dem Kern von *p*-Chlorotoluol auf. Die Abwesenheit von Chlorophthalsäure war bezeichnend, denn eine ähnliche Oxydation von  $\alpha$ -(*p*-Methylbenzyl)pyridin ergab eine 3%ige Ausbeute an Terephthalsäure wie auch eine 23%ige Ausbeute an 2-(4-Carboxybenzoyl)-pyridin. (2) Permanganatoxydation des gleichen Polymers in 25%iger Schwefelsäure ergab eine 27%ige Ausbeute an *p*-Chlorobenzoessäure. Dies ist die maximale Ausbeute an Halobenzoessäure, die von einem Polyvinylpyridin erwartet werden kann, welches Spuren von Halophenyl- und Pyridinkernen enthält, die durch eine Kette von zwei oder mehreren Kohlenstoffkernen getrennt sind. Im Gegensatz dazu ergaben ähnliche Oxydierungen von  $\alpha$ -(*p*-Bromobenzyl)- und  $\alpha$ -(*p*-Chlorobenzyl)pyridin in 25%iger Schwefelsäure viel kleinere Umsätze (16 beziehungsweise 14%) der entsprechenden Halobenzoessäuren. In konzentrierter Säure bilden die heterocyclischen Ringe beständige Salze, und Oxydation der Benzylpyridin-artigen Strukturen führt zu vorzugsweiser Spaltung des Benzolkernes. (3) Initiation der Polymerization von 2-Vinylpyridin mit *N*-Nitroso-*p*-bromoacetanilid bildete ein Polymer, welches bei Oxydation mit Kaliumpermanganat in 25%iger Schwefelsäure einen 31%igen (mittleren) Umsatz an *p*-Bromobenzoessäure ergab. Da dies die erwartete Ausbeute für ein Polymer ist, in welchem Pyridin und Bromobenzolringe durch eine Kette von zwei oder mehreren Kohlenstoffatomen getrennt werden, ist beta-Kohlenstoffatom-Addition in Ketteninitiation durch ein Bromophenylradikal bewiesen. (4) Polymerisation von 2-Vinylpyridin in Bromobenzollösung ergab ein Polymer, welches bei Oxydation mit Permanganat in 25%iger Schwefelsäure nur einen 6%igen Umsatz an Bromobenzoessäure ergab, was einer Bromobenzylpyridin-Struktur in dem Polymer entspricht. Es werden Gründe gegeben, warum diese Daten die Theorie unterstützen, aber nicht beweisen, dass Kettenübertragung aus Substitution in dem Bromobenzolkern durch ein Polymerradikal besteht, welches 2-Pyridylmethyl-Struktur besitzt.

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