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**SYNTHESIS AND POLYMERIZATION  
OF  $\beta$ -ALKYLSTYRENES**



**TECHNICAL REPORT**

*Ferrel E. Anderson*

March 1970

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TECHNICAL REPORT

RE 70-128

SYNTHESIS AND POLYMERIZATION  
OF  
 $\beta$ -ALKYLSTYRENES

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March 1970

DA 1G062105A109

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## ABSTRACT

Work was continued on the synthesis of poly( $\beta$ -alkyl-p-styrene sulfonate) salt corrosion inhibitors. A synthesis plan was followed which resulted in the synthesis of lauro-, palmito-, and stearophenone; octyl-, undecyl-, pentadecyl-, and heptadecyl-phenyl-carbinol;  $\beta$ -heptyl-,  $\beta$ -decyl-,  $\beta$ -tetradecyl-, and  $\beta$ -hexadecyl-styrene; and poly( $\beta$ -heptyl- and  $\beta$ -hexadecyl-styrene). Emphasis placed on the improvement of synthesis and analytical procedures resulted in significant progress. Results obtained from three polymerization attempts were useful in the solution of a major contamination problem encountered previously, but these results did not contribute to the formation of higher molecular weight polymers.

## FOREWORD

The work discussed in this report was performed under DA Project 1G062105A109, AMS Code 5025.11.803, "Corrosion Preventives and Specialty Compounds." The work unit title was "Development of an Improved Corrosion Preventive with Additives Having Single and Multiple Adsorption Groups." The information obtained and the techniques advanced in this study will lead to the development of new corrosion inhibitors and result in the formulation of improved corrosion preventives.

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## BACKGROUND

The work continued during the second year of a two-year continuing project is covered in this report. The results obtained during the first year of work are presented in Science and Technology Laboratory Technical Report 69-111 entitled "Development of Multiple Adsorption-Group Corrosion Inhibitors: Preliminary Results of the Synthesis of Poly( $\beta$ -Alkyl-p-Styrene Sulfonate) Salts."<sup>1</sup> In this report, the synthesis plan was completed for  $\beta$ -hexadecyl-styrene and was carried through to n-octaphenyl-carbinol for  $\beta$ -heptylstyrene, to laurophenone for  $\beta$ -decylstyrene, and to palmitophenone for  $\beta$ -tetradecylstyrene.

The synthesis of poly( $\beta$ -hexadecyl-p-styrene-sulfonate) salts revealed the weak points in the synthesis plan. These weaknesses occurred in the polymerization and sulfonation steps. The polymerization step resulted in a polymer of only two to three units rather than in a desired polymer of two-hundred monomer units. Sulfate residue analyses of the products gave an apparent result that indicated three sulfonate groups on each phenyl ring of the polymer. This result was inconsistent with infrared analyses which indicated that only one sulfonate group was present on each phenyl ring.

## APPROACH

Work was continued on the synthesis plan presented in Figure 1. Although octyl phenyl carbinol, laurophenone, palmitophenone, and stearophenone were available from previous syntheses, they were not present in sufficient quantity to ensure a large yield of end product. Because additional quantities were needed for subsequent syntheses and because a new purification procedure was initiated, the previously formed compounds were combined with the new materials for the sake of uniform purity.

Emphasis was placed on increasing the reaction yields and on developing a more efficient purification technique. The yields of Reaction-Steps 1, 2, and 3 were excellent; however, the yields of Reaction-Step 4 were from only 20 to 40 percent of theoretical. Purification was accomplished in earlier syntheses by recrystallization and fractional recrystallization techniques, and recovered by filtration or centrifugation. The compounds were relatively pure; but the significant effort expended in purifying these compounds by these methods and the attendant time loss

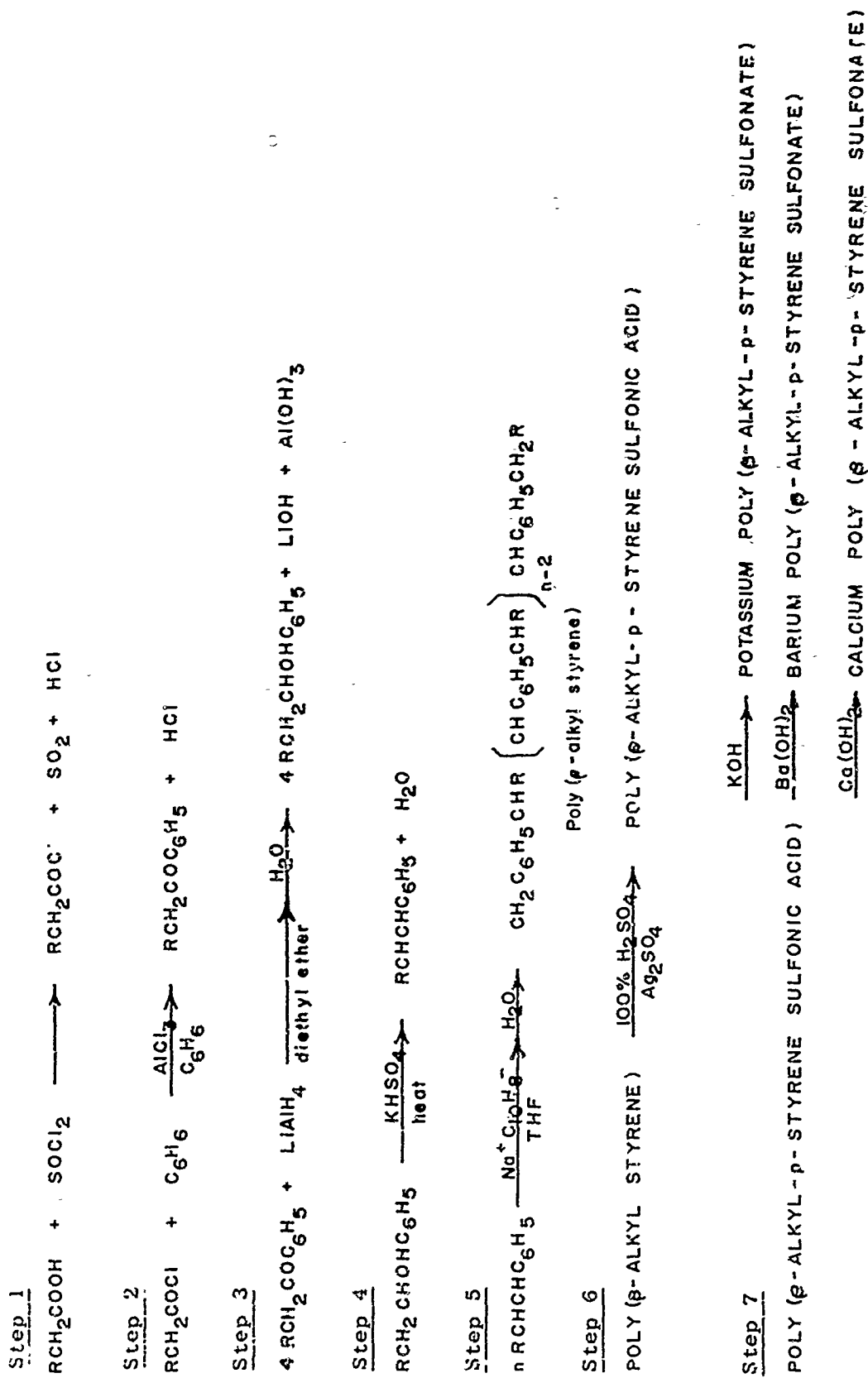


FIGURE 1  
 SYNTHESIS REACTION-STEP SERIES



incurred hampered progress. The obvious solution was believed to be high vacuum distillation.

The primary areas of concern were the polymerization and sulfonation steps. A solution to the problems experienced on these steps was essential to the future of this work. To solve these problems, it was assumed that the reaction would proceed under ideal conditions with no complications. Both reaction methods were proved successful by other workers on nonalkylated styrenes and polystyrenes.<sup>2,3</sup> Even though polymerization of  $\beta$ -alkylstyrenes can be seriously questioned on grounds of steric hindrance, it was believed that sufficient work had not been performed to establish such a conclusion. With this in mind, it was decided to improve the reaction technique and to incorporate changes that might reduce contamination rather than adopt another polymerization method. The sulfonation problem was second in priority to the polymerization problem and, as a result, was not attacked directly in the work included in this report. However, the solution to this problem also is suggested in the conclusions of this report based on the results gained in the polymerization investigation.

#### EXPERIMENTAL PROCEDURE

##### Synthesis

The reaction-step series followed is outlined in Figure 1. Detailed descriptions of reaction procedure are presented in Appendix A. The source and purity of the chemicals used in the reactions are presented in Table I of Appendix A. No changes were made in the detailed procedure used in previous syntheses for Reaction-Steps 1, 2 and 3. For improvement of the yields of Reaction-Step 4, a reaction-distillation procedure was instituted in which the product, in this case  $\beta$ -alkylstyrene, was distilled from the reaction mixture as soon as it formed. Although this method resulted in a more complicated procedure and additional apparatus, it also resulted in less complicated post-reaction procedures. It was obvious that the equilibrium of the reaction would require a shift to the right. Removal of the product offered the only solution and was easily accomplished because the styrenes had lower boiling points than those of the respective reactant carbinols.

The procedure in the first two polymerization reactions was changed only slightly from previous polymerization attempts. The third polymerization, to form

$\beta$ -heptylstyrene, was different in that no silicone lubricant was used where it might contaminate the reactant solution. This step was obvious after analysis of the infrared spectra of the first two polymer products displayed absorption bands typical of functional groups present in silicone lubricants.

No sulfonation reactions were conducted.

#### Isolation and Purification

The preliminary isolation and purification steps taken immediately after the reactions were similar to those used previously.<sup>1</sup> However, in the final step, all the products were distilled under high vacuum and isolated into four fractions. The majority of the product was collected as fraction three of each distillation. This material was then used in subsequent reactions. The distillation of the polymerization product was divided into the distillate and residue, the residue being the polymer and the distillate the remaining monomer.

#### Analyses

Molecular weight determinations were made with a Mechrolab Model 302 Vapor Pressure Osmometer. The determinations of the index of refraction of liquid products were made with a Bausch and Lomb Abbe-56 Refractometer. Gailbraith Laboratories<sup>4</sup> provided elemental analyses. Infrared analyses were conducted with a Perkin Elmer 621 Grating Infra-Red Spectrometer.

### RESULTS AND DISCUSSION

The properties and the results of analyses of the compounds synthesized in this work are presented in Table I. Infrared spectra of the compounds are indexed in Table I and can be found in Appendix B

#### Reaction-Steps 1, 2, and 3

As in the previous syntheses,<sup>1</sup> Reaction-Steps 1, 2, and 3 were carried out for all four styrenes without complications. Melting and boiling points for the four compounds in each step are internally consistent and correspond favorably with the few values found in the literature.<sup>5-12</sup>

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The infrared spectra for these compounds (Appendix B) have the important absorption bands marked with a diagram of the responsible functional group.

Note should be made of an interesting set of distinct absorption bands between  $1160$  and  $1340\text{cm}^{-1}$  present in the spectra of laurophenone, palmitophenone, and stearophenone. These bands represent  $-\text{CH}_2-$  group deformations and are similar to the  $-\text{CH}_2-$  absorption bands of long chain aliphatic carboxylic acids and soaps.<sup>15</sup> For these compounds, the number of absorption peaks in this region is indicative of the number of  $-\text{CH}_2-$  groups in the chain. This, of course, is directly related to the molecular weight of the compound.

#### Step 4

The reaction technique described in Appendix A resulted in a threefold increase in the yield of  $\beta$ -alkylstyrenes over that which was recovered in previous attempts.<sup>1</sup> All of the analyses were consistent and showed the compounds to be of high purity. Infrared analysis showed them to be  $\beta$ -alkyl styrenes with the phenyl group located trans to the alkyl group across the ethylene bond.

#### Step 5

Polymerization reactions were conducted with  $\beta$ -hexadecylstyrene,  $\beta$ -decylstyrene, and  $\beta$ -heptylstyrene. The products of these reactions were distilled under high vacuum to remove any remaining monomer or other low molecular weight products. Distillation of the  $\beta$ -hexadecyl product did not produce a distillate, whereas distillation of  $\beta$ -decylstyrene resulted in complete distillation at the boiling point of the monomer. Ninety percent of the product of the  $\beta$ -heptylstyrene product distilled over at the boiling point of the monomer. The residue was a clear, colorless viscous liquid.

Molecular weight determinations conducted on the distillation residue of the  $\beta$ -hexadecylstyrene and on the  $\beta$ -heptylstyrene polymerization reactions indicated that they had, indeed, polymerized, but only to the extent that dimer compounds probably formed.

Infrared analyses conducted on the  $\beta$ -hexadecylstyrene and on the  $\beta$ -decylstyrene polymerization products determined that the former had no unsaturation in the alkyl chain and that the latter had only approximately 25 percent of the monomer unsaturation concentration. This was

determined by comparison of the peak height of the  $965\text{cm}^{-1}$  band, indicative of the trans ethylenic bond, to the constant height of the  $710\text{cm}^{-1}$  band, indicative of the phenyl group. The infrared spectrum of the  $\beta$ -heptylstyrene polymerization product before distillation (Spectrum XV) was almost identical to the spectrum for  $\beta$ -heptylstyrene (Spectrum IX), except for the slope of a line drawn from the  $965\text{cm}^{-1}$  peak to the  $710\text{cm}^{-1}$  peak. The slope of the monomer spectrum was zero, whereas that of the polymerization reaction product was  $-0.037$ . This indicated that a loss of unsaturation occurred. After distillation, the spectra of the residue (Spectrum XVII) and distillate (Spectrum XVI) were compared with the spectrum of the mixture (Spectrum XV) before distillation. The spectrum of the residue, a clear viscous liquid, did not display an unsaturation peak at  $965\text{cm}^{-1}$ . The spectrum of the distillate, a clear, colorless, less viscous liquid, was identical in every respect to that of the monomer spectrum (Spectrum IX). Thus, the molecular weight determinations and infrared analyses on the polymerization reaction products of  $\beta$ -hexadecylstyrene and  $\beta$ -heptylstyrene substantiate that the polymers poly( $\beta$ -hexadecylstyrene) and poly( $\beta$ -heptylstyrene) were formed and that they were composed of 2.3 and 1.8 monomer units, or that unspecified dimer molecules were found instead. The infrared analysis of the product of the  $\beta$ -decylstyrene polymerization reaction and the boiling point of the distillate indicated that the monomer and, probably, the saturated monomer were the remaining products. In this reaction, very little, if any, polymerization resulted, even though the monomer was activated. The activated monomer was deactivated upon the addition of water to form dodecyl benzene. It is believed that the polymerization did not proceed because of an excessive amount of activated monomer, which in turn was due to an excessive amount of sodium in the polymerization vessel. This would also account for the conversion of approximately 75 percent of the beginning monomer to the saturated form.

In the discussion section of a previous report,<sup>1</sup> several possible causes for the low molecular weight of the polymers then being investigated were listed. One of these causes suggested the presence of impurities that might deactivate the activated monomer or polymers present. An examination of Spectra 8, 9, 10, and 11 of that report clearly indicates that an impurity was present. Very strong absorption bands, which cannot be associated with any of the structures of the monomers or polymers, appear as a sharp, strong band at  $1270\text{cm}^{-1}$  and as two broad bands centered at  $1100\text{cm}^{-1}$  and  $1040\text{cm}^{-1}$  that merge to form one large band, and a strong, sharp band at  $815\text{cm}^{-1}$ . The same peaks appear in the spectra of the

polymerization products of  $\beta$ -decylstyrene (Spectrum X) and of poly( $\beta$ -hexadecylstyrene) (Spectrum XII) discussed in this report. These peaks are definitely caused by the presence of silicone lubricant.<sup>14</sup> A spectrum of the silicone lubricant used in the apparatus of these polymerization reactions shows very strong bands at the frequencies listed above.

The polymerization of  $\beta$ -heptylstyrene and the subsequent separation procedures were conducted without the use of silicone lubricant. Only in the distillation of the product was silicone lubricant used, but here it was used very sparingly. The result was a silicone-free distillate and residue as displayed by the absence of absorption peaks at 1270, 1100-1000, and 815 $\text{cm}^{-1}$  in the spectra of these compounds.

The consequences of silicone polymer contamination were that the molecular weight of poly( $\beta$ -hexadecylstyrene), discussed in this report, is too high, as were the molecular weights determined for any of the polymers synthesized previous to the polymerization of  $\beta$ -heptylstyrene. In addition, this accounts for the high values obtained in the sulfate residue analyses conducted on the salts reported previously.<sup>1</sup> A more insidious consequence is the possible poisoning of the polymerization complex with a resultant decrease in the molecular weight of the polymer. The spectrum of the lubricant displays a hydroxyl absorption peak (3700 $\text{cm}^{-1}$ ) that is either due to a hydroxyl end group on the lubricant molecule or entrained water. In either situation, the sodium-activated polymer complex would be poisoned. In the former condition, the silicone lubricant could combine with the activated polymer as an end group and in the latter condition the water would dilute the complex. The fact that the lubricant did not significantly alter the extent of polymerization is indicated by the comparable molecular weights of poly( $\beta$ -heptylstyrene) and the earlier polymerization products that contained silicone lubricant. The slightly higher values that these compounds displayed were probably due to molecular weight contributions of the silicone polymer impurities and should not be taken to represent polymers that have silicone end groups.

#### CONCLUSIONS AND RECOMMENDATIONS

No problems were encountered in the prepolymerization reaction steps of the reaction plan (Figure 1); also the yields of Reaction Step 4 for the  $\beta$ -alkylstyrenes were improved three- to fourfold. With the discovery that silicone lubricant was contaminating the polymerization



product and the sulfonate salts of these products, a major problem was solved. However, the very limited polymerization of the uncontaminated polymer would indicate that the  $\beta$ -alkylstyrenes are difficult to homopolymerize by the Living Polymer method. For attainment of effective multiple-adsorption corrosion inhibitors, the polymers should be at least four monomer units in length<sup>15</sup> and should probably be from six to possibly 100 units long. For clarification of this problem, several additional polymerization attempts, including a control polymerization with styrene, will have to be run. It is believed that if very limited homopolymerization continues, copolymer polymerizations involving styrene and the  $\beta$ -alkylstyrenes should be attempted.

In lieu of any sulfonation reactions (Step 6) since those previously reported,<sup>1</sup> no additional information has been gained that would support their probable success. Even so, the infrared spectra (Spectra IX, X, and XII)<sup>1</sup> of the contaminated sulfonate salts previously reported<sup>1</sup> show definite absorption peaks which indicate that they are monosulfonated in the para position only.

It is concluded that once the polymerization is modified, or the reaction method changed, to yield polymers of desired molecular weights no problem should be encountered in synthesizing the corrosion inhibiting polymer end products. The products, if attained, should also show promise as lubricity agents. Since work proposed in FY70 is concerned with polymeric lubricity agents, it is recommended that the work to synthesize poly( $\beta$ -alkyl-p-styrene sulfonate) salts be continued into FY70.

## APPENDIX A

### DETAILED EXPERIMENTAL PROCEDURE

The source and purity of the chemical reagents used in the reactions are presented below in Table I.

TABLE I

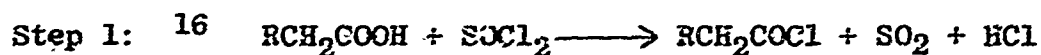
#### SOURCE AND PURITY OF CHEMICAL REAGENTS

| <u>Reagent</u>               | <u>Source</u>   | <u>Purity</u>            |
|------------------------------|-----------------|--------------------------|
| Stearic Acid                 | Fisher          | Fisher "Reagent Grade"   |
| Palmitic Acid                | Fisher          | Fisher "Reagent Grade"   |
| Lauric Acid                  | Eastman         | Eastman "Grade"          |
| Nonanophenone                | Eastman         | Eastman "Grade"          |
| Thionyl Chloride             | Fisher          | Fisher "Reagent Grade"   |
| Benzene                      | Fisher          | Fisher "Reagent Grade"   |
| Aluminum Chloride<br>(anhyd) | Fisher          | Fisher "Certified Grade" |
| Ethyl Ether                  | Fisher          | ACS Specification        |
| Lithium Aluminum Hydride     | Alfa Inorganics | "Reagent Grade"          |
| Potassium Bisulfate          | Fisher          | Fisher "Certified Grade" |
| Naphthalene                  | Eastman         | Eastman "Grade"          |
| Tetrahydrofuran              | Fisher          | Fisher "Reagent Grade"   |

All of the reagents except thionyl chloride, benzene, tetrahydrofuran, and nonanophenone were used without further purification. Thionyl chloride was purified by distillation

from quinoline under vacuum. Benzene was stored with Safe Potassium and distilled to remove remaining water azeotropically. Tetrahydrofuran was purified by treatment with lithium aluminum hydride followed by distillation in an argon atmosphere. Nonanophenone was purified by distillation under high vacuum.

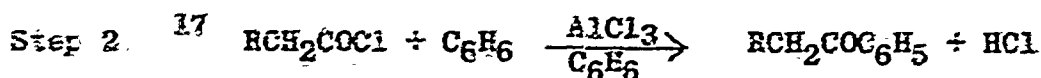
The detailed procedure followed in each chemical reaction is recorded below. Each reaction is referenced by the step number and chemical equation presented previously in Figure 1. Ground-glass jointed glassware sealed with Dow Corning High-Vacuum Grease Silicone Lubricant was used for the reactions, distillations, and storage of materials, unless otherwise noted.



STOICHIOMETRY

| <u>Reaction Product</u> | <u>SOCl<sub>2</sub> (moles)</u> | <u>RCH<sub>2</sub>COOH (moles)</u> |
|-------------------------|---------------------------------|------------------------------------|
| Lauroyl Chloride        | 1.04                            | 0.51                               |
| Palmitoyl Chloride      | 0.95                            | 0.41                               |
| Stearoyl Chloride       | 0.91                            | 0.36                               |

The reaction was conducted in a 250-milliliter, two-necked, flask, fitted after the introduction of the acid, with a water-cooled reflux condenser and a pressure-equalizing addition funnel. Before the addition of thionyl chloride to the funnel, the system was purged of atmospheric gases with anhydrous argon. Thionyl chloride was then poured into the addition funnel and subsequently allowed to drip over a ten-minute period into the flask. The mixture was heated to a temperature at which the acid melted and then allowed to remain at this temperature until the evolution of hydrogen chloride and sulfur dioxide gas had subsided. The solution was then heated to reflux and allowed to cool; the condenser was arranged for vacuum (water aspirator) distillation; and the excess thionyl chloride, hydrochloric acid, and sulfur dioxide fumes were distilled from the product remaining in the flask. The aryl chloride product was then recovered by high-vacuum (0.010 - 0.020 mm Hg) distillation into a receptacle flask cooled with dry ice. Yields ranged from 90 to 96 percent of theoretical.

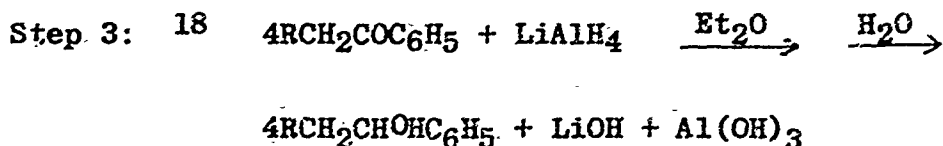


STOICHIOMETRY

| <u>Reaction Product</u> | <u>RCH<sub>2</sub>COCl (moles)</u> | <u>C<sub>6</sub>H<sub>6</sub> (moles)</u> | <u>AlCl<sub>3</sub> (moles)</u> |
|-------------------------|------------------------------------|---|---------------------------------|
| Laurophenone            | 0.50                               | 4.1                                       | 1.25                            |
| Palmitophenone          | 0.39                               | 4.1                                       | 1.25                            |
| Stearophenone           | 0.34                               | 4.1                                       | 1.25                            |

The reaction was conducted in a four-necked, 2000 milliliter, round-bottomed, flask, fitted with a thermometer, a motor-driven stirrer, a gas inlet tube, and a two-necked adapter which was in turn fitted with a funnel and a water-cooled reflux condenser. The system was flamed while atmospheric gases were purged with a stream of argon gas. A benzene solution of the acid chloride was poured into the flask (a large excess of benzene was used to reduce the probability of double arylation of one benzene ring), and the flask and its contents were cooled in an ice-water bath. Aluminum chloride powder was slowly added over a period of one hour. The mixture was then warmed to 60°C, cooled, and poured with stirring into a beaker containing two kilograms of ice and 200 milliliters of concentrated hydrochloric acid. As soon as the ice melted, the benzene phase was recovered, washed with dilute aqueous hydrochloric acid, distilled water, and dilute sodium hydroxide solutions. Upon addition of the hydroxide, a white, gelatinous suspension formed. This was removed by centrifugation and discarded (the precipitate was assumed to be the sodium salt of the alkyl acids that formed by the hydrolysis of the respective aryl chlorides by atmospheric water). The clear benzene solution was then washed twice with distilled water and dried over magnesium sulfate. After a gravity filtration, the benzene solution of the phenone was distilled to dryness, hexane was added to "sweep off" any remaining benzene, and the solution was again distilled to dryness. The produce was then distilled under high vacuum and received into receptacle flasks cooled with dry ice. Yields ranged from 50 to 60 percent of theoretical. The melting points of the products compared well with those reported in the literature.<sup>9-17</sup>

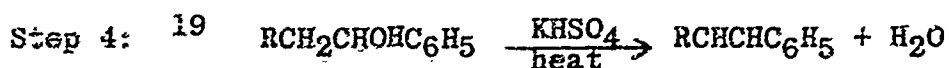
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#### STOICHIOMETRY

| <u>Reaction Product</u>   | <u><math>RCH_2COC_6H_5</math> (moles)</u> | <u><math>LiAlH_4</math> (moles)</u> |
|---------------------------|---|-------------------------------------|
| Octylphenyl-carbinol      | 0.49                                      | 0.31                                |
| Undecylphenyl-carbinol    | 0.39                                      | 0.31                                |
| Pentadecylphenyl-carbinol | 0.29                                      | 0.30                                |
| Heptadecylphenyl-carbinol | 0.21                                      | 0.25                                |

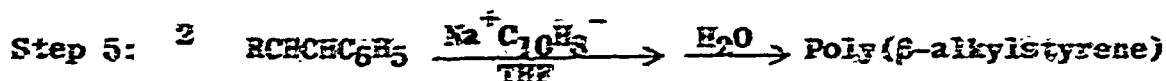
The reaction was conducted in a 2000-milliliter reaction kettle fitted with a motor-driven stirrer, a gas inlet tube, a dry ice reflux condenser cooled with dry ice, and a funnel. Before entry of the reactants, the kettle was flamed and purged of atmospheric gases by a stream of anhydrous argon gas. Throughout the reaction, the kettle was maintained with a slight positive pressure by a constant renewal of argon gas. Three hundred milliliters of anhydrous ether were then added, the lithium aluminum hydride powder was introduced, and an additional 200 milliliters of anhydrous ether were finally added. The funnel was replaced by a pressure-equalizing, addition funnel containing either nonanophenone or stearophenone in ether solution. The phenone was then added at a very slow rate. After its addition, the reaction mixture was stirred for one hour. This was followed by the addition of distilled water in a quantity sufficient to "kill" the excess lithium aluminum hydride. The white hydroxide precipitate which formed was neutralized by a 1/1 solution of sulfuric acid. The ether phase was then removed, washed three times with distilled water, dried with magnesium sulfate, and filtered. The product was isolated by distillation of ether, and was purified by distillation under high vacuum. Yields averaged 85 percent of theoretical.



STOICHIOMETRY

| <u>Reaction Product</u> | <u>RCH<sub>2</sub>CHOHC<sub>6</sub>H<sub>5</sub> (moles)</u> | <u>KHSO<sub>4</sub> (moles)</u> |
|-------------------------|--|---------------------------------|
| β-heptylstyrene         | 0.34   | 1.4                             |
| β-decylstyrene          | 0.41   | 1.5                             |
| β-tetradecylstyrene     | 0.16   | 1.5                             |
| β-hexadecylstyrene      | 0.18   | 1.5                             |

The reactions were conducted in a two-necked, round-bottomed flask. One neck was fitted with a carry-over adapter fitted with a thermometer and a 500 milliliter receiving flask. The other neck was fitted with an addition funnel for the β-heptylstyrene reaction and with an addition tube for the other three reactions. The tube was filled by melting the respective carbinol, pouring it into the tube and allowing it to solidify. For the reactions, the KHSO<sub>4</sub> was added to the flask with one milligram picric acid inhibitor and the system evacuated with a water aspirator vacuum. Sufficient reactant was added to the KHSO<sub>4</sub> to wet it completely. The mixture was then heated to a temperature at which distillation commenced. As the product distilled over to the receiving flask, additional reactant was added to the reaction flask to maintain the distillation at a constant rate. The solid carbinols were added to the reaction by melting a portion of the carbinol solid in the tube with a heat lamp. When the reaction was completed, the distillate was dissolved in benzene, washed twice with dilute hydrochloric acid, and three times with distilled water. The solution was then dried with calcium sulfate. Next, the benzene was filtered and then distilled from the product. The product was then distilled under high vacuum into four fractions that were stored under anhydrous argon gas and refrigerated. Yields ranged from 80-90 percent of theoretical.



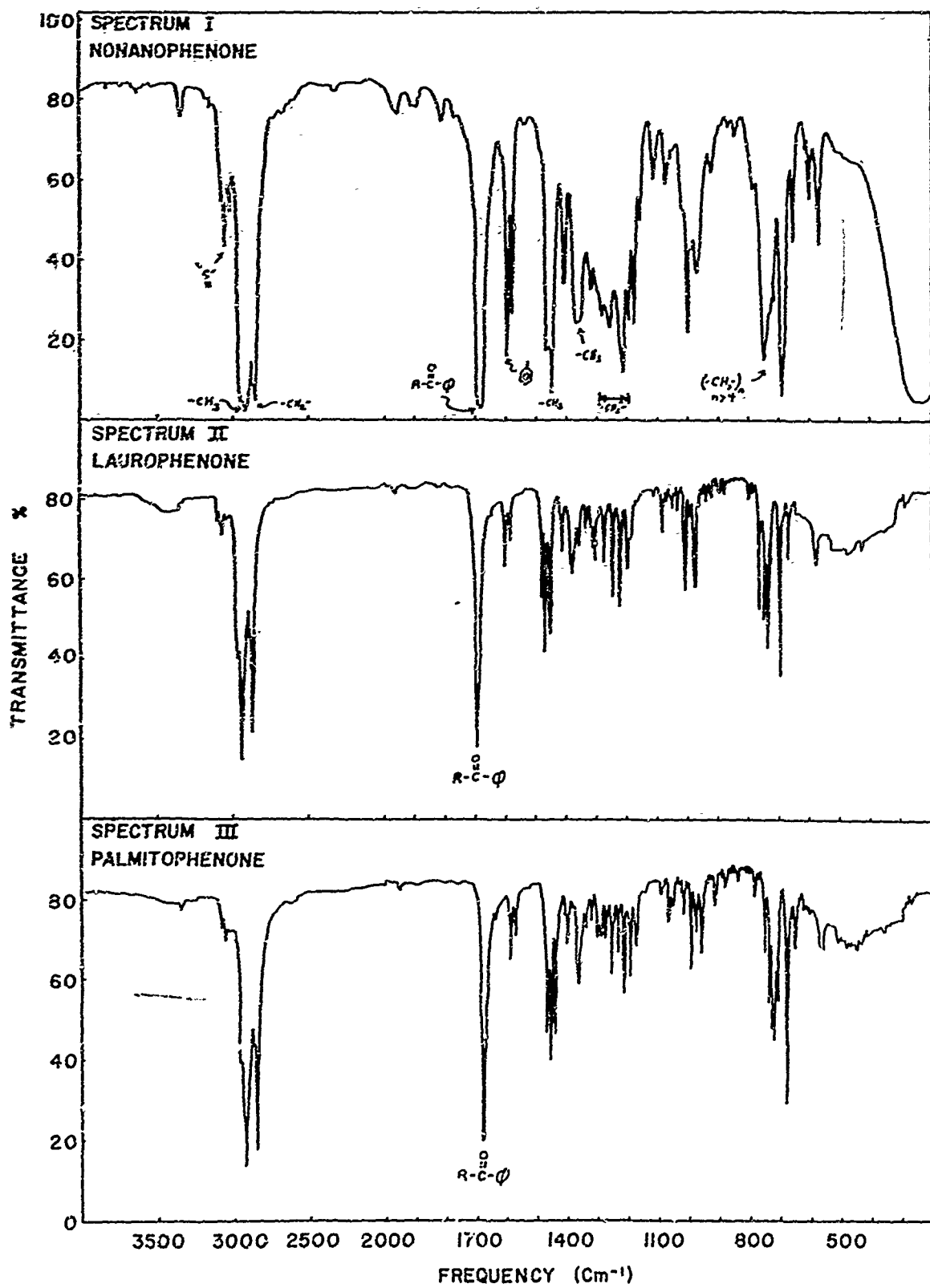
#### STOICHIOMETRY

| Reaction Product                 | $\text{RCHCHC}_6\text{H}_5$ (moles) | $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (moles) | THF (moles) |
|----------------------------------|-------------------------------------|--|-------------|
| Poly( $\beta$ -hexadecylstyrene) | $0.95 \times 10^{-2}$               | $0.93 \times 10^{-3}$                          | 1.4         |
| Poly( $\beta$ -decylstyrene)     | $2.09 \times 10^{-2}$               | $1.10 \times 10^{-3}$                          | 1.4         |
| Poly( $\beta$ -heptylstyrene)    | $3.37 \times 10^{-2}$               | $1.7 \times 10^{-3}$                           | 1.4         |

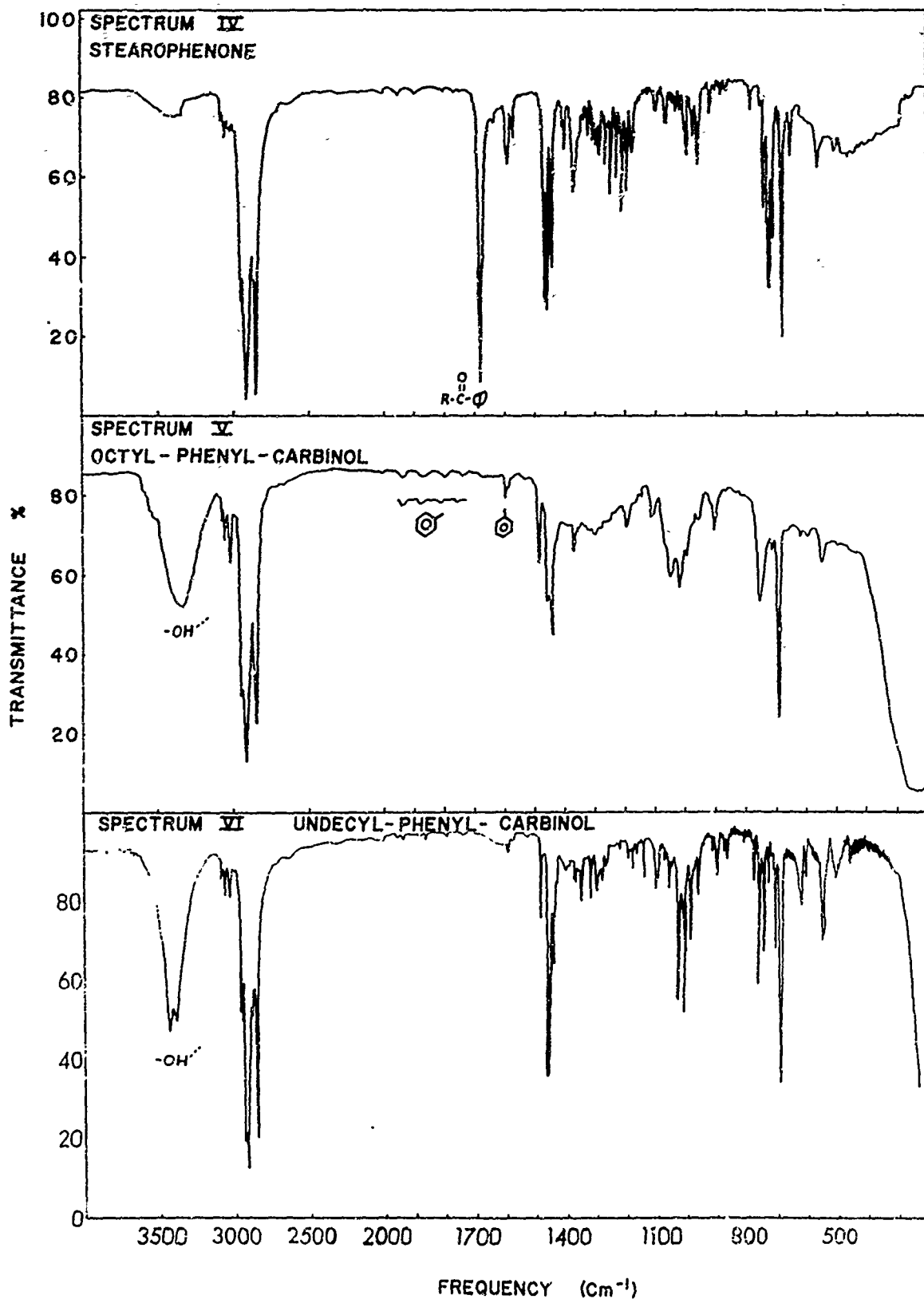
The reactions were conducted in a 100-milliliter cylindrical kettle fitted with a four-necked cap. Dow Corning Silicone lubricant was used in the ground-glass joints for the first two reactions listed above. Teflon tape was used as a sealant in the poly( $\beta$ -heptylstyrene) reaction. The reactions were conducted under a positive pressure of anhydrous argon that had been dried by a molecular sieve column. The reaction vessel was fitted with a gas inlet tube, a gas-equalizing addition funnel, an immersion thermometer, and a stirrer. Tetrahydrofuran (THF) was distilled from  $\text{LiAlH}_4$  into an erlenmeyer flask containing sodium chips and kept under an anhydrous argon atmosphere. A portion of the THF was added, along with a small amount of molecular sieve, to the addition funnel. The monomer was added to the THF in the funnel from a hypodermic syringe. The catalyst was prepared in a 50-milliliter flask fitted with a glass tube spout and glass inlet tube arranged so that, when the spout tube was lowered into the catalyst solution, gas pressure would transport it through the tube into the reaction flask. The monomer was added to the reaction flask followed by additional solvent to bring the volume to the correct level. The flask was then cooled to  $-20^\circ\text{C}$ . The catalyst was added and the reaction allowed to continue 24 hours for poly( $\beta$ -hexadecylstyrene), 24 hours for poly( $\beta$ -decylstyrene) and 5 hours for poly( $\beta$ -heptylstyrene) at  $-20^\circ\text{C}$ ,  $-45^\circ\text{C}$  and at  $-85^\circ\text{C}$ , respectively. The polymers were "killed" with water.

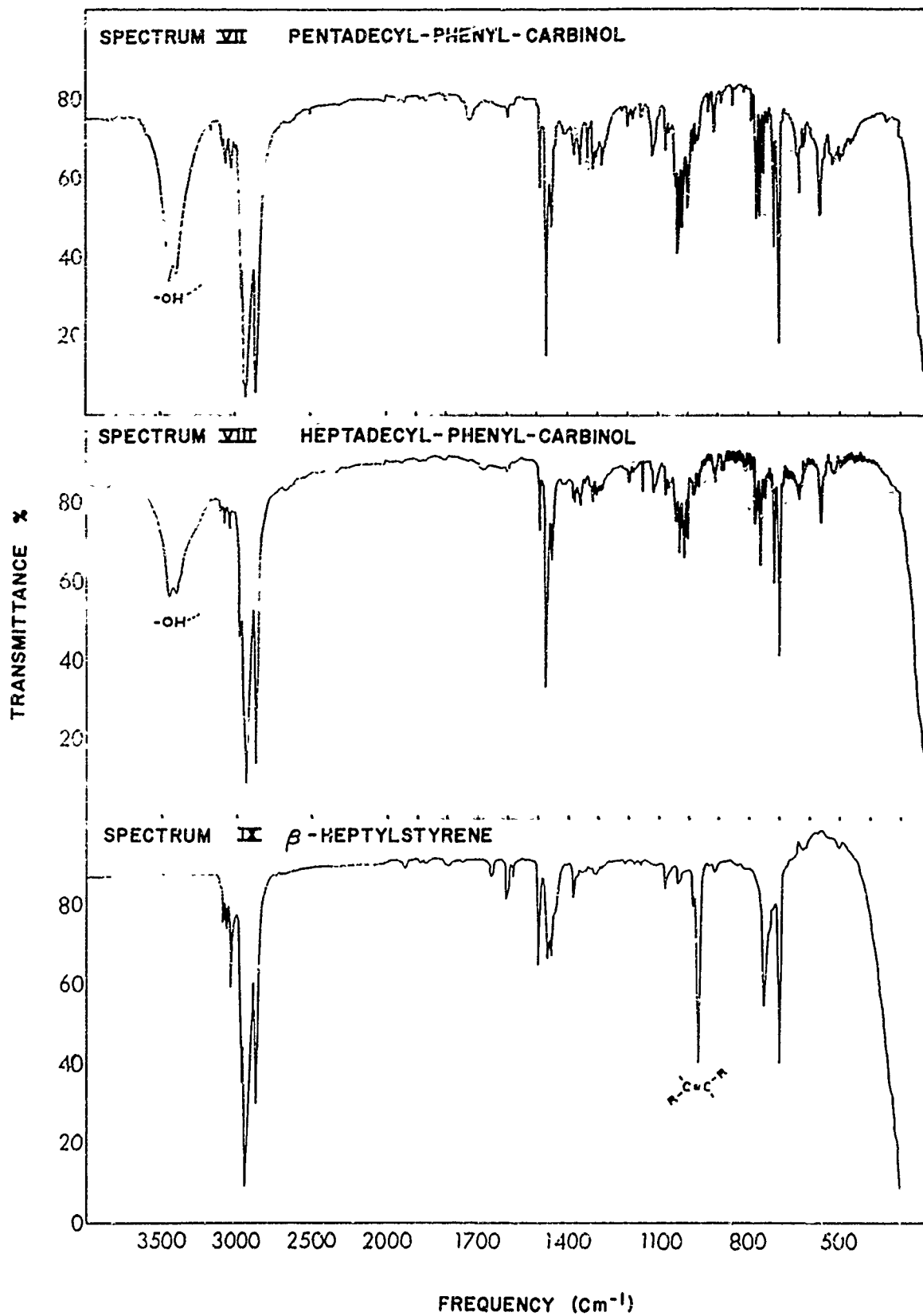
The THF was distilled from the residue and the residue dissolved in benzene. This solution was filtered and the benzene distilled from it. The residue was then distilled under high vacuum and the residue and distillate retained for analysis. The yields were 50 percent polymerization for poly( $\beta$ -hexadecylstyrene), zero percent for poly( $\beta$ -decylstyrene) and 10 percent for poly( $\beta$ -heptylstyrene)

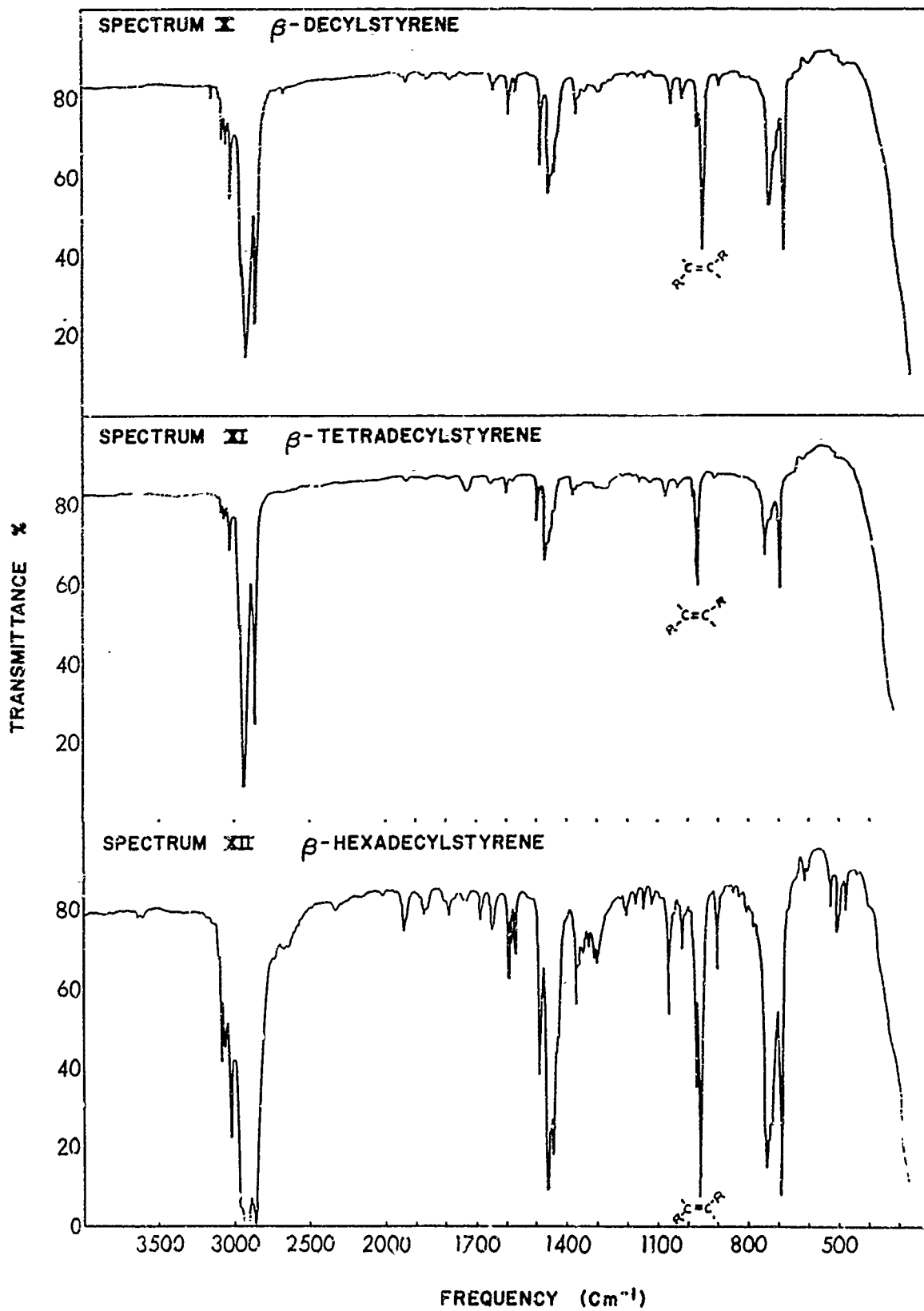
APPENDIX B  
INFRARED SPECTRA

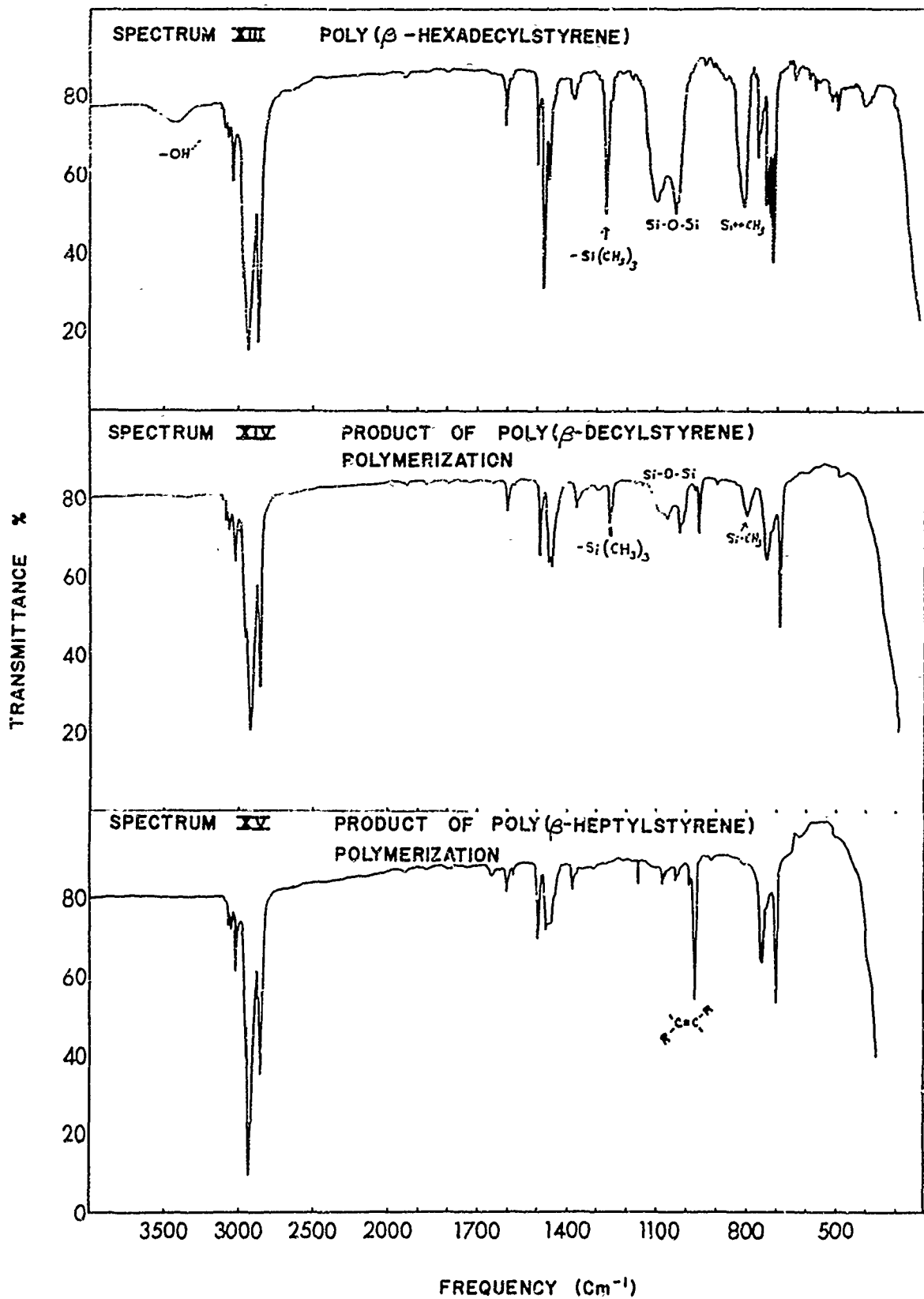


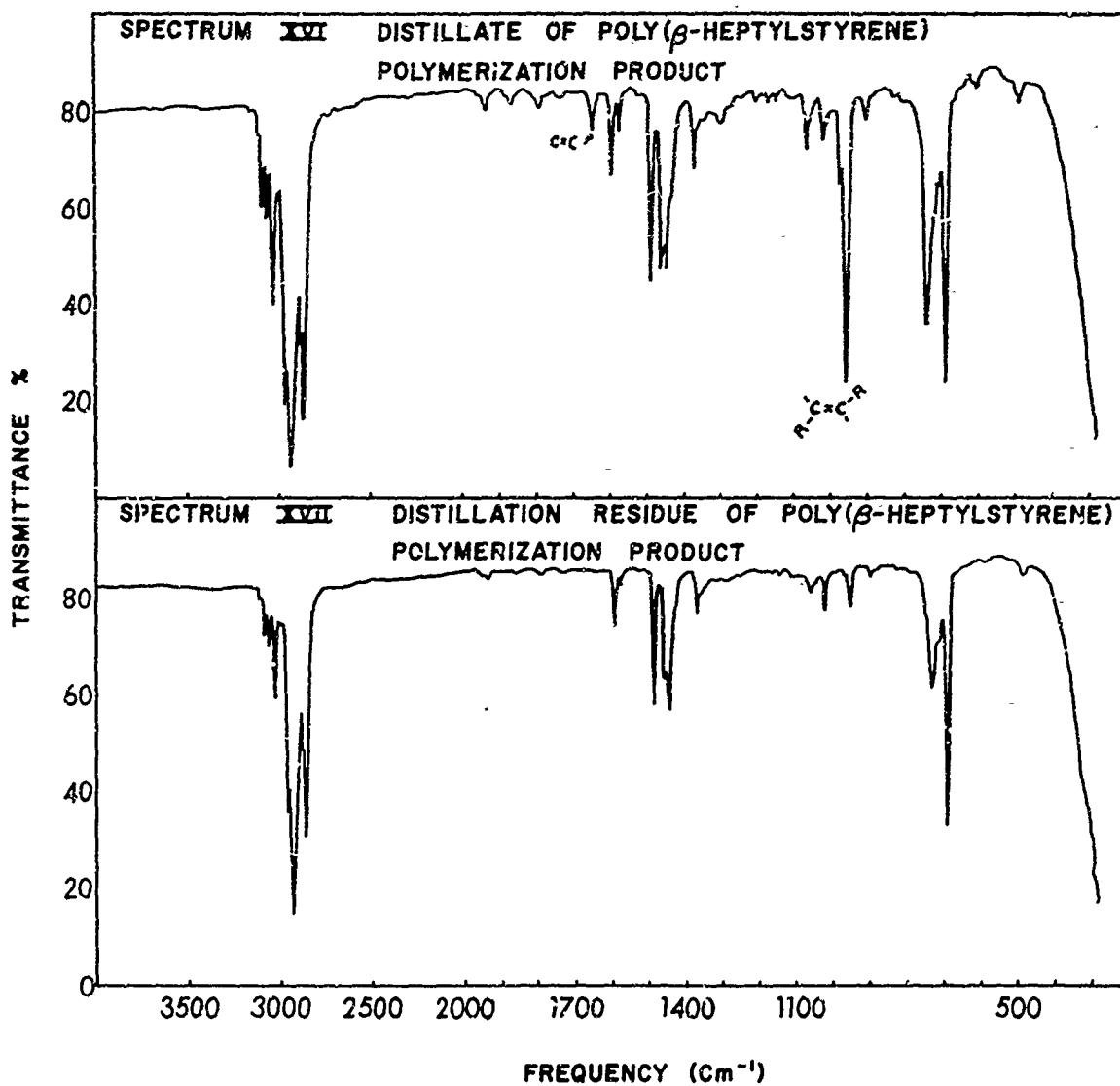












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| 13. ABSTRACT<br><br>>Work was continued on the synthesis of poly( $\beta$ -alkyl-p-styrene sulfonate) salt corrosion-inhibitors. A synthesis plan was followed which resulted in the synthesis of lauro-, palmito-, and stearophenone octyl-, undecyl-, pentadecyl-, and heptadecyl-phenol-carbinol; $\beta$ -heptyl-, $\beta$ -decyl-, $\beta$ -tetradecyl-, and $\beta$ -hexadecyl-styrene; and poly( $\beta$ -heptyl- and $\beta$ -hexadecyl-styrene). Emphasis placed on the improvement of synthesis and analytical procedures resulted in significant progress. Results obtained from three polymerization attempts were useful in the solution of a major contamination problem encountered previously, but these results did not contribute to the formation of higher molecular weight problems. (U) (Author) |   |  |

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