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## Isolation and Characterization of the Dimers Formed in the Free-Radical and Anionic Initiated Polymerization of Alpha-Methylstyrene

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ISOLATION AND CHARACTERIZATION OF THE DIMERS FORMED IN THE  
FREE-RADICAL AND ANIONIC INITIATED POLYMERIZATION OF  
ALPHA-METHYLSTYRENE

by

Kevin S. Bosman

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Chemistry

Western Michigan University  
Kalamazoo, Michigan  
August 1986

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Kevin S. Bosman, M.A.

Western Michigan University, 1986

Alpha-methylstyrene was polymerized near its ceiling temperature using two different initiators. First, sodium was used as an anionic initiator, primarily in an effort to provide an experimental link joining the work of S-L Ou with that of Kolobielski and Pines. The structure of the sodium initiated product was determined to be 1,3-diphenyl-1-methylcyclopentane, a dimer of  $\alpha$ -methylstyrene, thus providing the desired link. Second, tertiary-butylperoxide was used as a free-radical initiator under similar reaction conditions, and the product was compared with that from the anionic reaction.

The product of the free-radical initiated polymerization has an undetermined structure, although the data are indicative of a combination of  $\alpha$ -methylstyrene with the breakdown products of the initiator. Compared with the product of the sodium initiated reaction, as well as with the products of several other polymerizations reported in the literature, this product is not dimeric in nature. This is manifested in the mass spectrum, where this product has a unique major peak at 162 daltons. Other unexpected peaks are at 220, 205, and 194 daltons, again, major peaks unique to this product.

#### ACKNOWLEDGEMENTS

I would like to thank Dr. George G. Lowry for his direction, advice, and understanding through the course of this research. I would also like to thank Drs. Iffland, Howell, and Berndt for their aid in answering some of the questions encountered in the course of the work.

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Kevin S. Bosman

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## CHAPTER I

### INTRODUCTION

Polymers have been utilized by humanity throughout history, but it was not until 1839 that the science of polymer chemistry was born. In that year, Charles Goodyear (1) accidentally discovered that the addition of sulfur to rubber along with a little heat resulted in a marked improvement in the versatility and usefulness of rubber. Since that time, the discovery of various synthetic methods for the preparation of rubber and other polymers has led to many new products and applications.

In the course of the development of these syntheses, it has been observed that there are two generic types of polymerization stoichiometry. These two types of polymerization are called addition and condensation polymerization. The mechanism of condensation polymerization normally results in the generation of small, simple molecules such as water or hydrogen chloride as byproducts of the polymerization. Condensation polymerizations yield shorter polymer chains than do addition polymerizations, and generally require a longer time to go to completion. Addition polymerizations require the input of sufficient energy to weaken a  $\pi$ -bond system to the point where electrons may be either donated to another molecule, or accepted from another molecule. This may be facilitated by the direct application of energy as by irradiating with light, or

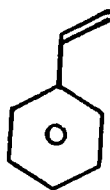
through the addition of an initiator or catalyst as an electron source or sink. This energy activates the molecule at specific sites, and as any of the active sites can attack at any inactive site, the chain grows very rapidly and tends to be composed of many more monomer units than that resulting from a condensation polymerization. Addition polymers tend to be more branched than condensation polymers, also as a result of the many active sites present in the polymerization process. Polymers resulting from the condensation of, for example, formaldehyde and phenol and those resulting from the addition of, e.g., styrene to itself are very versatile and important. The commercial value of phenolic resins or of polystyrene resins reside in their relative ease of manufacture, low cost, and chemical and thermal stability.

Alpha-methylstyrene (AMS) is very similar to styrene structurally (See Figure 1); but it is much more difficult to polymerize, and under many conditions all but impossible. AMS polymers, when made, are generally lower in molecular weight and lack the thermal stability characteristic of polystyrene. Often these AMS polymers have no commercial value as a result. Nonetheless, polymers and copolymers of AMS are commercially available, although the difficulty in polymerizing AMS makes it an ideal research tool for the exploration of the mechanisms of polymerization reactions. The comparison of AMS reactions to styrene reactions is not limited to an area of polymerization as evidenced by the recent literature (2,3).





$\alpha$ -Methylstyrene



Styrene

Figure 1. Comparison of  $\alpha$ -Methylstyrene and Styrene.

## CHAPTER II

### HISTORICAL BACKGROUND

#### The Early Workers

Although AMS is now known to polymerize with difficulty, the acquisition of that knowledge came through the many attempts that were made to polymerize the substance. Like many other addition polymers, AMS requires a catalyst or initiator to commence polymerization.

There are three types of initiators commonly used for chemical initiation of addition polymerization. Cationic polymerization proceeds through the generation of a carbocation on a monomer molecule that subsequently adds across the double bond in another monomer molecule. Anionic polymerization proceeds through the generation of a carbanion on a monomer molecule that subsequently acts as a nucleophile in opening up the double bond in another monomer molecule. Free-radical initiation is similar to anionic polymerization in that the free radical generated on a monomer molecule also acts as a nucleophile. This nucleophilic character migrates along the chain, as does the electrophilic center from cationic initiation, as the polymer chain increases in length.

The earliest workers often used several of these catalytic systems in their attempts to polymerize AMS, and the earliest work

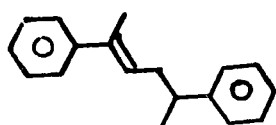
relevant to the present work appeared in 1929 (4). In that report, Staudinger and Breusch discussed several such techniques for the polymerization of AMS.

The initiators used in Staudinger and Breusch's work included various metal chlorides, "Florida-erde" (a bentonite clay), heat, and ultraviolet light. Their work yielded no high polymers, and the only substance to initiate polymer chains having more than three monomer units in length was  $\text{SnCl}_4$ . The major products found by Staudinger and Breusch were the dimers of AMS. They concluded that there were at least two dimeric structures formed, and that each structure had two stereoisomers, 1a, 1b, 2a, 2b. The cyclic structure, 2, proposed by Staudinger and Breusch had been proposed in 1902 by Klages in a study of the synthesis of AMS (5).

Klages prepared the dimer of AMS by two distinct procedures. One procedure was the Grignard reaction of benzylmethylketone with magnesium isopropylbenzene iodide, and the other involved heating 2-phenyl-2-propanol in the presence of 85%  $\text{H}_3\text{PO}_4$ . In both cases the dimer Klages reported was a solid melting at  $55-56^\circ \text{C}$ . Klages suggested that the structure of the dimer was either 1,2-dimethyl-1,2-diphenylcyclobutane, 2, or tetramethyldiphenylethane (2,3-dimethyl-2,3-diphenylbutane, 3). Klages was unable to conclusively establish either structure, but he did report a third structure as the byproduct of the synthesis of AMS from 2-phenyl-2-propanol. This structure, 2,5-diphenyl-2-hexene, 1, was the only structure reported by Tiffeneau (6) in 1907 after attempting to duplicate Klages' dimerizations.

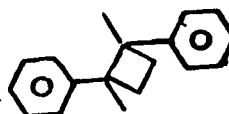
Staudinger and Breusch's (1929) work demonstrated that the dimer found by Klages most likely incorporated the cyclobutane structure; in so doing, they also showed that Klages' confusion about the dimeric structure was justified by observing that the cyclobutane ring was prone to open up under oxidative conditions. The reaction catalyzed by  $\text{SnCl}_4$  was the only one to yield appreciable amounts of the various oligomers, and all those oligomers were less than eight monomer units in length. These polymers incorporated the cyclobutane structure, and the dimer accounted for over 70% of the total yield. Only part of the dimer could be crystallized, and that part was assumed to possess the trans-cyclobutane structure, 2b. The crystalline portion had a very sharp melting point about  $80^\circ$  higher than the amorphous remainder, and was 1.1 times as dense. The crystalline portion was also shown to be saturated through its resistance to bromine attack. The amorphous portion of the dimer appeared to contain both the cis-cyclobutane, 2a, structure and the structure Tiffeneau favored, the unsaturated 2,5-diphenyl-2-hexene, 1.

Two years later, in 1931, Bergmann and his coworkers (7) duplicated the work of Klages (5) and of Staudinger and Breusch (4). The work of Bergmann's group led to the proposal of two additional dimeric structures, 4 and 5. The structure they proposed for the unsaturated dimer, 5, is slightly different from that proposed by Tiffeneau, 1, and they also suggested a mechanism for its formation.



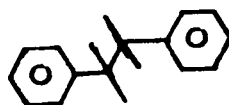
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1

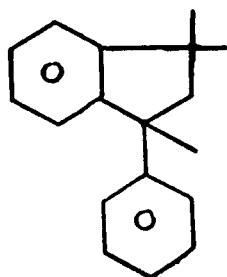


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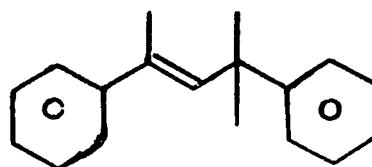
2



3



4



5

Bergmann's group used  $\text{AlCl}_3$  as a polymerization initiator for AMS for the first time, but they found that the results were almost indistinguishable from those obtained when using  $\text{SnCl}_4$ . As an alternative to the cyclobutane structure, they suggested that the dimer possessed an indane structure, 4. As proof of the dimer's structure, they developed two direct, unambiguous syntheses leading to the indane structure.

While running the metal chloride initiated polymerization at room temperature, Bergmann's group (7) found that the yields of dimers approached 90% of the initial AMS charge. When they ran polymerizations using sodium metal as the initiator, the total yield and that of the dimer in particular, was much less. The dimers that were observed after sodium initiation were generally unsaturated in structure, but two of them, while chemically similar, remained undetermined. Further efforts led to the proposal of a mechanism for the formation of the unsaturated dimer via the reaction of a sodium salt of AMS with a corresponding acid. It was also observed that upon standing over  $\text{AlCl}_3$  in benzene for two days, the unsaturated dimer was converted to the saturated dimer in 20% yield.

The work of the early investigators cited above gave somewhat different results depending upon the initiator used. Free-radical initiated polymerization was all but ignored, but studies devoted exclusively to either anionic or cationic initiation of the polymerization of AMS appeared in the middle and later 1950s. Toward the end of the 50s, researchers could routinely use sophisticated

instrumental techniques for structure elucidation in combination with the more traditional physical and chemical methods.

#### Cationic Dimerization of AMS

In 1956, Vander Zanden and Rix discussed some dimers of AMS (8,9). They attempted to repeat Bergmann's et al. work, and although they were able to rule out the cyclobutane structure, they were unable to repeat and confirm the work leading to Bergmann's proposed indane structure, 4. Additionally these researchers worked with a variety of substituted  $\alpha$ -methylstyrenes, and  $\alpha$ -methylstyrene (BMS) as well as AMS itself.

Vander Zanden and Rix's results indicated that electron delocalization effects that they presented as a series of resonance structures, could enhance the reactivity of AMS compared to other substituted styrenes. That conclusion is also supported by the work of Seymour and Wolfstirn dealing exclusively with the effects of substituents upon reaction rates for a variety of styrene and AMS species (10,11). The reaction mechanism is illustrated in Figure 2. BMS gave Vander Zanden and Rix dimerization products that were very similar to those obtained from AMS, although the reaction times were much longer. To account for these results, it was proposed that BMS rearranged to AMS under common reaction conditions, and subsequently dimerized via the same reaction mechanism.

This mechanism suggests that the electrons in the pendant  $\pi$ -bond system of a monomer molecule are somewhat delocalized, with

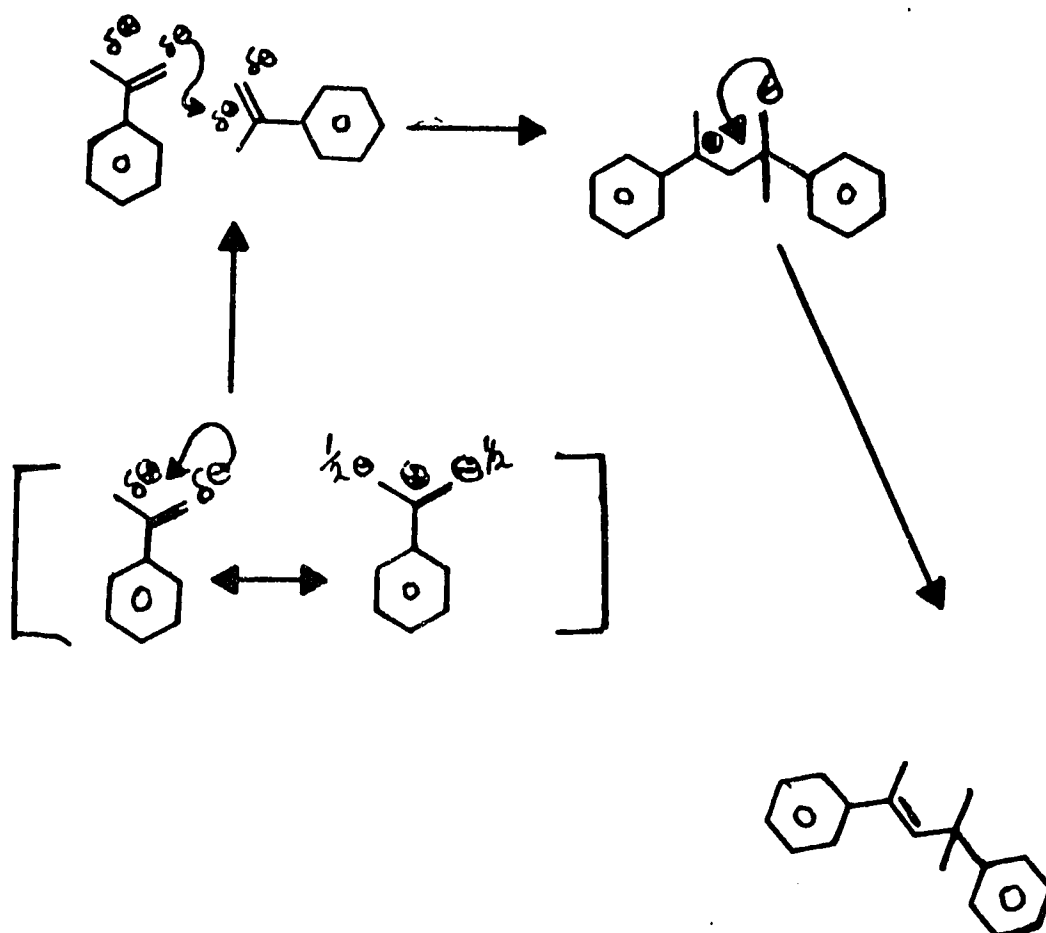


Figure 2. VandenZanden and Rix's Proposal for Dimerization Mechanism(8,9).



an increased negative charge at the  $\beta$  carbon, and a corresponding positive charge at the  $\alpha$  carbon. The dimer is then formed via the addition of the  $\beta$  carbon to the  $\alpha$  carbon on another monomer molecule. In an ionic system, the charge is presumed to be full, and thus, this mechanism might apply to a variety of initiation conditions and polymerization reactions with very little alteration. In support of this mechanism, it should be mentioned that the relative stability of tertiary carbocations compared to secondary carbocations is well established, rearrangements of secondary to tertiary carbocations are not unknown, and the probability of stabilization through electron delocalization is high.

Concurrently with the work of Vander Zanden and Rix, the use of aluminosilicate catalysts was being explored in the Soviet Union (12). In the Soviet work, three different dimeric structures were reported. The mechanisms proposed for the formation of these dimers are primarily carbocationic in nature (See Figure 3), and as such are very similar to the mechanism proposed by Vander Zanden and Rix. The proposed mechanisms are different in that rearrangement of the intermediate may be a requirement, and that the monomer undergoes rearrangement prior to, rather than during, the reaction (Figure 3).

Support for these mechanisms is derived from the comparison of various dimers of AMS and BMS, including those resulting from a mixture of the two monomers. A new dimeric structure, a saturated hexane, was reported in addition to the 2,5-diphenyl-2-hexene, 1,

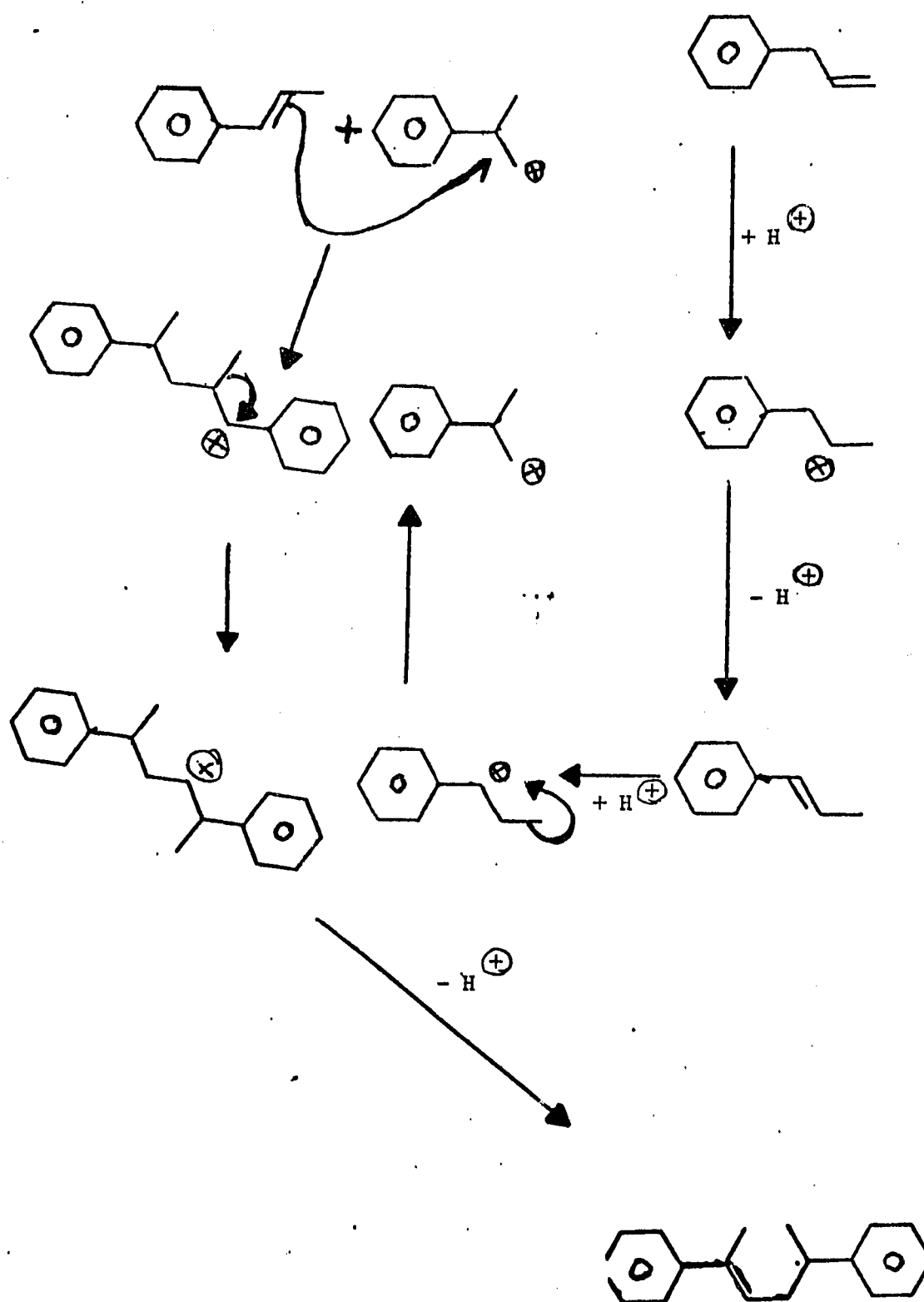


Figure 3. Scheme for Formation of 2,5-diphenyl-2-hexene After Topchieva et al. (12).

previously reported. A third dimer, sharing the physical characteristics of the hexene structure was also reported, but it possessed a grossly different infrared (IR) spectrum. The cyclobutane structure, 2, was reported as well, and along with the hexane structure, rearrangement of the intermediate is required in the reaction mechanism in order to account for its presence.

In 1975, Mehta (13) was working exclusively with the dimers of AMS. In his procedure, AMS was dissolved in  $\text{CCl}_4$  and the reactions were initiated by  $\text{SnCl}_4$ . Mehta observed and tentatively identified four different dimeric structures. The cyclic and three linear dimeric structures Mehta reported have all been described previously, 1a, 1b, 4, 5 (3,6,11).

Since Mehta was dealing exclusively with the dimers of AMS, he had to separate the dimers from the other oligomers formed under the reaction conditions. Mehta reported using analytical size exclusion chromatography, and subsequently preparative scale, column, size exclusion chromatography for the separation of the dimers from monomer and trimers. Size exclusion chromatography (SEC) was chosen to separate the reaction mixture because the only significant difference between the oligomeric species is that of size. The differences in chemical functionality between the oligomers are so slight as to make "traditional" chromatographic techniques prohibitively inefficient. Distillations might be possible, but the nature of AMS and its homologues is such that further polymerization or possible depolymerization might occur, thus having a deleterious

effect upon an attempted purification.

#### Anionic Dimerizations of AMS

In 1957, Kolobielski and Pines (14) initiated polymerization of AMS with sodium metal. As a result, they reported yet another dimeric structure. This structure, a 1,3-diphenyl-1-methylcyclopentane,6, was confirmed through a direct unambiguous synthesis beginning with the Grignard product of 3-phenylcyclopentanone and methylmagnesium bromide followed by reaction with potassium bisulfate to eliminate water and the addition of benzene catalyzed by hydrogen fluoride. This gave the desired 1,3-diphenyl-1-methylcyclopentane in approximately 17% yield (See Figure 4). Kolobielski and Pines reported the physical characteristics of this dimer, such as refractive index and boiling point, but neglected to detail the results of instrumental analysis.

Richards and Williams initiated the polymerization of AMS using an alloy of sodium and potassium (15). While their primary interest was in the study of the tetramers, they found that the bulk of the product recovered from the reaction mixture was dimer, about eight times more than the tetramer by weight. They used preparative scale thin layer chromatography to purify their products and found that their dimer possessed the 2,5-dimethyl-2-hexene structure,1.

S-L Ou was working in the same laboratory as B. Mehta (13), but was exploring the anionic polymerization system as opposed to the cationic system Mehta investigated (16). Initially, Ou's intention

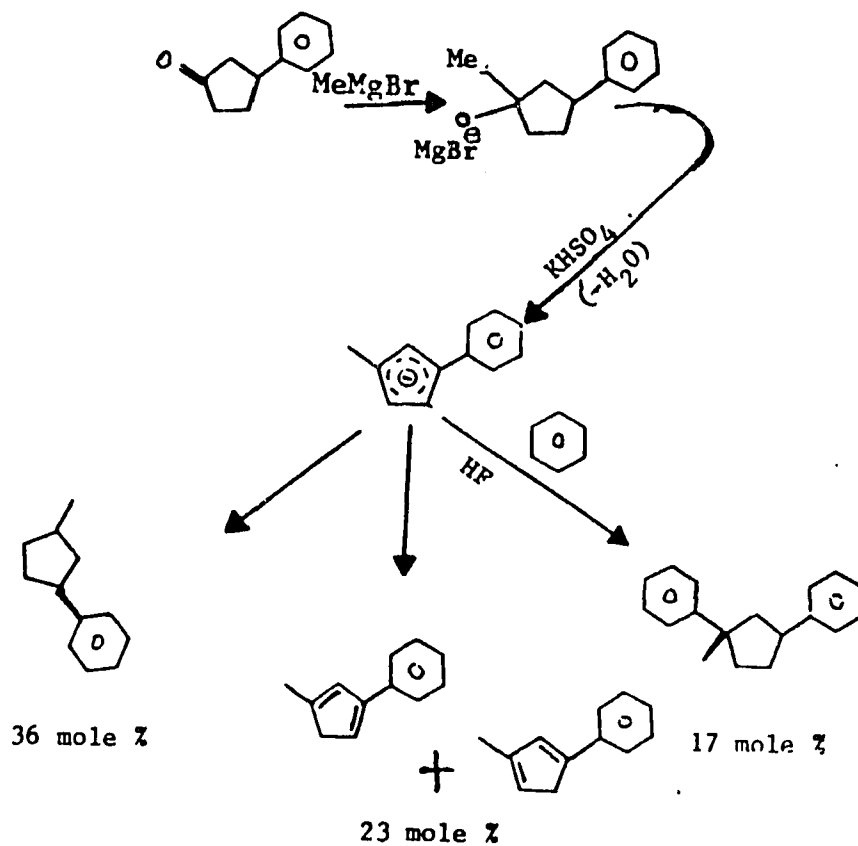


Figure 4. Kolobielski and Pines Unambiguous Synthesis of 1,3-diphenyl-1-methylcyclopentane (14).

was to examine the equilibria among the various oligomers of AMS. As mentioned above, AMS is an addition polymer. Addition polymers grow rapidly as active sites are formed (either an excess of electrons, unpaired electrons, or an electron deficiency) and subsequently attack unactivated molecules. The initial active site is deactivated, and a new active site is formed, with a net growth in the size of the molecule and migration of the active site along the growing molecular chain (see Figure 5). On occasion, the propagation reaction can be made to reverse itself, that is depropagation can be induced. Under certain conditions, equilibrium can be established between the rates of propagation and depropagation. The conditions necessary to establish the series of such equilibria for AMS are easily accommodated in the laboratory. Above the ceiling temperature for AMS, it does not readily form high polymers, and thus the number of equilibria is relatively small. Ou expected perhaps eight equilibria to be established for AMS, while the use of styrene under comparable conditions would have probably required the study of several thousand such equilibria.

Ou's results led him to conclude that AMS catalyzed by sodium did fit into the category of reversible equilibrium polymerizations. The rate of depropagation was difficult to manipulate, and based upon the work of Szwarc (17), Ou expected that the AMS oligomer mixture would be "alive" after the initial reaction had gone to completion. Ou found that the addition of excess monomer after the reaction had gone to completion caused the reaction to resume and

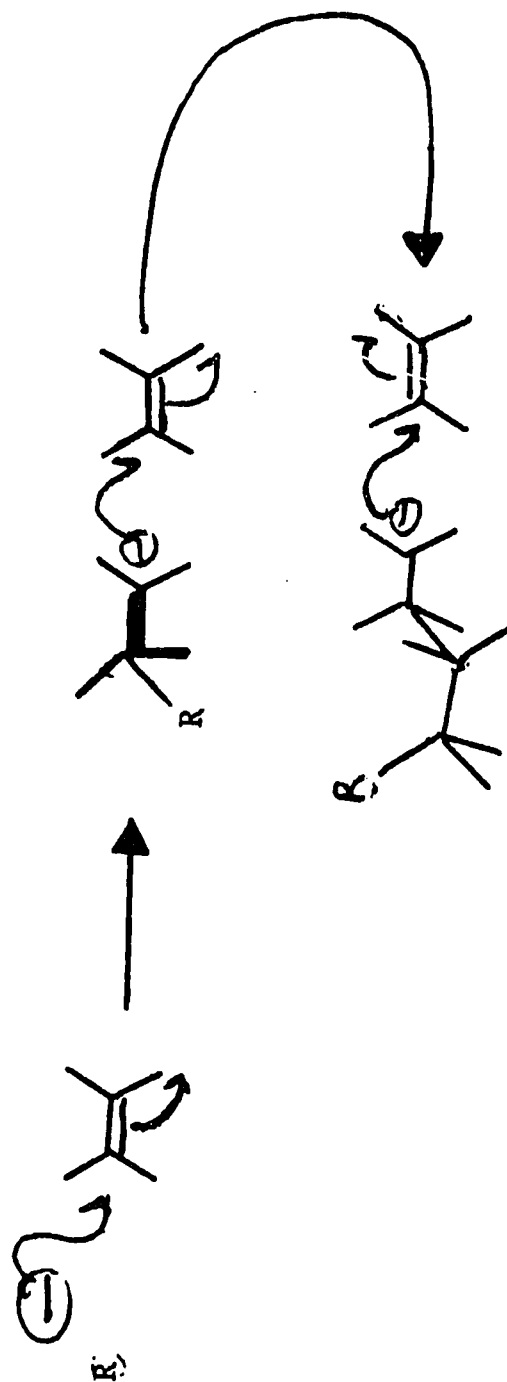


Figure 5. Propagation of an Addition Polymerization

further polymerization to occur, thus the results were indicative of AMS forming a living polymer. The results were also suggestive of a chain transfer mechanism participating in the course of the reaction.

Ou found no oligomers larger than the hexamer, but found evidence suggesting two structures for each oligomer. By using size exclusion chromatography under high performance analytical conditions, Ou was able to resolve the pairs (16). The dominant structures were cyclic in character, and the minor structures linear. For the dimer, these were the 2,5-diphenylhexane reported previously (11,12,14), and the 1-methyl-1,3-diphenylcyclopentane also reported previously (14). The cyclopentane structure supported the chain-transfer mechanism in that if the active sites migrate to another location within the polymer chain, or if those sites "jump" from chain without resulting in some sort of polymer growth (i.e. change in chain length, or formation of a branch chain); cyclic end groups consisting of five to seven carbon atoms are often formed. These end groups are believed to form as the polymer chain writhes about. The size of end group is due to the ease of close approach of the carbon atoms five to seven units from the active sites to those active sites and the steric stability of the cyclic structure that results (See Figure 6). While not determined, the stability of the cyclic structure and its expected reluctance to dissociate into two monomer molecules is likely to have contributed to a slower rate of depropagation than would be expected for a linear dimer.



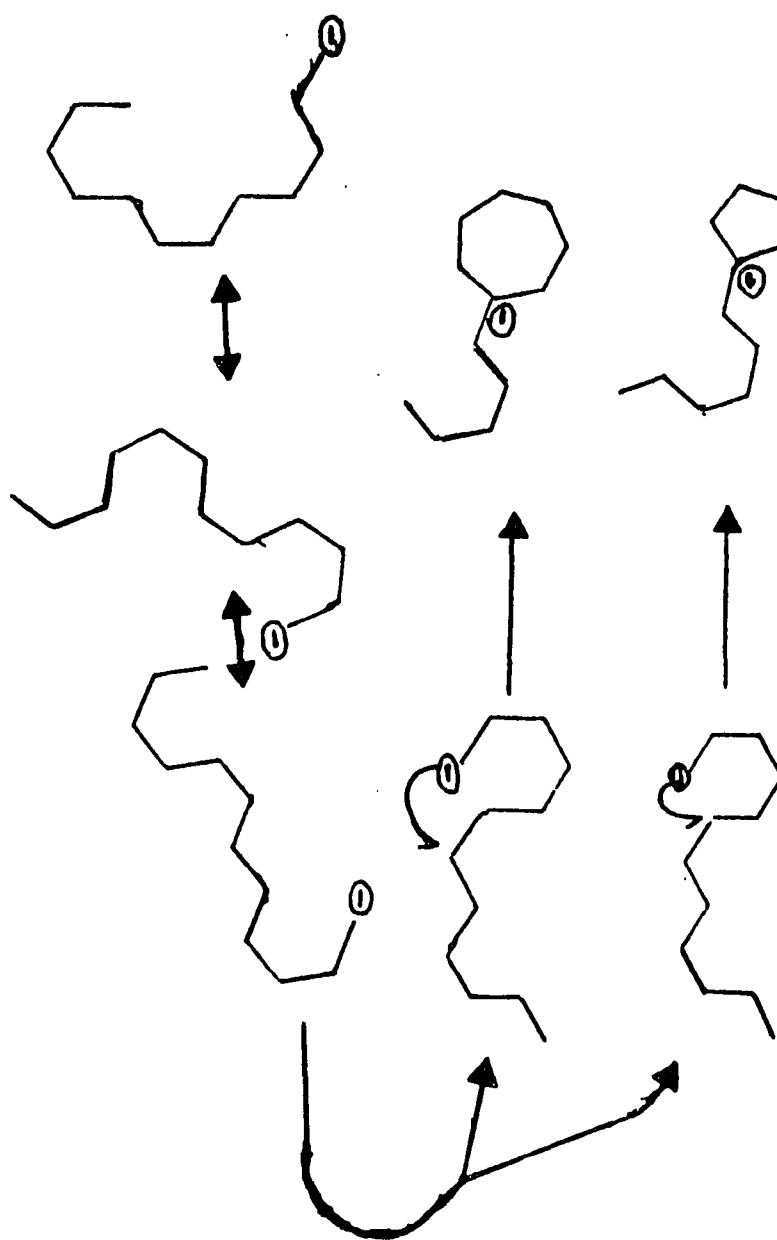


Figure 6. Formation of Cyclic Endgroups.

Ou's selection of the cyclopentane structure was based on several factors. Most prominently, nuclear magnetic resonance spectroscopy (NMR) showed a single isolated peak indicative of an methyl group with no hydrogens on adjacent carbon atoms. All of Ou's results were indicative of a cyclic structure, but the NMR results combined with the report of Kolobielski and Pines of the 1-methyl-1,3-diphenylcyclopentane structure caused him to make the specific choice. Although Kolobielski and Pines ran their reaction under similar but somewhat different conditions, Ou found that by making some slight adaptations, the mechanism they proposed would also fit his reaction conditions and structural proposal (see Figure 7).

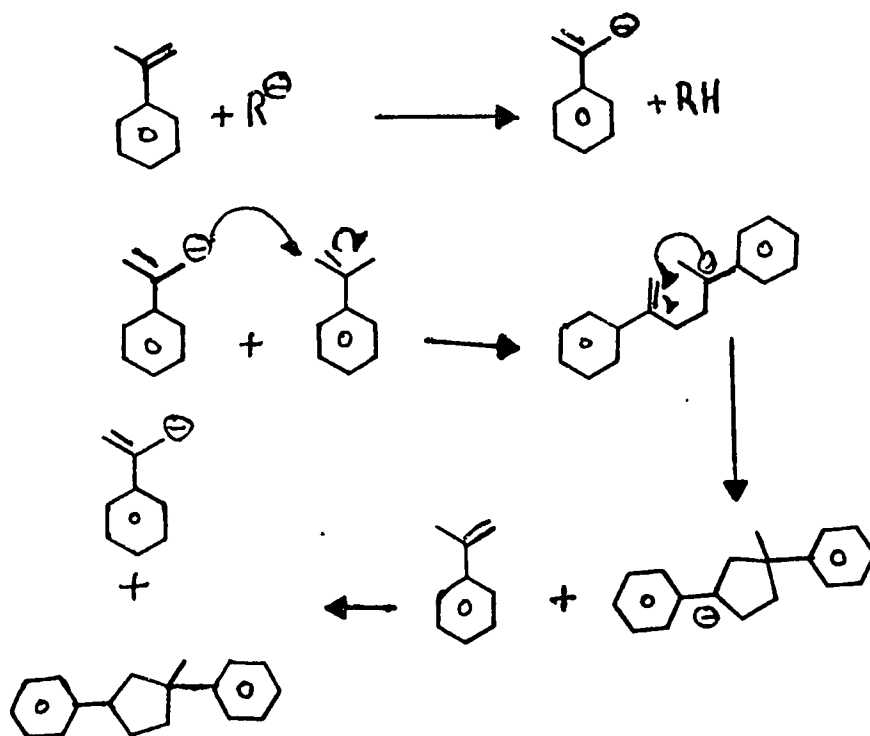


Figure 7. Mechanism for Formation of 1,3-diphenyl-1-methylcyclopentane with Anionic Initiation.

## CHAPTER III

### OBJECTIVES OF THE PRESENT STUDY

This research had two distinct objectives and they were:

1. To independently establish that the dimers found in anionic dimerization by Ou (16) and by Kolobielski and Pines (14) were identical and of the 1-methyl-1,3-diphenylcyclopentane structure; and
2. To study the structures of the dimer(s) formed in the free-radical initiated polymerization of AMS at or above its ceiling temperature.

#### Anionic Dimerization

The structure reported by both Ou and Kolobielski and Pines was the result of similar, but not identical syntheses. While each report complemented the other, neither one provided sufficient evidence to link it to the other. Thus, one goal of this work was to provide that link. Since Kolobielski and Pines confirmed their structure definitively, it was decided to repeat their polymerization and compare the spectral results with those of Ou.

#### Free-Radical Initiated Dimerization

The attempted free-radical initiated polymerization of AMS with

t-butylperoxide has not been reported anywhere in the literature, particularly in regards to structural studies. Given the wide variety of dimeric structures reported from other initiation mechanisms, it was decided that this technique should be attempted as another goal of this work. It was decided to approximate as closely as possible, save the nature of the reactive species, the conditions used for the anionic polymerization in recognition of the superficial similarity between the two procedures.

## CHAPTER IV

### EXPERIMENTAL PROCEDURES

The AMS used in this work was commercial grade monomer obtained from The Dow Chemical Company. As the monomer had been in storage for some time, a distillation was performed to ensure the purity of the monomer, and the distillate was subsequently refrigerated until it was needed.

The distillation utilized an eleven-plate glass bubble and cap column placed between a one liter round bottom flask and the condenser head as illustrated in Figure 8. This apparatus was charged with about 900 mL of AMS, and had a small lump of sodium metal ( 2g) added as an ion, active hydrogen, and water scavenger as well as a reducing agent.

The distillation system was heated to the reflux temperature of 157°C and maintained there for approximately 48 hours. The distillate was then collected, with the first 50 mL of distillate and the approximately 50 mL of residue being discarded. The 800 mL recovered from the distillation was stored in a refrigerator. A second batch of AMS was then distilled, with part of the distillate being used immediately and the remainder joining the first batch in the refrigerator awaiting subsequent polymerization.

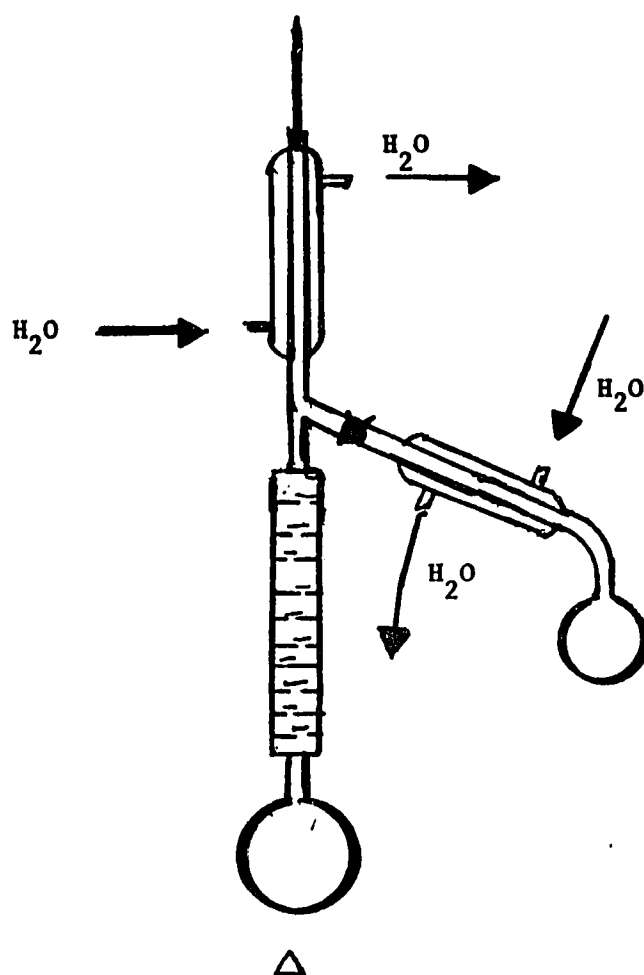


Figure 8. Eleven-Plate Bubble and Cap Distillation Apparatus.

### Anionic Initiated Polymerization

Purified AMS (121 g, 1.025 mol) and sodium metal (4.13 g, 0.180 mol) were placed in a 300 mL three neck round bottom flask containing a teflon coated stirring bar and fitted with a reflux condenser as illustrated in Figure 9.

Upon heating, a reddish solution was formed that darkened as the reaction proceeded. The reaction temperature stabilized at 130-131°C and was maintained at that temperature for six hours. The resulting mixture was then allowed to cool with stirring for a day.

Pesticide grade pentane was added to the cooled reaction mixture and allowed to mix over night. Celite filter aid was added to the mixture and an attempt was made to filter the resulting slurry by applying vacuum to a buchner funnel and flask. As the slurry did not filter efficiently, the solid was allowed to settle and the mother liquor decanted onto another buchner filter apparatus. The second filtration yielded a brownish-black filtercake that included metallic sodium, and a dark orange liquid. Finally, the filtercake was washed with two 25 mL portions of pentane.

The filtrate was distilled under 15 torr of vacuum, and the fraction boiling between 130°C and 160°C was collected for a subsequent distillation. For the second distillation, the pressure was reduced still further, to 2 torr, and the fraction that boiled between 130°C and 140°C was collected and assumed to be the desired product based on Kolobielski and Pines (14).

The 7.41 g of distillate recovered from the double distillation

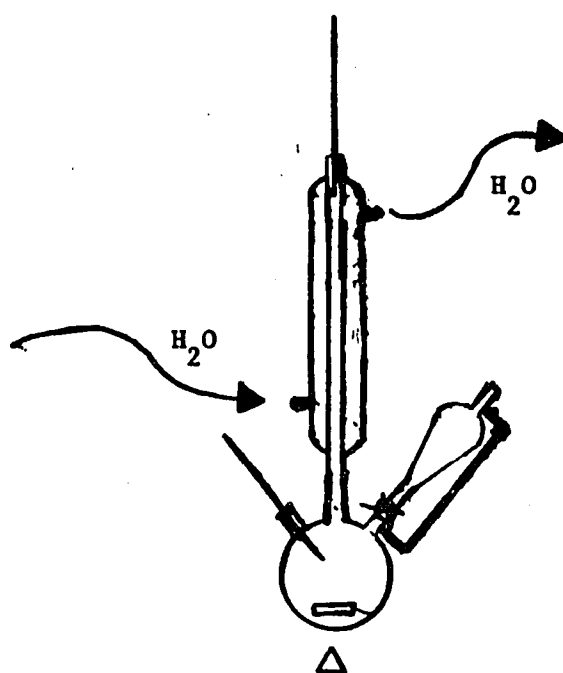


Figure 9. Reaction Apparatus.



was tested for purity by thin layer chromatography (TLC). The TLC used commercially available plastic backed silica gel sheets impregnated with a fluorescent indicator (Silica gel F-254, Merck) and pesticide grade pentane was used as eluent.

The TLC results indicated that the dimer was relatively pure, so preliminary spectral data were obtained for the sample. The sample was further purified by preparative size exclusion chromatography as described following the next heading. Spectra were obtained after the chromatographic purification, and were compared to those obtained prior to that step to ensure that no change in the dimer had occurred.

#### Free Radical Dimerization

To 118 g (1.00 mol) of purified AMS was added 7.3 g (0.05 mol) of  $t\text{-BuO}_2$ . This was refluxed for six hours in the apparatus illustrated in Figure 9 and described above. Then an additional 4.0 g (0.028 mol)  $t\text{-BuO}_2$  was added and the reflux continued. Twenty-four hours after the start of the reflux, a final 4.0 g (0.028 mol)  $t\text{-BuO}_2$  was charged to the system and the reflux continued for twenty-four hours more. The reaction mixture was then allowed to cool as described above. Approximately 100 mL of reagent grade pentane was added to the cooled reaction mixture and mixed over night. After the pentane addition, 50 mL of distilled water was added to the system to quench the reaction. By that it is meant that the water would be expected to cool and dilute the reaction

mixture and therefore effectively eliminate the possibility of the reaction recommencing.

The quenched reaction mixture was processed with the same double distillation procedure as the sodium initiated material was. After the distillation, suspected final product was tested by TLC as before, and passed through the preparative SEC column. TLC seemed to indicate that the product was impure relative to the material obtained from the sodium initiated procedure, but repeated attempts to purify this product by preparative size exclusion and analytical high performance reverse phase chromatography proved unsatisfactory. To eliminate the possibility of contamination by water or alcohol, a 1 mL sample of product was treated with  $\text{LiAlH}_4$ . The  $\text{LiAlH}_4$  was added stepwise to the product, the sample was shaken vigorously until cessation of effervescence, and an IR spectrum taken after each step. After about 0.3 g of  $\text{LiAlH}_4$  had been added to the sample, no further effervescence was observed. There was also no change observed in either the TLC or the IR spectrum done at this time. A second sample of monomer was polymerized, with  $\text{CaSO}_4$  added to the double distillation as a drying agent, but no improvement in the apparent purity was observed.

#### Size Exclusion Chromatography

About one quarter of the raw dimer produced by each of the two polymerization techniques was introduced onto a 5 cm x 50 cm glass column packed with silicar<sup>™</sup> cc-7 200-300 mesh (Mallinkrodt)(16). The

column packing was added to analytical grade tetrahydrofuran (THF) (Mallinkrodt) and allowed to swell up over two days. The swollen packing material was then slurry packed into the column. The eluting solvent was more of the same THF. An automatic fraction collector was used to take 15 mL fractions of the eluent stream as it came off the gravity fed column. The experimental apparatus illustrated in Figure 10.

Thin layer chromatography was used to determine which of the fractions contained products by observing which ones gave dark spots when observed under short wavelength ultraviolet light. The fractions thus selected were then combined and a second set of spectra obtained from them. These recombined fractions were also tested for purity by repeating the TLC procedure described previously.

### Instrumental Analysis

#### Infrared Spectroscopy (IR)

Samples were prepared neat on NaCl plates and analyzed with a Beckman Acculab 8 infrared spectrophotometer. Figure 11 depicts the IR spectra of the sodium initiated product, while Figure 12 is that of the free-radical initiated product. The a and b versions of the spectra are before and after the size exclusion chromatography respectively in both figures.

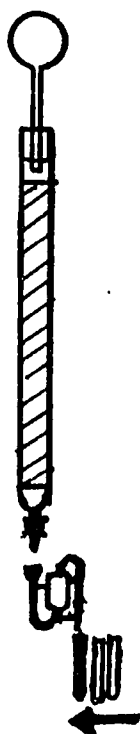


Figure 1Q. Size Exclusion Column Set-up.

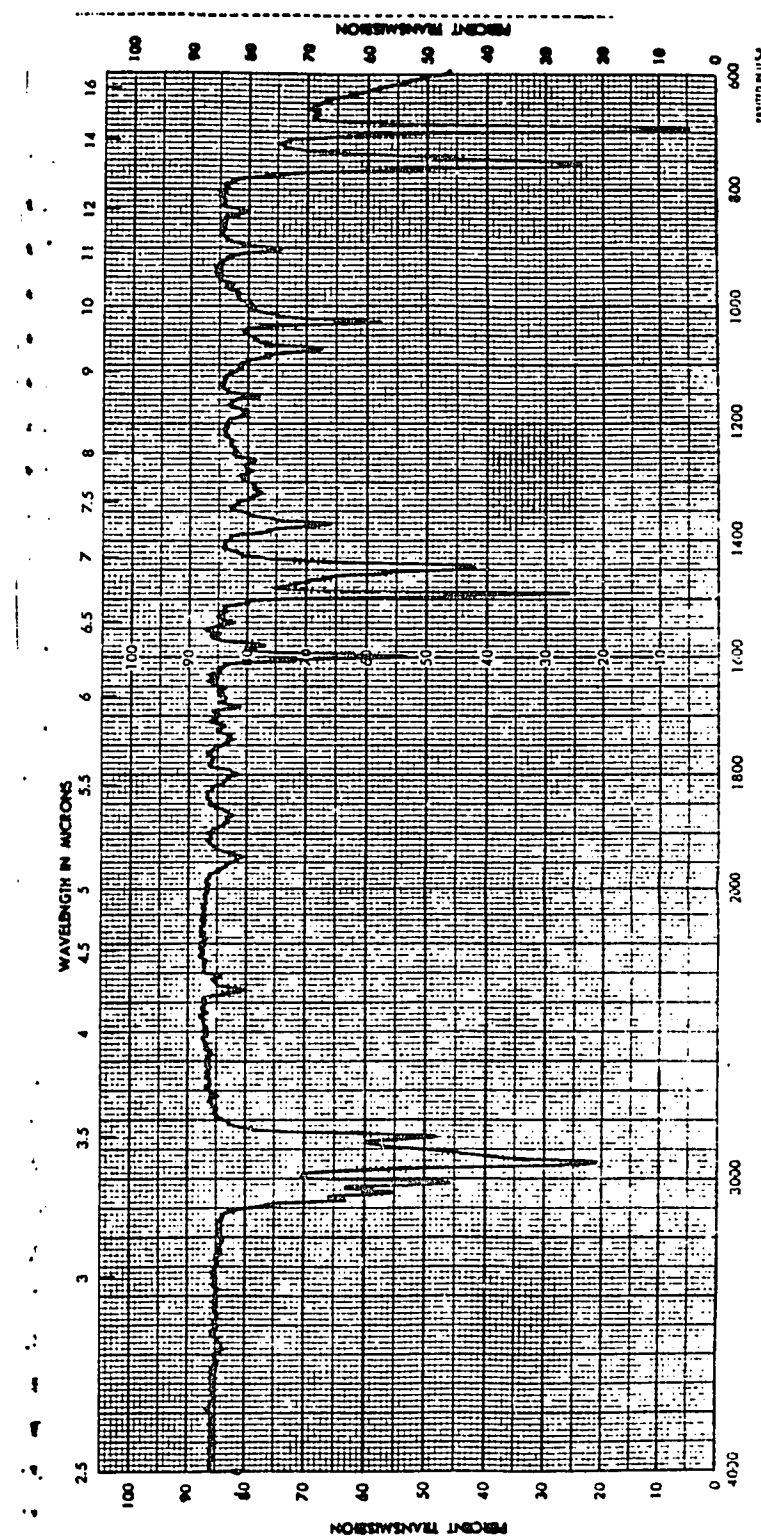


Figure 11a. Initial IR Spectrum of Na Initiated Product.

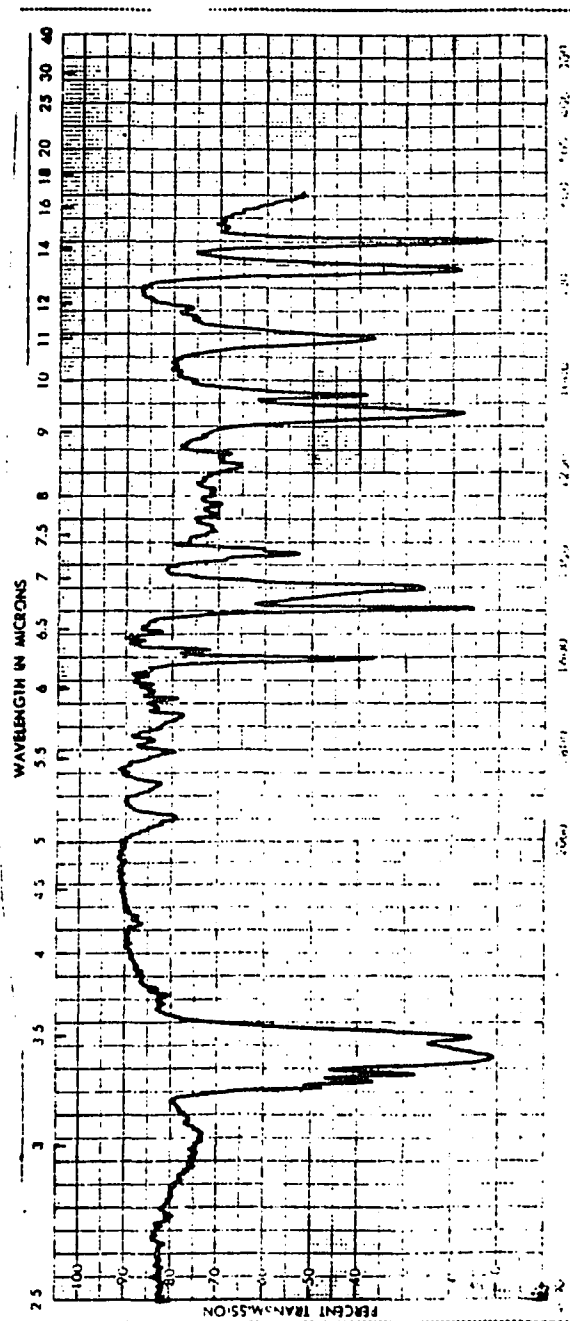


Figure 11b. Final IR Spectrum of Na Initiated Product.

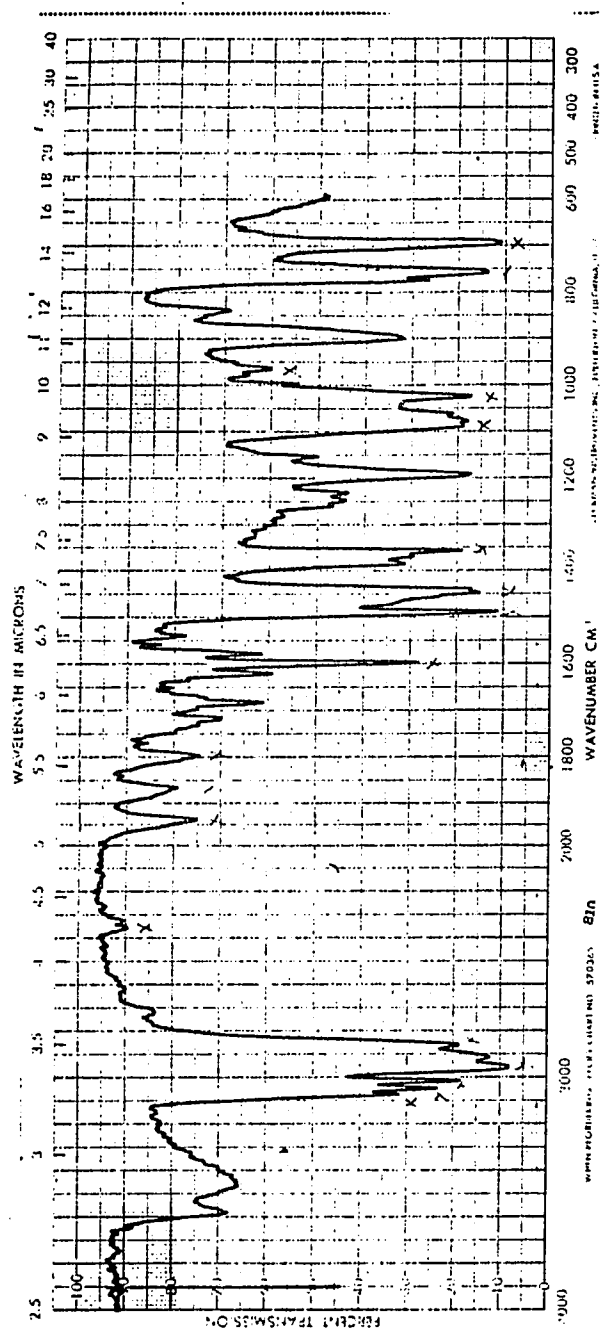


Figure 12a. Free Radical Product Prior to Column Run.

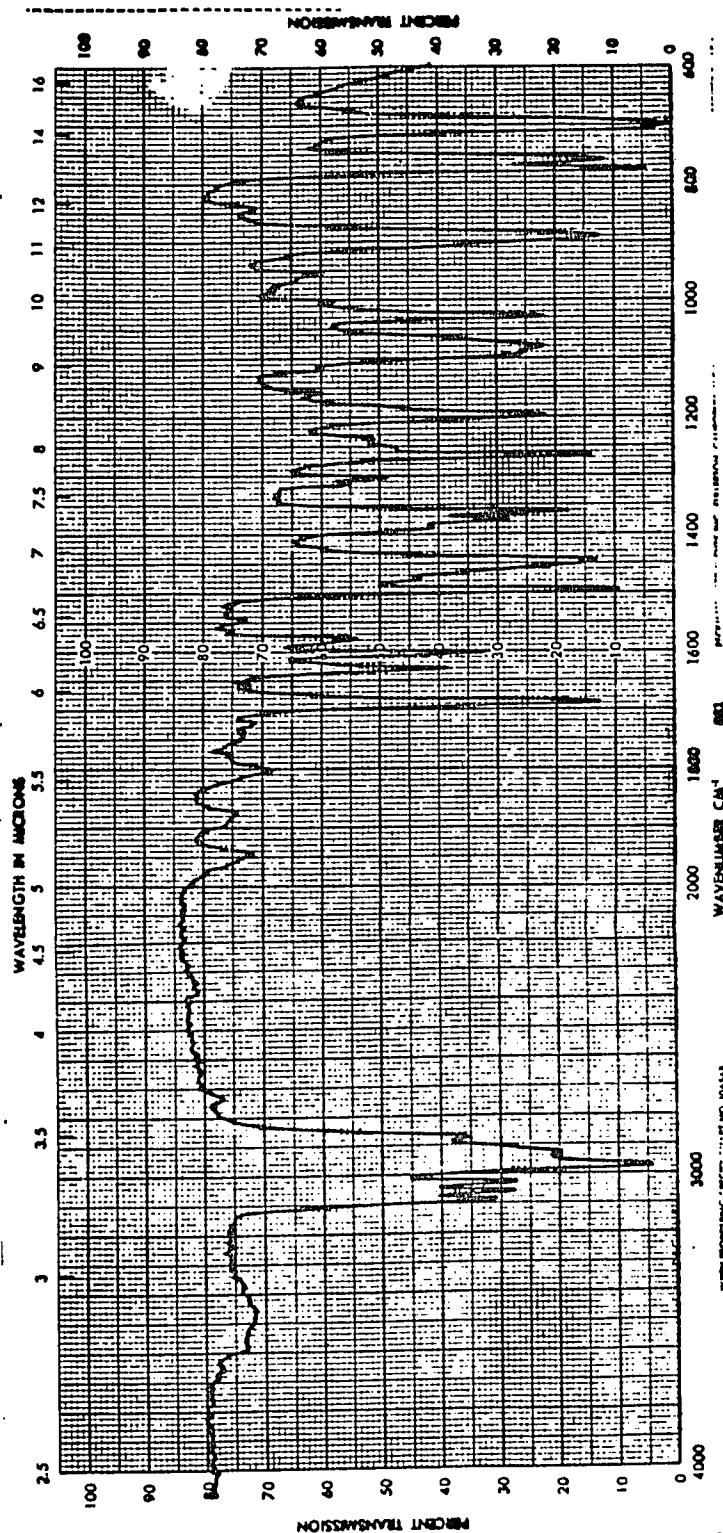


Figure 12b. Free Radical Product Following Column Run.



### Nuclear Magnetic Resonance Spectroscopy (NMR)

The sample were dissolved in  $\text{CDCl}_3$  in all cases but one, where  $\text{CCl}_4$  was used. The spectra were taken using a Varian A-60 NMR spectrometer at 60 MHz having tetramethylsilane as an internal standard. Figures 13 and 14 are the spectra corresponding to the sodium and the free radical initiated polymerization respectively. The figures correspond to the spectra for the product after the SEC step.

### Mass Spectroscopy (MS)

Mass spectra were obtained with a Dupont model 29-490B mass spectrometer operating at 70 eV, with the sample applied directly to the ion probe at  $20^\circ$ , and at  $10^{-7}$  to  $10^{-8}$  torr.

### High Performance Liquid Chromatography (HPLC)

Samples were dissolved in acetonitrile and diluted to give concentrations in the range of 100-500 ppm. The samples were separated on an MCM-10  $\text{C}_{18}$  octadecylsilane endcapped  $10\mu$  particulate packing in a 3 mm x 30 cm stainless steel column. The eluents were isocratic mixtures of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  at flow rates between 1 and 3 mL per minute. The ultraviolet spectra of the samples were examined over the range 204-320 nm. The peak absorption occurred around 290 nm. Optimum separations were obtained at 1.6 mL per minute of a

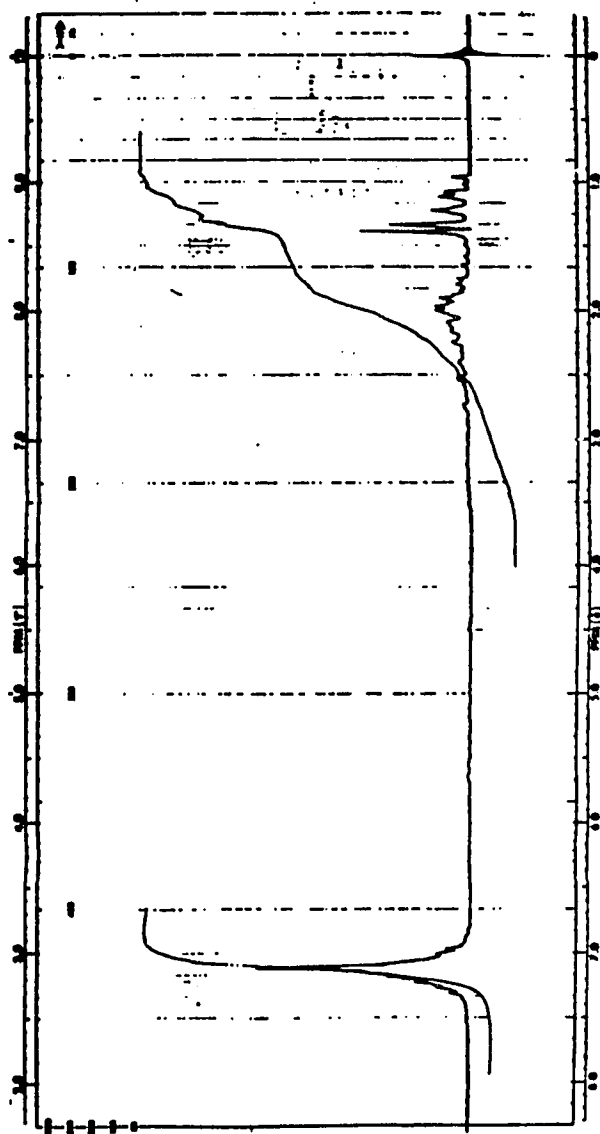


Figure 13. NMR Spectrum of Na Initiated Product.

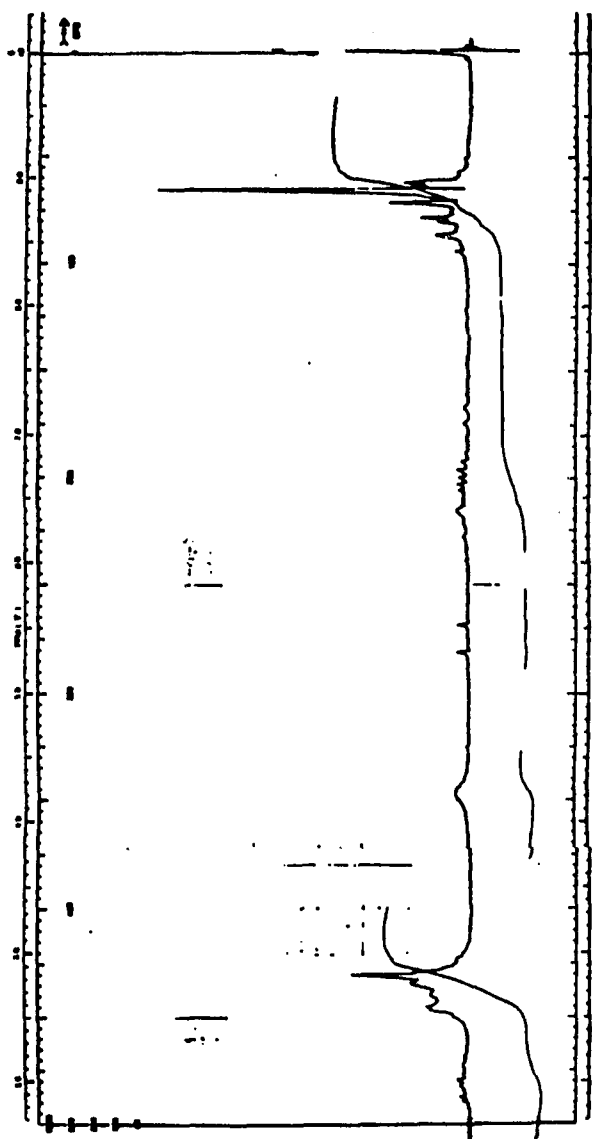


Figure 14. NMR Spectrum of Free-Radical Initiated Product.

60/40  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  eluent. The system was a Varian Instruments 5000 HPLC with a variable wavelength UV detector set at 290 nm (Varian Vari-chrom).

## CHAPTER V

### DISCUSSION

#### Separation By Size Exclusion Chromatography

Chemical difference among a series of oligomers are practically nonexistent; and for higher polymers, the only difference becomes one of size. Thus, traditional chromatographic techniques based upon such chemical differences as solubility and volatility range from insufficient for short oligomer chains to useless for high polymers. The change in size caused by the addition of one or two monomer units to a polymer chain may not be very significant for a high polymer, but the corresponding difference in size for an oligomer is substantial. A separation based upon size differences should be very efficient for oligomers, and useful for high polymers.

In the more common types of chromatography, the column packing has either a distinct chemical functionality, or is coated with a fluid having a distinct functionality. As a sample passes through the column its components interact with the column to varying degrees. Those components of the sample mixture having the fewest or shortest interactions with the column packing come out of the column first, while those having the most or the longest come out last. Thus, the desired separation is achieved. By analogy, a

person walking down a downtown street may travel one block in ten minutes at night when the stores are closed. If the store windows are lit, it will take longer to examine the goods on display, and the block may take twenty minutes to traverse. If the stores are open for business, walking a block may take an hour if one goes into the stores stocking goods of interest, or longer if one goes into all the stores.

Size exclusion packings are highly porous, chemically inert particles. Again, the molecules having the fewest interactions with the packing will come off the column first and those having the most will come off last. Smaller molecules can fit into more of the pores than the larger ones can, so the larger molecules in a mixture will come off the column first (having entered fewer pores) while the smaller ones come off later. By analogy, one might consider attempting to cross a snow covered field. If one attempts to merely walk through deep snow, progress is slow as one sinks into the snow and is reduced to plowing through the snow in order to get anywhere. With snowshoes, progress is more rapid as one's weight is distributed over a larger surface area and does not sink as deeply into the snow. Skis facilitate even faster movement over snow as they have even more surface area than snowshoes (remember that skis are solid, snowshoes are open lattices).

#### Anionic Initiated Polymerization

Both the polymerization reaction used by Kolobielski and Pines

(14) and the direct unambiguous synthesis of 1,3-diphenyl-1-methylcyclopentane were described in considerable detail. It was decided to essentially repeat their polymerization procedure as the direct synthesis was devised as a means of proving that they had a dimer with the 1,3-diphenyl-1-methylcyclopentane structure. By using the term "essentially repeat" it should be understood that there were two differences between this work and that of Kolobielski and Pines. One was intentional, the lack of a selective hydrogenation at any point during the procedure; and the other was little more than an observation, that the reaction temperature was six degrees (Celsius) higher than that reported in 1957. Neither change was deemed significant to the goals of this work.

The lack of a hydrogenation step resulted in obtaining one third of the product yield previously reported. Specifically, the yield dropped from 18.8% (22.2 g) obtained by the previous workers, to the 6.14% (7.41 g) obtained in the present work. Testing for purity by thin layer chromatography showed that following the double distillation the product relatively 95% pure. At this point, preliminary infrared and nuclear magnetic resonance spectra were obtained for the sample.

Following the size exclusion chromatographic purification, the fractions numbered 25-30 were determined to contain the product of interest. This product was believed to be purified dimer, and infrared, nuclear magnetic resonance, and mass spectra were again obtained on the product. Only the IR spectrum showed any changes

after the SEC run; and those changes were attributable to the purification of the raw dimer. Thus, armed with the knowledge that size exclusion chromatography had no deleterious effect upon the product, and that the dimer was reasonably pure following the two vacuum distillations, the research proceeded into the free-radical initiated polymerization reaction. While the anionic initiated reaction gave almost exactly the results anticipated, i.e., a dimer having the 1,3-diphenyl-1-methylcyclopentane also found by Kolobielski and Pines, as well as giving spectra with point for point, peak for peak matches with the corresponding spectra Ou obtained for his "oligomer B", the free-radical initiated reaction gave something else again.

#### Free-radical Initiated Polymerization

In an attempt to approximate the anionic reaction conditions, the procedure was modified slightly to accomodate the difference in catalytic behavior of t-butylperoxide ( $\text{tBuO}_2$ ) compared to sodium metal. The reason for the modification was two-fold; first,  $\text{tBuO}_2$  was used up during the course of the reaction in contrast to sodium being recovered essentially in toto; second, the  $\text{tBuO}_2$  has to break down into two t-butyloxy radicals before it can react with the monomer, this slow reaction step is not necessary in the sodium initiated reaction. Thus, the reaction time was extended and more than one charge of initiator was made for the free-radical initiated polymerization.



While the attempted polymerization of AMS with free-radical initiation has met with even less commercial success than the other methods of polymerization, a variety of free-radical initiated polymerizations have been studied. In the literature, free-radical initiated polymerizations have been reported as early as 1945 (18). Free-radical initiated polymerizations are different from ionic initiated polymerizations in several ways. Most importantly, there is no charge carried on the polymer chain or anywhere else in the polymerization system. But while essentially all of the initiator charged to a reactor for ionic polymerization is available throughout the polymerization reaction, only a portion of the free-radical initiator is available at any given time. An ionic initiator is generally active as soon as it is introduced to a polymerization system, a free-radical initiator, on the other hand, is relatively inactive as activation requires bond breakage of some sort. Thus, active sites take time to form for free-radical initiators, or more precisely, dissociation of, e.g., peroxide to oxy-radicals is the rate controlling step of the reaction. Additionally, any free radical produced can be deactivated by encountering another free radical or electron acceptor.

Periodic additions of the initiator are required throughout the course of the reaction to maintain the concentration of free radicals at an appropriate level. Additionally, the reaction time was extended in order to accomodate the relatively slow formation of the free radicals. Based upon its previously reported behavior in

similar solvents, the half-life for conversion of  $t\text{-BuO}_2$  into  $t\text{-butoxy}$  radicals was presumed to be approximately seven and one half hours (19).

One of the differences between the two reaction systems was that the free-radical initiated polymerization left less residue after the double distillation than the sodium initiated polymerization did. The residue was less tarry and oily as well as lighter in color as well. The water that was added to the free radical system was later recovered as a distinct layer containing dissolved  $t\text{-butanol}$ .

Most of the pentane added to the systems was recovered in the cold trap located between the receiving flask and the vacuum pump. The lowest boiling fraction was examined by IR, and found to consist of unreacted AMS with a trace of dissolved pentane. Between 110 and 115 mL (105-108 g) of AMS was recovered from the free-radical initiated polymerization (89-92.5% of the initial charge). The uncertainty in the amount is due to several factors. There is some residual pentane in the AMS layer, intermixing of the water layer with the organic layer, and unreacted AMS is present in some of the higher boiling fractions containing an indeterminate amount of the higher oligomers formed in the polymerization reactions.

Instrumental analysis of the products of the two types of initiation showed some similarities, but also some significant differences. The free radical product showed more aliphatic character than the sodium product, and it also showed the presence

of a hydroxyl group that the sodium product did not (20). The NMR spectrum of the free radical product showed a "mobile" hydrogen peak (one that shifted with changes in pH) indicative of a hydroxyl group, and a set of peaks containing a strong singlet suggestive of a t-butyl group. The preliminary conclusion was that the dimer resulting from the free-radical initiated polymerization was possibly contaminated with either water or t-butanol.

Attempts to purify the product through size exclusion chromatography or high performance liquid chromatography were fruitless, as the sample did not show any changes after passage through the SEC column, and fewer peaks were observed for the free-radical initiated product than for the sodium initiated product when both were examined using HPLC. Indeed, the peaks that were observed for the free radical corresponded exactly to the major peaks found for the sodium initiated dimer. Additional efforts to clean up the product via chemical reaction were equally unsatisfactory.

Although the results of IR and NMR were both indicative of an impure product similar to that resulting from the sodium initiated reaction, mass spectroscopy gave very substantial differences. Combined with the apparent impossibility of purification for the free radical product, this led to the conclusion that the product was not the same as the sodium initiated product (but impure), but rather that the product was a different compound altogether.

Table 1 shows comparative infrared spectra for several different dimers reported from the polymerization of AMS. It should be

Table I  
Comparative IR Spectra

t-Butyl Peroxide	Na	Ou's Oligomer B	V <sub>p</sub>	Mehta's Dimers		XIV <sub>p</sub>	Richards and Williams' Dimers	
				VIII <sub>p</sub>	XIII <sub>p</sub>			
3620								
3080	3080	3110 <sup>w</sup> 3092 <sup>m</sup>	3067 <sup>m</sup>					3104 <sup>w</sup> 3083 <sup>m</sup>
3050	3050	3068 <sup>ms</sup> 3035 <sup>s</sup>	3030 <sup>m</sup>					3061 <sup>ms</sup> 3027 <sup>s</sup>
3020	3020	3005 <sup>w</sup> 2965 <sup>vs</sup>						3001 <sup>w</sup>
2960	2955	2935 <sup>s</sup>	2959 <sup>s</sup>	S				2959 <sup>vs</sup>
2920			2925 <sup>s</sup>					2927 <sup>vs</sup>
2860	2960	2875 <sup>ms</sup>	2865 <sup>m</sup>	M				2870 <sup>ms</sup> 2854 <sup>m</sup>
1940	1941	1943 <sup>vw</sup>	1957 <sup>w</sup>	1942 <sup>w</sup>				
1865	1870	1875 <sup>vw</sup>	1869 <sup>w</sup>	1835 <sup>w</sup>				
1795	1800	1800 <sup>vw</sup> 1742 <sup>vw</sup>	1805 <sup>w</sup>					
1720			1727 <sup>m</sup>	1724 <sup>s</sup>				
1680								
1620								
1595	1600	1602 <sup>ms</sup>	1600 <sup>s</sup>	1592 <sup>m</sup>				1602 <sup>ms</sup>
1572		1583 <sup>w</sup>						
1489	1490	1496 <sup>vs</sup>	1495 <sup>s</sup>	1493 <sup>m</sup>	S	1488 <sup>m</sup>		1493 <sup>vs</sup>
1455	1475		1481 <sup>m</sup>		1471 <sup>m</sup>	M		
		1452 <sup>s</sup>						
1445	1448	1446 <sup>s</sup>	1445 <sup>s</sup>	1439 <sup>m</sup>	S	S		1452 <sup>vs</sup>
1382			1387 <sup>m</sup>		1379 <sup>m</sup>			
1367	1372		1364 <sup>m</sup>	1361 <sup>w</sup>	1370 <sup>m</sup>	M		
1355					M			
1310								
1244								
1225								
1205								
1195			1183 <sup>w</sup>	1170 <sup>s</sup>	1176 <sup>m</sup>	M		
1150			1156 <sup>w</sup>					
1115				1117 <sup>w</sup>		w		
1082								
1072	1073							
1021	1028							
895	905							
755	760	765 <sup>s</sup>	754 <sup>s</sup>	755 <sup>s</sup>	752 <sup>s</sup>	755 <sup>s</sup>		759 <sup>vs</sup>
696	698	700 <sup>vs</sup>	696 <sup>s</sup>	695 <sup>s</sup>	697 <sup>s</sup>	S		698 <sup>vs</sup>

noted that the product of the free-radical initiation ( $t\text{-BuO}_2$ ) has a reasonably similar infrared spectrum compared to the others, although it appears to be slightly more complex. The available nuclear magnetic resonance spectra show even fewer differences, save the hydrogen peak mentioned previously, and thus are not repeated here. In comparing the IR spectra, one does see some differences among them. These differences appear minor when considering the structural difference that give rise to them. Even dimers presumed to have identical structures show slight differences even though they give essentially identical spectra. The free-radical initiated product has several peaks unique to it, and several of them are major in character. The spectra of Ou's "oligomer B" and the sodium initiated dimer reported in the present work are identical except for resolution of some adjacent peaks, and some minor peaks also indicative of enhanced resolution and the use of a different instrument.

The unique peaks found for the free-radical initiated product and the more complex nature of the spectrum are not so easily accounted for. The spectrum on inspection appears to be a combination of the spectra found for both cyclic and non-cyclic dimers with that of water, or of the cyclic dimer contaminated with  $t$ -butanol. As described above, this was shown not to be the case.

The mass spectral data presented in Table 2 leave no doubt that the product resulting from the free radical initiation is different from the other dimers. This product alone has peaks at

Table 2  
Comparative Mass Spectra\*

t-Butyl Peroxide	Na	Ou's Oligomer B	V <sub>p</sub>	Mehta's Dimers			Richards and Williams' Dimer
			VIII <sub>p</sub>	XIII <sub>p</sub>	XIV <sub>p</sub>		
	238						238
	236	3.0%	236	2.2%	236	2.2%	
		1.4%	222	3.3%	222	2.7%	
	221	221	221	221	221	221	
220							
206							
205							
194							
	41%	0.8%	191	1.9%	4.3%	1.4%	
					186	5.8%	
162							
		158					158
	156						
145		145					3.2%
		143			143	1.4%	0.6%
134							
	131						0.7%
		129	129	3.6%			
			128	2.3%	128	2.7%	2.1%
	121	5.5%	121	121	121	121	2.1%
	120				120		
119	119	119	119	119	119	119	3.6%
118	118	118	118	118	118	118	7.4%
117	117	117	117		117	6.7%	3.8%
		116					0.9%
115	45%	4.9%	115	5.2%	115	4.9%	2.3%
105	105	105	105	105	105	105	105
104	45%	104	104	2.1%	5.5%	2.7%	6.9%
103	103	103	103	103	103	103	5.8%
	41%	1.3%	102	1.1%	5.1%	1.7%	0.8%
	41%	2.5%	92	3.9%	7.8%	3.6%	1.6%
91	91	91	91	91	91	91	91
		1.9%	89	2.5%	89	2.7%	
					88	5.4%	
			87	87	87	87	
			86	86	86	86	
			85	85	85	85	
				83	83	83	
				82	82	82	
82							
80							
79	79						79
78		78	78	78	78	78	78
	77	77	77	77	77	77	77
		0.5%	76	76	76	76	

\*±8% unless otherwise specified

205, 206, 162, and 194 mass units. It is also the only "dimer" to give a spectrum having no peak at either 236 or 238 mass units (corresponding to unsaturated and saturated dimers), and it also gives fewer peaks below 120 mass units than any of the others.

To further confuse the issue, the hydroxyl peak in the IR and the mobile hydrogen peak in the NMR spectra, as well as some of the minor peaks in the IR were not in the spectra obtained from the product after it had been exposed to the air for about six months. The spectra of the product did not change with time if it was not exposed to the air. The spectra resulting from the exposure of the product to the air are virtually indistinguishable from the spectra of the known dimers, especially that of the cyclopentane based structure. The cause and significance of this phenomenon remains undetermined, although the logical explanation requiring a simple rearrangement or "loss of a contaminant" would appear to be ruled out in view of the inability to remove or react such contaminants. The original mass spectrum shows no peak that would correspond to the parent ion of any dimeric species, any higher oligomeric species, or combination of dimer or oligomer with a contaminant.

The highest molecular weight peak observed for the free-radical initiated "dimer" is at 220; this does not correspond to the loss of a methyl group from a dimer structure as do the peaks found at 222 and 221 for the other dimers, nor is there any other convenient and logical explanation found. If the peak at 220 is presumed to be the parent ion, the unique peak at 205 corresponds to the loss of a

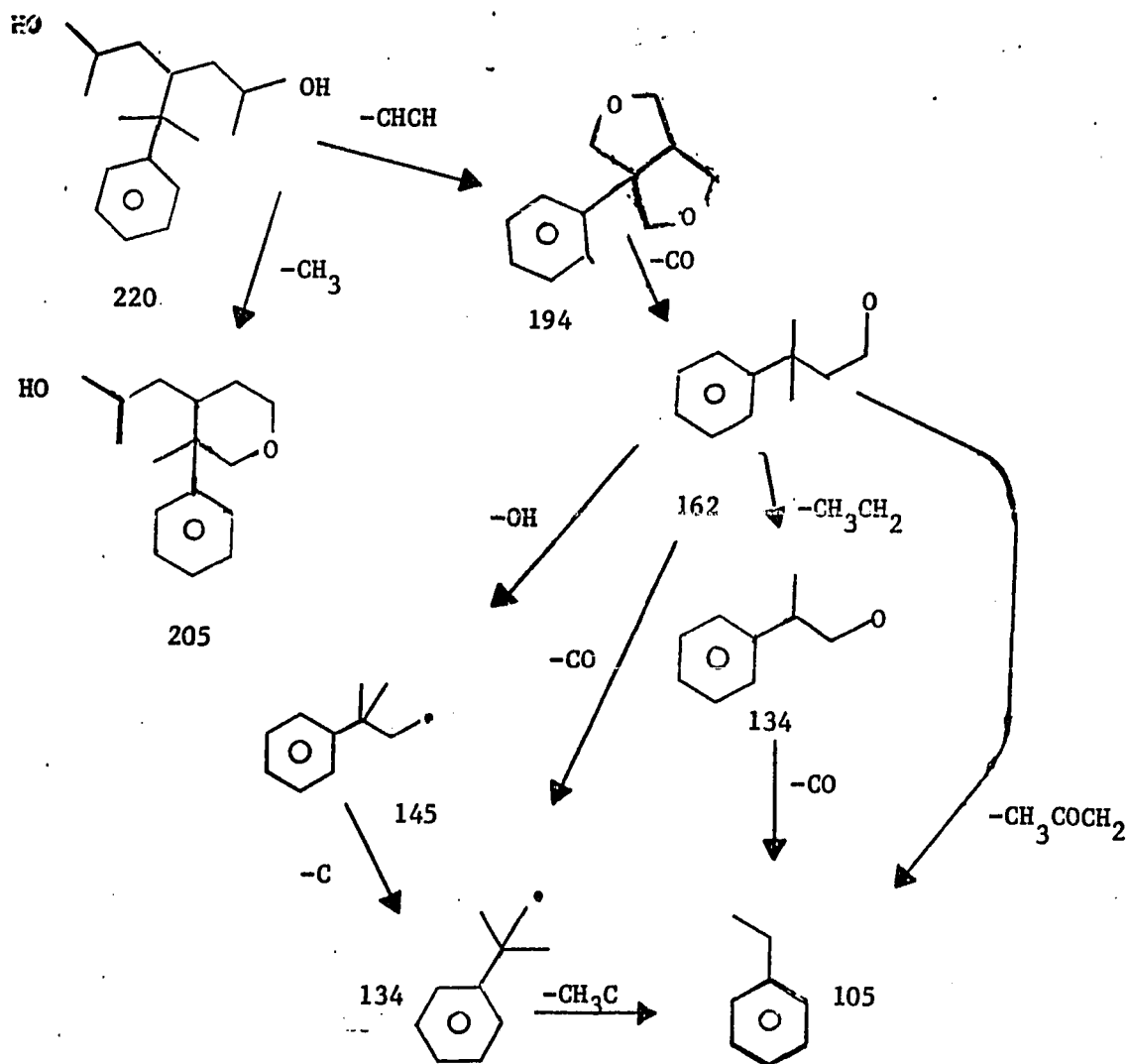
methyl group from the parent. The peak at 134 is explicable if methane is added to AMS (most likely across the double bond) to form t-butylbenzene. Alternatively, the addition of oxygen to AMS would also account for the peak at 134. While either event may occur during the acquisition of the mass spectrum, the stability of t-butylbenzene precludes the observed rearrangement with time. Indeed, given the lack of stability of an epoxide ring, and the convoluted route a mechanism for its formation would require, it too would appear to be an impossible reaction byproduct.

The addition of t-butanol across the double bond of AMS or of a t-butoxy radical to the AMS molecule would result in a peak at 192 or 191. The product of the free-radical initiation has a peak at 194, but not at 191 or 192. t-Butoxy radicals are formed by the dissociation of t-butylperoxide, and t-butoxy radicals can dissociate into methyl radicals and acetone. Adding acetone (m.w. 58) to a structure having a molecular weight of 162 would account nicely for the peak at 220. The loss of a methyl group from a structure having a molecular weight of 220 accounts for the peak at 205 which is the second largest peak found in the mass spectrum of the free-radical initiated product. The largest peak for the free radical product is at 57, that peak corresponds nicely with acetone after the loss of a hydrogen atom. The loss of a hydroxyl group from a structure having a molecular weight of 162 is the simplest explanation for the peak at 145. The loss of hydrogen from t-BuO<sub>2</sub> would also explain the peak at 145, but t-BuO<sub>2</sub> is far more likely to dissociate into



t-butoxy and give a peak at 73. However, a peak at 73 is nonexistent for this and the other dimers, while the peak at 145 is common to some of them. The peak at 105 is common to all dimers, and corresponds to ethyl benzene. If acetone is added to ethyl benzene, the resulting structure would have a molecular weight of 162. The addition of acetone to a structure having a weight of 134 would give a peak of 191 or 192, not 194. The addition of carbonyl (CO) to a structure having a weight of 134 would result in a structure with a weight of 162. The conclusion that at least one acetone molecule adds to an AMS molecule in the course of the reaction appears to have some validity. Figure 15 shows some known and some speculative structures along with fragmentations that may account for the above observations.

The change in structure observed for that portion of the sample exposed to the air for several months remains inexplicable. Attempts to duplicate and accelerate that change in structure by bubbling oxygen through it were unsuccessful.



**Figure 15.** Speculative and Known Fragmentations Accounting for the Mass Spectral Observations for the Product of the Free-Radical Initiated Reactions.

## CHAPTER VI

### SUMMARY OF RESULTS AND CONCLUSIONS

1. It has been demonstrated that the product obtained by Ou (16) was the same as that obtained by Kolobielski and Pines (14). The anionic initiated polymerization of AMS with sodium as initiator appears to result in the formation of a dimer having the 1,3-diphenyl-1-methylcyclopentane structure when the polymerization is conducted at or near the ceiling temperature.

2. Attempting to duplicate the reaction conditions for the sodium initiated polymerization but with t-butylperoxide, a free-radical type initiator, instead of sodium, did not give the 1,3-diphenyl-1-methylcyclopentane product. In fact, the product of the free-radical initiated polymerization did not appear to correlate with any of the other dimeric species reported in the literature. The only result that seems to fit the data would necessitate the incorporation of the breakdown products of the initiator into the AMS molecule.

## CHAPTER VII

### SUGGESTIONS FOR FURTHER STUDY

1. The structure of the free-radical initiated product is not established, although it appears to have a pendant methyl group, at least one hydroxyl group, aliphatic, and aromatic character. The other key structure is that having a molecular weight of 162, and it should either follow from the establishment of the structure of the product itself or lead to the establishment of that structure.

2. What happens to the structure of the free radical product over time when it is exposed to the air is also rather odd. The transformation to the actual dimer, if it occurs, would seem to require a complicated mechanism. The forced transformation and establishment of the mechanism would seem to follow from the establishment of the initial product structure.

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