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SYNTHESIS AND ANALYSIS OF DIMERS OF ALPHA-METHYLSTYRENE

by

Bhadreshkumar J. Mehta

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

Western Michigan University
Kalamazoo, Michigan
August 1975

ACKNOWLEDGEMENT

An expression of gratitude is extended to Professor G. G. Lowry for his competent advice and understanding during this research. I am also very thankful to Professors J. Howell and D. Warren for their help and advice.

I am indebted to the Chemistry Department for providing financial support in the form of teaching assistanceships.

A special thanks is also given to my family in India for their moral support.

Bhadreshkumar J. Mehta

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INTRODUCTION

The heat of polymerization Δ Hp, of Alpha-methylstyrene (AMS) has been a source of study for many years. The structure of AMS is shown in Figure 1.

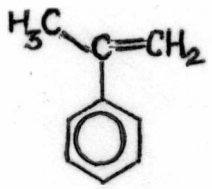


Figure 1
Alpha-methylstyrene

Roberts and Jessup carried out the first quantitative work to determine Δ Hp of AMS.[1] Their data displayed a Δ Hp dependence on the degree of polymerization, DP. Several other reports were also published with new values for Δ Hp and new explanations for the apparent DP dependence.[2,3,4,5].

Samples of dimers of AMS have been prepared by various workers.[6,7,8] The reactions were mostly carried out by using sulfuric acid as an initiator. It has been shown that in carbon tetrachloride solution the polymerization by anhydrous stannic chloride will produce dimer with a cyclic endgroup at the ceiling temperature.[9] By regulating the solvent system and initiator concentration, it may be possible to optimize the production of one isomer and exclude the other isomers.

The original outline for this thesis called for carrying out the oligomerization of AMS by using anhydrous stannic chloride as initiator.

Gel permeation chromatography can be used to separate a mixture of oligomers. Preparative column chromatography could be used to obtain samples of pure dimer. The identification of isomers of dimer called for use of various spectroscopic methods. Once a pure sample of dimer having a known amount of a particular isomer, is obtained its true heat of polymerization can be determined.

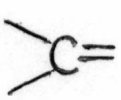
The structure of the "cyclic" isomer, 1, 3, 3-trimethyl -1-phenyl indane, has been established previously.[10]

THEORY

The monomer unit is a 1, 1-disubstituted ethylene. It is selective as to where and how the ethylene group may be attacked.[11]

The steric interference of the methyl group and phenyl group severely limit the possible orientations of the attacking ion or radical. After a few monomer units have been added, the orientation of subsequent adding monomer units is even more restricted. The propagating chain becomes more bulky, rigid and inhibited in its ability to orient itself to the monomer for further addition. This effect would be more pronounced near the ceiling temperature, where depropagation is also significant. The elimination of a monomeric unit from the end-group of a growing polymer chain is called depropagation. At the ceiling temperature, the rate of depropagation becomes equal to the rate of propagation.

The steric hindrance of the benzene ring in AMS is of the same order as that caused by a methyl group, although the phenyl group is much more bulky.[12] It is necessary to realize that the substituents are bound on the alpha carbon atom with coplanar valences and not the tetrahedral ones. The axis of benzene ring lies then in a plane parallel to the plane of the valences as the carbon atom, so interferences are of about the same order as in methyl group even if aromatic ring is bulky.

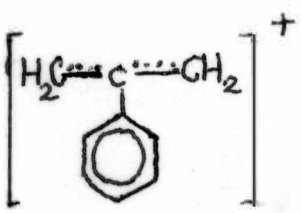


planar

tetrahedral

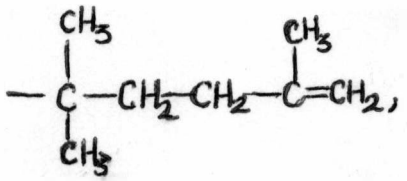
The linear ''head-to-tail'' addition, which is typical for polymerization species having a tertiary carbonium ion, is disturbed by the aryl substitution. The process of alkylation of the aromatic nucleus can take place intramolecularly and lead to the stabilization by cyclization with the formation of an indane skeleton at the end of the macromolecule.[13] The intramolecular process is relatively easy, and the resulting break of the growth occurs very often.

Initiation occurs by the removal of an allylic hydrogen atom, in the form of a hydride ion from the nucleophilic monomer by a Lewis acid such as stannic chloride. Monomer provides its own initiator, its first carbonium ion. Allyl hydride transfer yields a favorable resonance stabilized structure.[14]

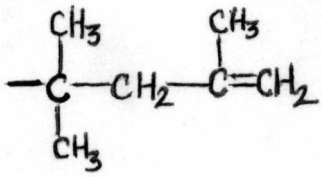


The stability of the allylic carbonium ion is relatively high and the rate of formation is fast. Thus even the less acidic associated stannic chloride is able to remove hydride ion from AMS. AMS has been previously polymerized by titanium tetrachloride alone.[15,16] AMS has not been polymerized by anhydrous stannic chloride alone.

Self-initiation via hydride transfer is most likely a slow process relative to other types of initiations and it results in unsaturated endgroups that are structurally very similar to endgroups arising in common chain transfer to monomer (proton transfer).[17] For example, in the case of self-initiation with isobutylene, the headgroup would be

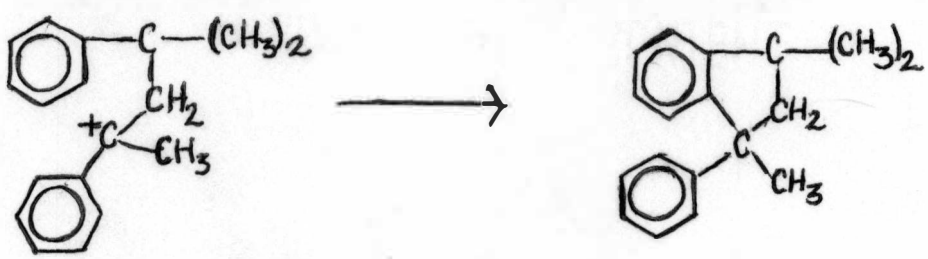


a structure which is very similar to the endgroup that is formed on chain transfer.



The role of the solvent is due on one hand to its polarity and on the other hand to its basicity. If the solvent is equally acid or more acid than monomer in the sense of Lewis definition, and is capable of combining with an aprotic acid, it can take over the role of cocatalyst. For example, it is impossible to polymerize isobutene or styrene in diethyl ether, while vinyl ether can be polymerized in this solvent.[18] If the solvent is more basic than monomer it will cause inhibition. The initiation reaction is affected by the basicity of the solvent; the growth is affected by the polar effects.

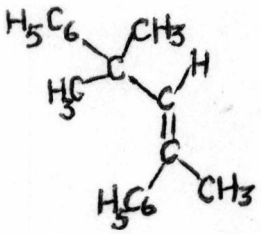
Unsaturated dimer reacts to form a saturated dimer as follows.[8]



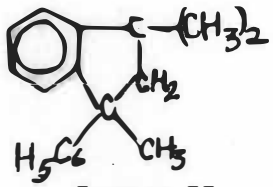
There are four possible isomers of the dimer of AMS as shown in Figure 2.

Termination in cationic polymerization occurs by the removal of

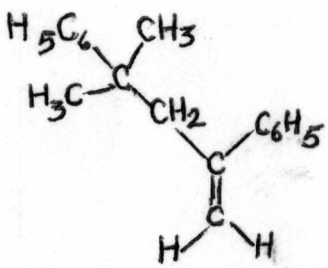
a hydride by the propagating carbonium ion from suitable olefins.



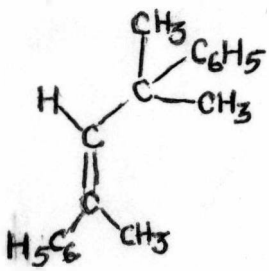
Isomer I
"Cis"



Isomer II
"Cyclic"



Isomer III
"Terminal"



Isomer IV
"Trans"

Isomer I: Cis 2,4-diphenyl-4-methyl-2-pentene

Isomer II: 1,3,3-trimethyl-1-phenylindane

Isomer III: 2,4-diphenyl-4-methyl-1-pentene

Isomer IV: Trans 2,4-diphenyl-4-methyl-2-pentene

Figure 2
Isomers of Dimer of Alpha-Methylstyrene

The present theory of self-initation via hydride transfer is closely related to the earlier self-consistent theory of termination via hydride

transfer; in this sense the monomer may provide its own initiating and terminating agents.

EXPERIMENTAL

Synthesis of Alpha-methylstyrene Oligomers

In an attempt to obtain a sample of dimer of AMS, the reactions were carried out near the ceiling temperature, i.e. 60°C. To obtain a particular isomer of the dimer, the reactions were carried out at various initiator-to-monomer ratios, (Table 1).

Carbon tetrachloride was used as solvent to favor low DP and the formation of "cyclic" isomer. Anhydrous stannic chloride was used as the initiator and the reactions were quenched with dilute hydrochloric acid solution, (approximately 0.1M).

The solvent was distilled with a 12 plate bubble cap distillation apparatus. The distillation flask was filled with 1500 ml of solvent. The first 100 ml of the distilled solvent was rejected and last 100 ml of solvent was left in the flask. The distilled solvent was used within one week of its distillation.

Each synthesis was carried out in an integrated distillation reaction apparatus (IDRA, Figure 3). The experimental procedure was essentially the same as used by Humbert.[19] Except for the ball joints which had little or no lubricant, the ground glass joints of the IDRA were sealed with polytetrafluoroethylene sleeves. A minimum of silicone lubricant was used, because both AMS and carbon tetrachloride dissolved it.

Once the IDRA was sealed, it was purged with high purity dry nitrogen for a period of 24 hours before each batch of reactions.

Table 1
Synthesis of Alpha-Methylstyrene Oligomers

Sample	Monomer Molarity	Initiator Molarity	(Initiator)/(Monomer)	Reaction Time in Hours
I	0.5	0.15	0.3	5
II	0.5	0.25	0.5	5.5
III	0.5	0.45	0.8	5.5
IV	0.5	0.60	1.2	5
V	0.8	0.24	0.3	5.5
VI	0.8	0.40	0.5	5
VII	0.8	0.72	0.8	5
VIII	0.8	0.96	1.2	5
IX*	0.25	0.075	0.3	5
X	0.25	0.18	0.5	5
XI	0.25	0.225	0.8	5
XII	0.25	0.30	1.2	5
XIII	1.0	0.5	0.5	5
XIV	1.0	0.8	0.8	5
XV	1.0	1.2	1.2	5
XVI*	0.5	1.0	2.0	5.5
XVII	0.5	0.5	1.0	5.5
XVIII	0.25	0.5	2.0	5.5
XIX	0.25	0.25	1.0	5.5
XX	0.10	0.1	1.0	5

For all reactions: Temperature: $60° \pm 0.2°C$
Solvent : Carbon Tetrachloride
Initiator : Anhydrous Stannic Chloride

* Some catalyst was lost due to leak from the stopcock 12.

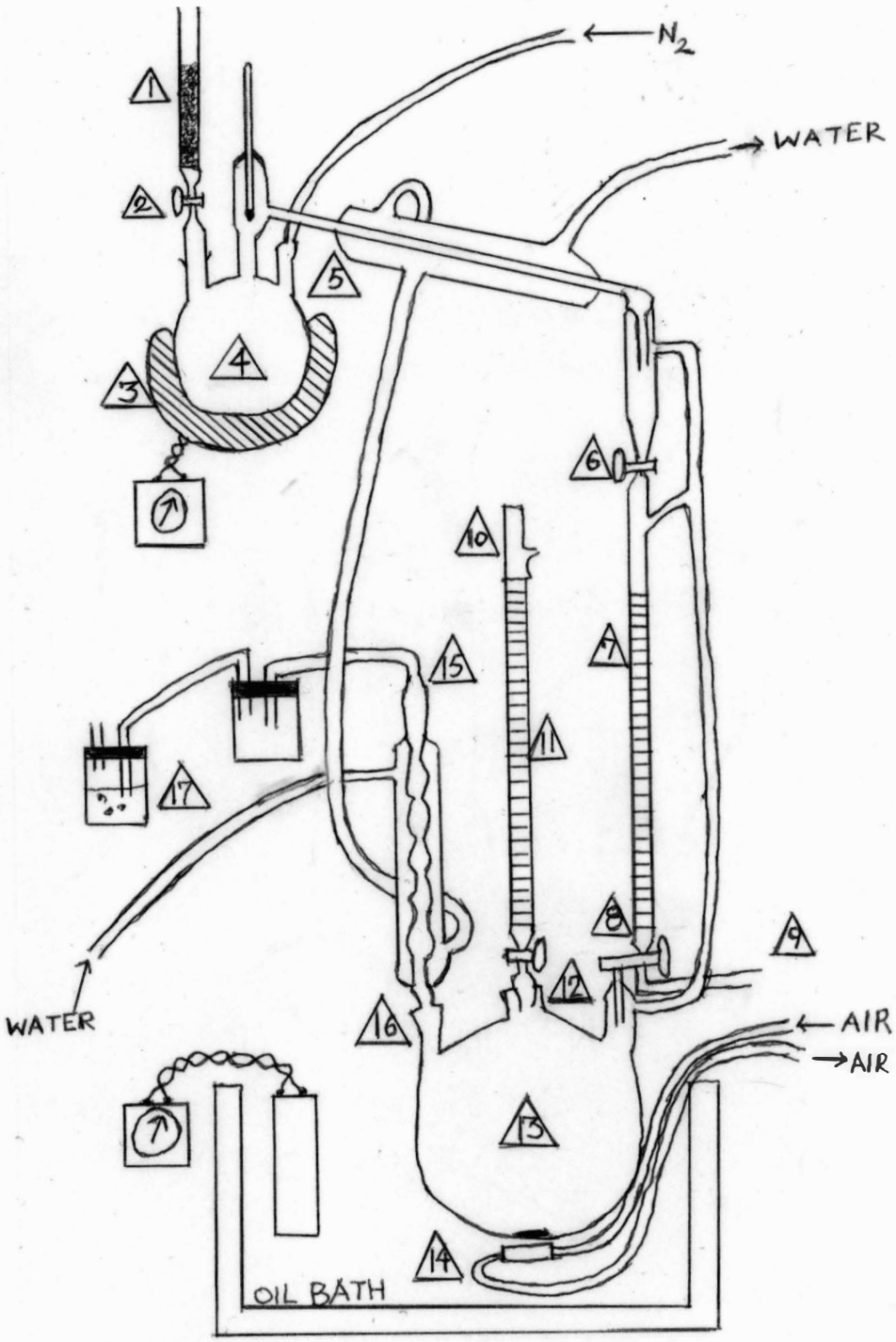


Figure 3: Integrated Distillation-Reaction Apparatus (IDRA)

Each batch was limited to five reactions or five consecutive days. After each batch, the IDRA was disassembled and cleaned. All the glassware was cleaned by keeping them in a solution of alkaline isopropyl alcohol for two days and washed with distilled water. All the glassware was dried in the oven before reassembly.

The following will refer to the IDRA in Figure 3 and the individual parts will be referred to by the numbered triangles. Column 1 was filled with activated alumina. Alpha-Methylstyrene was poured into column 1 and allowed to drain slowly into flask 4 through stopcock 2. Approximately 0.5 g of sodium metal was cut into small pieces and placed in the distillation flask 4 through the nitrogen gas inlet 5. The nitrogen was then allowed to flow at a slow rate and the flow was monitored by the bubbler 17, containing silicone oil to a level of several inches. After approximately 100 ml of AMS was in the flask, stopcocks 2 and 6 were closed and the heating mantle 3 was turned on just high enough to allow refluxing. The 50 ml graduated buret 11 was then filled under the hood with anhydrous stannic chloride and then replaced into joint 12. The drying tube 10 was filled with anhydrous calcium chloride and closed until the stannic chloride was needed. The required amount of carbon tetrachloride was placed in the flask of 13 through joint 15.

The amount of carbon tetrachloride used for each reaction was calculated separately, by considering the volume of monomer and initiator at the reaction temperature. The total volume at the reaction tempera-

ture was maintained at 300 ml.

After the monomer had refluxed in the presence of amber colored anion for about one hour, it was allowed to distill into the 50 ml graduated buret 7. First the stopcock 6 was opened and the three way stopcock 8 was closed. The first 15 ml of AMS was discarded through the outlet 9. After the desired amount of AMS was collected in 7, the distillation was discontinued and 6 was closed. Here it was necessary to adjust the nitrogen flow because of temperature changes and consequently, the pressure changes within the flask 4.

The required amount of AMS (± 0.2 ml) was then slowly drained into 13 and allowed to equilibrate with the constant temperature oil bath for about fifteen minutes. The air driven stirrer 14 was used to obtain a homogeneous solution. The required quantity of stannic chloride (± 0.2 ml) was then added continuously through stopcock 12 into flask 13 and the time was recorded. The required amount of stannic chloride was added continuously and in a short period of time.

Approximately five hours after initiation, the reaction was quenched with 200 ml of dilute hydrochloric acid. The water terminated the reaction and the small amount of hydrochloric acid prevented the oligomers from forming an emulsion with the wash water. The crude product was washed several times with distilled water, until the evolution of gas ceased. The product mixture was allowed to stand over calcium chloride for about eighteen hours and then filtered through the filter paper. The solvent and the unreacted monomer were removed by

employing a rotating evaporator with the flask partially immersed in a warm water bath. The remaining viscous oil was again filtered with the filter paper under nitrogen atmosphere. The final product was stored under nitrogen at 5°C.

When the analytical experiments were performed, the samples were allowed to come to room temperature before exposing them to the atmosphere. This was done to prevent water vapor from condensing on the sample.

Analysis of Oligomers

Gel Permeation Chromatography

Gel Permeation Chromatography was used to separate and identify the presence of oligomers and the monomer. Gel Permeation Chromatography (GPC) is a separation technique in which the components are separated in accordance with their molecular size. The larger molecules exhibiting less permeation into the gel are eluted first from the column. The pores have different diameters. The molecules of various sizes separate by their perferential permeation into the pores of the gel.

A Perkin-Elmer model 1250 Liquid Chromatograph was used. The columns were packed with Bio-Beads S-X2 and Poragel. Bio-Beads from Bio-Rad Laboratories had particle size of 200-400 mesh. Two different Poragel materials, manufactured by Waters Associates were used. One, Poragel/60 A had particle size less than 37 microns and the other, Poragel/100 A had particle size 37-75 microns.

These soft gel materials were lightly cross-linked. They had capability of imbibing large quantities of solvent into their pores. These materials swell many times their dry volume and gain their porosity in proportion to the volume of solvent imbibed. When used at low flow rates these soft gels offer a high efficiency and high capacity, but at high flow rates these gels deform easily.[20] All columns were made of stainless steel and had the same internal diameter of .0625 inch. Columns were packed according to the procedure described by Bombaugh.[20]

A special effort was made to maintain a uniform suspension of the slurry. Packing was carried out at low transport velocity. A slurry of the packing material was prepared by soaking these soft gels in pure tetrahydrofuran for 24 hours. Tetrahydrofuran was chosen as solvent for several reasons. The oligomers dissolve very easily at room temperature. The columns can be operated at room temperature because of low viscosity of the solvent. The gels had swollen about six times their dry volume after 24 hours in the solvent.

The slurry of solvent-swollen gel was poured into the column, which was partially filled with tetrahydrofuran. The columns were packed straight and used as such. This maintained the homogeneity obtained during the packing of the gel. The columns were fitted with a filter and an adaptor for connections, at each end of the column.

The gel was allowed to settle until a gel bed was formed of a sufficient thickness to retard the flow solvent from the column. The slurry was then added in small amounts until each column was packed to

the top. The solvent was allowed to pass through the column at slow flow rate for a few hours. The filter and the adaptor were removed from the top of the column and small amount of slurry was added to keep the column fully packed. Once the columns were filled to the desired height, they were not allowed to dry. The total length of the column was varied to achieve a good separation of the oligomers. Various combinations of Bio-Beads S-X2 and Poragel columns were also tried to achieve a good resolution.

Tubings connecting various columns were of 0.625 inch o.d. and 0.03-0.04 inch i.d. The column couplers were made of stainless steel and were semi-circular in shape. The columns were kept at room temperature during use.

Tetrahydrofuran was degassed with constant stirring at 50°C. The degassed solvent was then passed through a Millipore filter (cat. no. LSWP02500) to remove dust particles and then into a Milton Roy pump (See Figure 4). A pulse damper having a zero dead volume and zero back pressure design was used to maintain the noise level (observed on the recorder trace due to the pump stroke) to a minimum.[21]

The solvent coming out of the pump was passed through the reference section of an ultraviolet detector. The solvent was then passed through the sample injector.

The sample was introduced through a loop injector which had a fixed volume of 30 microliters. After the sample injector, solvent was introduced at the top of the column. The solvent coming out of the last section of the column was then introduced to the sample

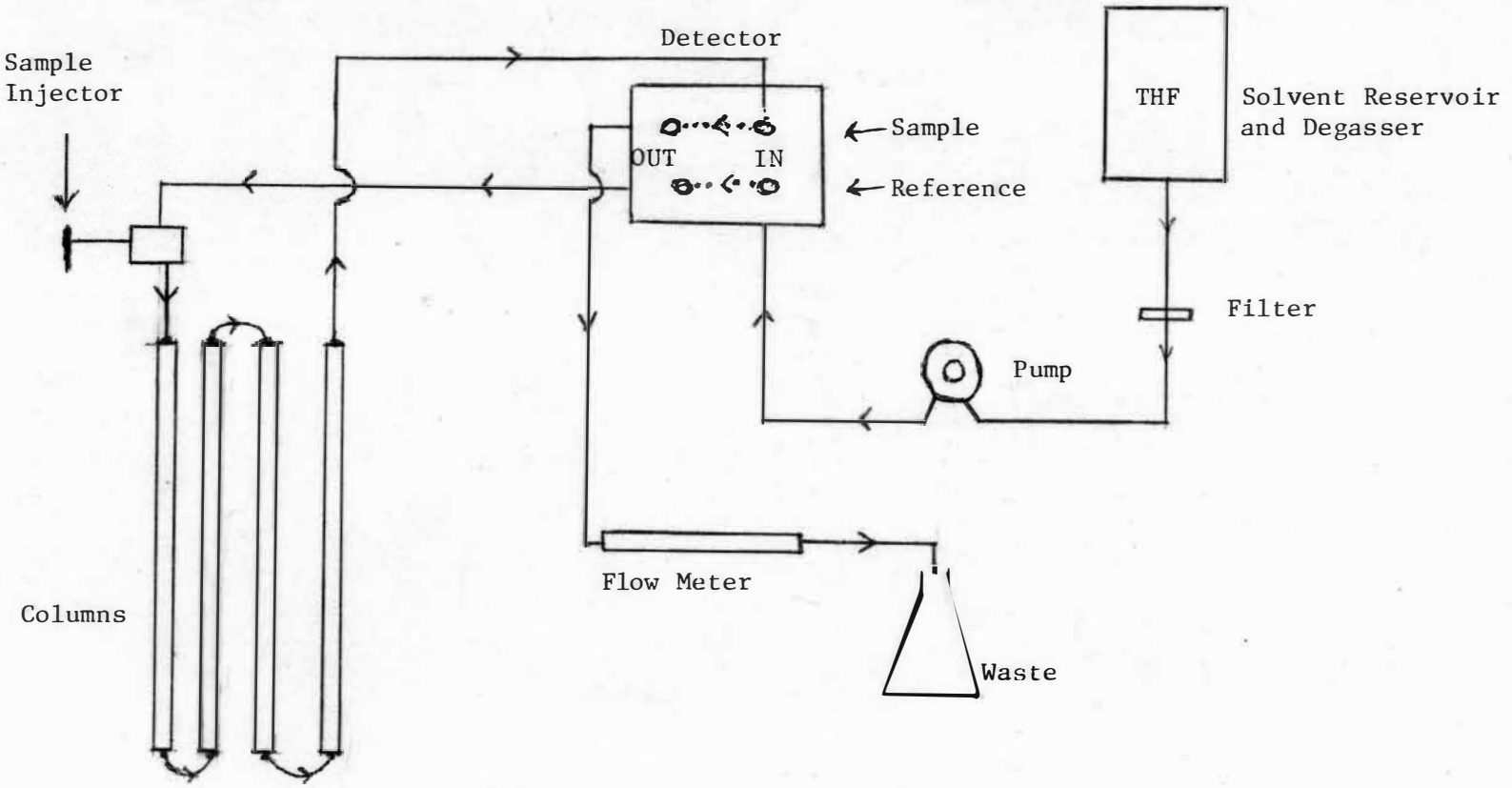


Figure 4. Schematic Diagram of the Perkin-Elmer Model 1250 Liquid Chromatograph.

section of the detector. The solvent from the detector was then passed through a flow meter to observe the flow rate. The solvent was collected in a reservoir and distilled for reuse.

The detector used in this instrument had a mercury vapor lamp as a source of ultraviolet radiation. A fixed wavelength of 253.7 nm was selected to detect the presence of any oligomer and the monomer. Tetrahydrofuran has an ultraviolet cut-off at 220 nm. This detector offered a great sensitivity, i.e. 0.001 absorbance units.[22]

Both a reference and sample cells had a 10 mm path length and 12 microliter volume. AMS has an molar absorptivity of the order of 10^4. Using this detector amount of AMS as low as 10^{-8} g. can be detected.[21]

A 5 to 8% sample of the mixture of oligomers synthesized was prepared for introduction into the column. The loop injector was rinsed with pure solvent before and after the introduction of the sample. A syringe was used to fill the loop with solution of the sample. Care was taken to prevent any air being introduced in the system.

Before injection of the sample, flow rate was adjusted so that it was between 0.15 and 0.30 ml/min. and the pump pressure was adjusted so that it operated between 700 and 900 psi. Detector controls, range o.d. (optical density) and attenuator, were adjusted so that a stable and noise free baseline was obtained on a 1 mv Beckman 10 inch recorder.

The detector response was linear for various concentrations of dimer and the monomer. The response for monomer and dimer also gave an indication of relatively low molar absorptivity for the dimer.

See Figure 5 and Figure 6.

GPC was also used to detect the presence of monomer or dimer in the fractions collected of the effluent from the preparative column. A sample of oligomers was obtained by carrying out the polymerization of AMS by anhydrous stannic chloride in benzene at 10°C. This was synthesized by Humbert.[9] Upon analysis it was found to contain oligomers up to the hexamer. This sample was used for identifying the peaks obtained with Perkin-Elmer Liquid Chromatograph.

The data obtained from the chromatographs of each sample are given in Table 2 and Table 3. The columns were connected as shown in Figure 7 for the data in Table 2 and as in Figure 8 for data in Table 3. A typical gel permeation chromatograph is shown in Figure 9.

A quantitative determination was made for each sample to find out the amounts of trimer and dimer. The amount of monomer left behind after the reaction and the removal of carbon tetrachloride was also determined. Cut and weigh method was used for such determinations in the following manner. A baseline was drawn for each peak on the chromatogram. The curve was traced carefully on Albanene paper by superimposing the paper on the chromatogram. The weight of each peak was obtained on a Sartorius balance. One square inch of the tracing paper weighed 0.0293 g. The weights for all peaks of trimer, dimer and monomer were calculated. Data obtained are shown in Table 4.

Solvent obtained from the rotary evaporator was introduced into the GPC to find out if any trimer was lost during the removal of carbon tetrachloride and the monomer. Only a slight amount of dimer

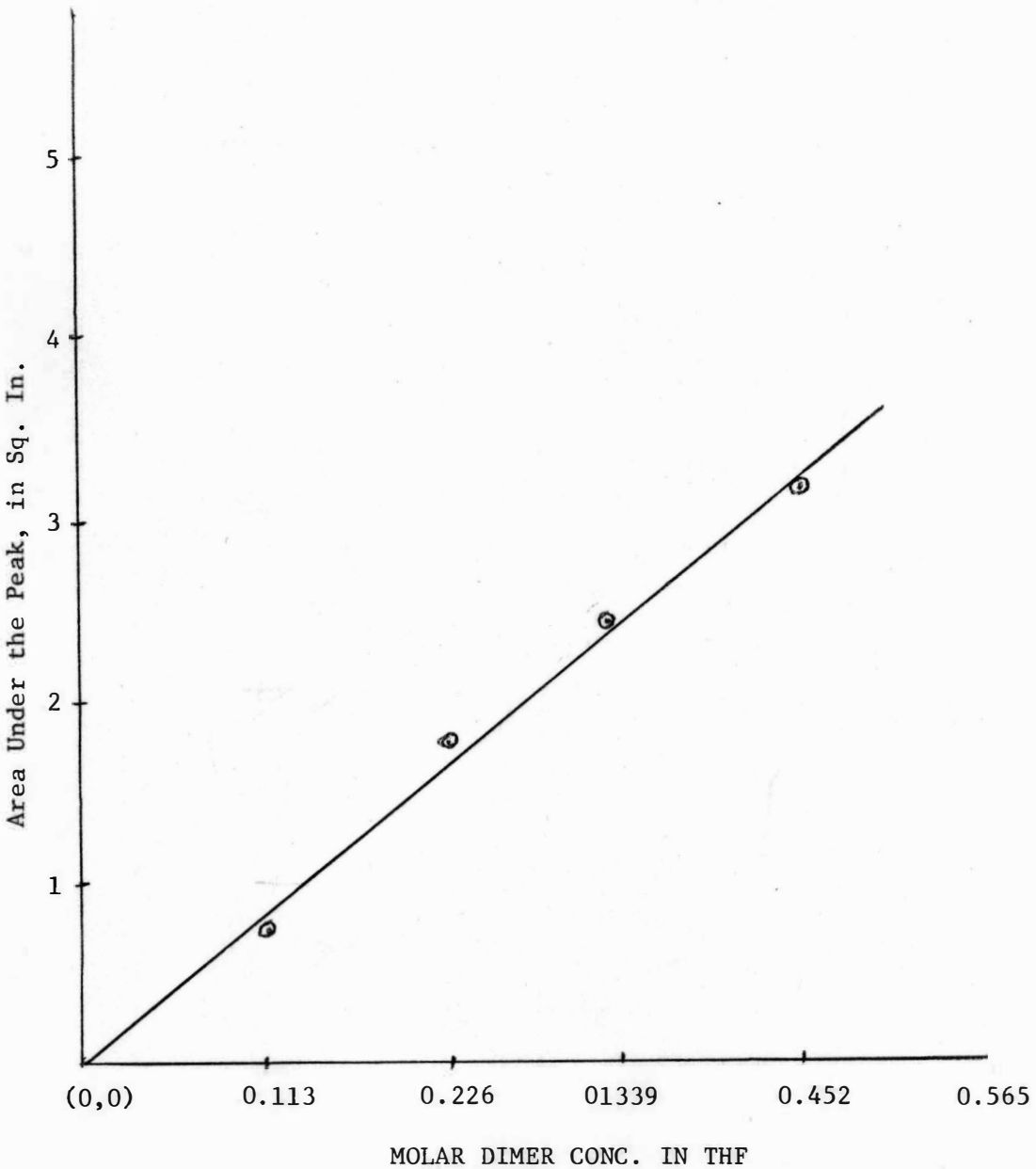


Figure 5. Detector Response vs. Dimer Concentration, Sample XIV_p.

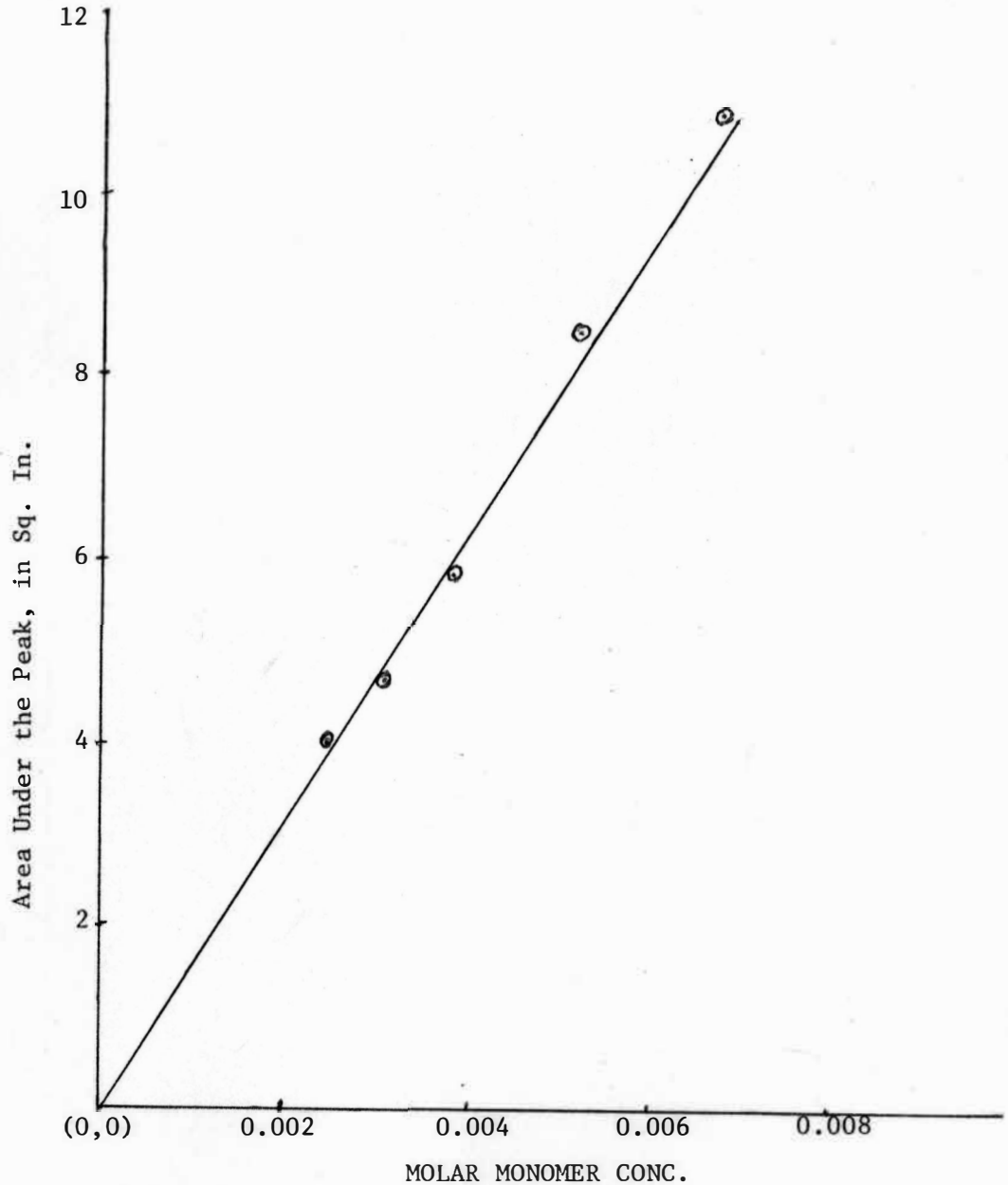


Figure 6. Detector Response vs. Monomer Concentration

Table 2
Gel Permeation Chromatographic Data For Column Arrangement in Figure 7

SAMPLE	FLOW RATE ml/min.	ELUTION VOLUMES V_e (in mls.) Trimer	Dimer	Monomer	$\frac{Ve\ Dimer}{V_e\ Monomer}$
I	0.17	69.7	75.8	85.0	0.892
II	0.17	69.7	75.7	84.8	0.896
III	0.15	61.4	66.6	74.4	0.895
IV	0.17	61.8	67.1	75.0	0.895
V	0.17	70.8	75.7	86.2	0.878
VI	0.17	69.7	75.7	84.7	0.893
VII	0.16	65.6	71.2	79.5	0.896
VIII	0.14	60.5	65.8	73.5	0.895
IX	0.16	65.3	71.4	79.5	0.894
X	0.16	65.1	70.7	79.2	0.893
XI	0.16	74.7	80.3	88.6	0.906
XII	0.16	64.7	70.6	78.9	0.895
XIII	0.15	69.5	75.3	84.2	0.894
XIV	0.17	79.1	74.8	83.8	0.893
XV	0.15	68.7	74.6	83.6	0.892

Table 3
Gel Permeation Chromatographic Data For Column Arrangement in Figure 8

SAMPLE	FLOW RATE ml/min.	ELUTION VOLUMES V_e (in mls.) Trimer	Dimer	Monomer	$\frac{V_e \text{ Dimer}}{V_e \text{ Monomer}}$
I	0.28	84.6	91.3	104.0	0.880
II	0.28	84.0	90.4	103.0	0.880
III	0.24	86.2	91.7	103.0	0.890
IV	0.24	86.4	91.9	103.0	0.892
V	0.30	85.5	95.4	109.0	0.875
VI	0.20	74.2	79.0	89.0	0.888
VII	0.28	92.7	98.8	110.0	0.898
VIII	0.20	74.8	79.6	89.0	0.894
IX	0.26	85.5	91.0	102.0	0.892
X	0.27	87.8	93.2	103.0	0.905
XI	0.28	89.6	95.5	107.0	0.893
XII	0.28	88.2	94.4	108.0	0.875
XIII	0.27	84.0	89.4	100.0	0.894
XIV	0.29	87.0	93.1	104.0	0.895
XV	0.29	85.6	91.1	98.0	0.901
XVI	0.22	82.5	88.4	102.3	0.897
XVII	0.20	78.8	84.4	94.0	0.890
XVIII	0.22	83.8	91.2	101.8	0.894
XIX	0.22	90.3	94.9	105.2	0.898
XX	0.20	81.5	88.7	99.7	0.891

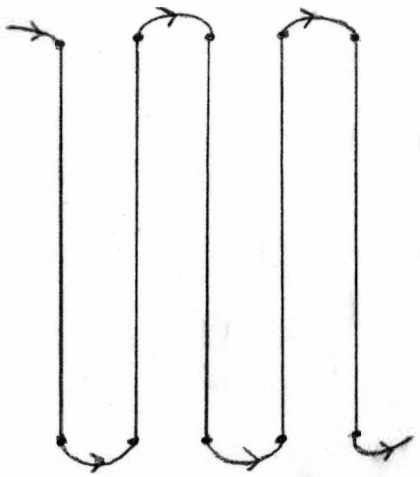


Figure 7. Column Arrangement Used to Obtain Data In Table 2

TOTAL LENGTH: 530 cm COLUMN PACKING: Bio-Beads S-X2

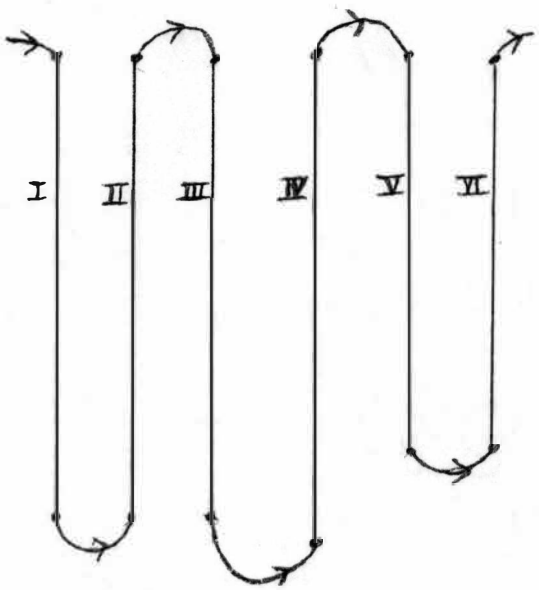


Figure 8. Column Arrangement Used to Obtain Data in Table 3.

TOTAL LENGTH: 560 cm

COLUMN PACKING:
COLUMN I, II, & III: Porage1/100 A 300 cm
COLUMN IV: Bio-Beads S-X2 110 cm
COLUMN V, VI: Porage1/60A 150 cm

peak was observed for a few samples. Amount of dimer lost during evaporation was estimated to be no greater than 1%.

Preparative Column Chromatography

Preparative column chromatography was used to obtain pure samples of dimer. A glass column 4.5 cm X 200 cm, schematically shown in Figure 10, was packed with Bio-Beads S-X2 gel. The gel was swollen in freshly distilled tetrahydrofuran. The column was first washed with the solvent and then filled with the solvent about half full. The flow rate through the Teflon stopper was maintained slow. The gel with solvent was introduced at the top of the column in small amounts at a time. The whole column wsas packed over a period of twelve hours. The gel was prevented from drying by keeping some solvent above the gel at all times.

When the solvent was allowed to flow through the stopper at the lower end of the column, the solvent level was maintained at overflow level from the reservoir of tetrahydrofuran at the top of the column as shown in the Figure 10. Before introducing the sample, the reservoir was removed and the flow rate was adjusted as required (about 0.25 ml/min.). When the solvent level fell down to about 1-2 mm above the gel, a concentrated sample solution (0.5 g in 2 ml of THF) was introduced using a dropper. The solution was spread over the whole area of the gel at the top. This was done to prevent overcrowding at the center of the column. After the sample solution was well into the gel, the solvent reservoir was replaced and solvent was

Table 4
Percentage of Monomer, Dimer and Trimer as Determined From the Chromatograms by Cut and Weigh Method

SAMPLE	% MONOMER	% DIMER	% TRIMER
I	10.54	85.13	4.33
II	6.72	88.63	4.64
III	7.55	85.80	6.65
IV	8.30	82.90	8.80
V	6.60	86.47	6.93
VI	7.15	81.70	11.15
VII	6.68	83.19	10.13
VIII	1.29	86.23	12.48
IX	59.51	38.01	2.48
X	10.82	85.40	3.78
XI	10.17	84.00	5.83
XII	4.80	90.05	5.15
XIII	3.81	86.71	9.48
XIV	6.63	82.85	10.52
XV	5.25	81.62	13.13
XVI	61.11	30.05	8.74
XVII	5.88	87.25	6.87
XVIII	2.46	90.69	6.85
XIX	22.36	74.19	3.45
XX	-	67.56	32.44

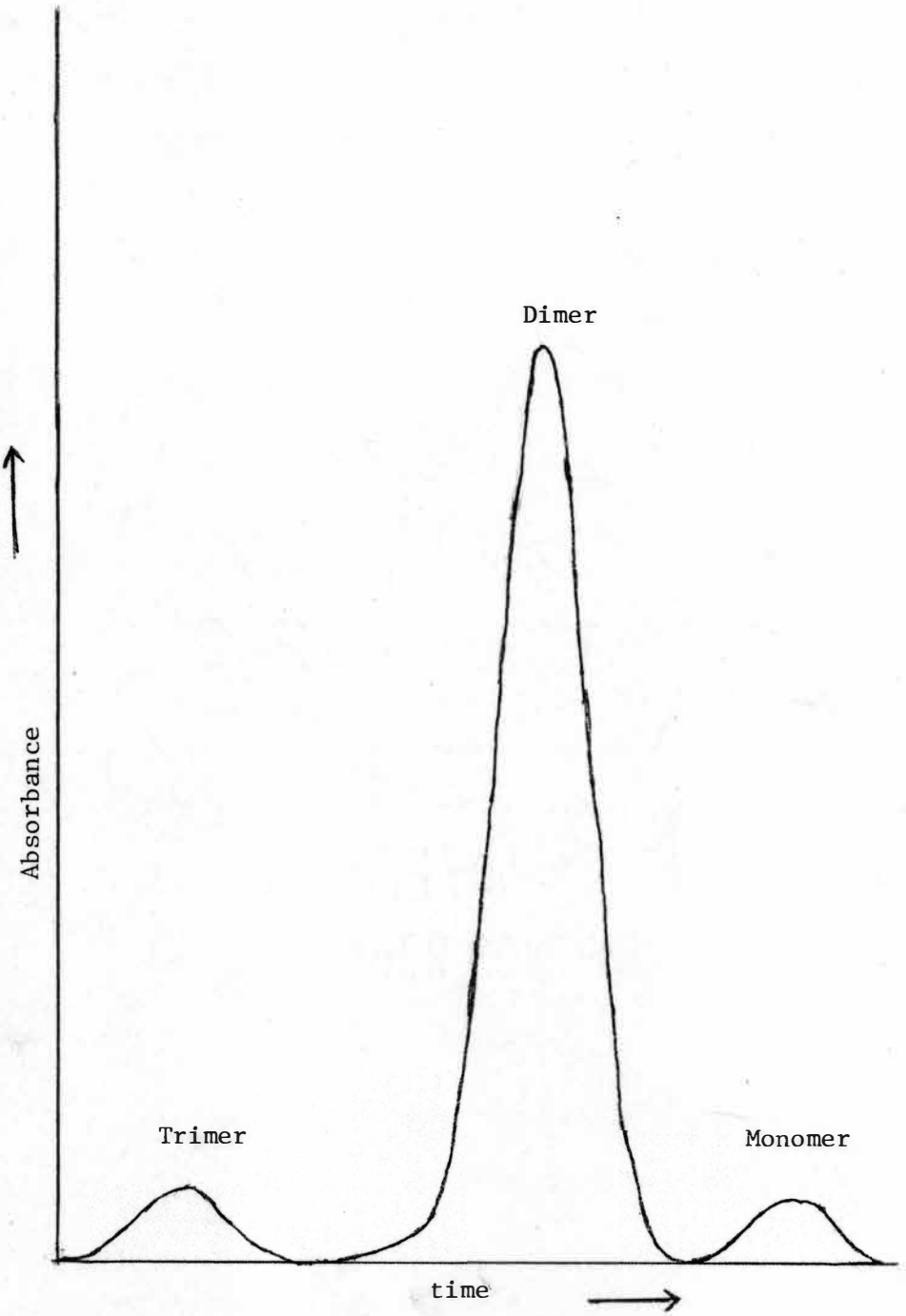


Figure 9. A Typical Gel Permeation Chromatogram

added at a slow flow rate from the reservoir. After a while the flow rate was adjusted to allow a small overflow.

After 24 hours of flow, the effluent was collected in test tubes placed in the fraction collector. Normally, each fraction was collected for 30 minutes.

Absorbance of the fractions collected was determined to detect presence of any oligomer in the fraction. A Beckman DB Spectrophotometer was used. The wavelength dial was set at 254 nm and the hydrogen lamp was used as the light source. Fractions which showed absorbance of 2 or more were kept aside and solvent was recovered from the others. Since, the separation was schieved for the difference in the size of the molecules, the larger trimer molecules emerged first and the monomer was eluted last. The first increase in the absorbance of 2 or more indicated emergence of trimer molecules. The time at which the first continued increase was observed varied with the samples. It was determined from the GPC previously that each sample had only monomer, dimer and trimer after solvent removal. Only three peaks, with the elution volumes equal to those of the monomer, dimer and trimer were observed.

The first decrease in the absorbance indicated separation between the trimer and other molecules. The fractions collected after that which had absorbance of 2 or more were mixed in a round bottom flask. The solvent and the monomer were removed by employing a rotating solvent evaporator. The viscous liquid which remained in the flask was transferred in the sample vial. Preparative column chromatography was

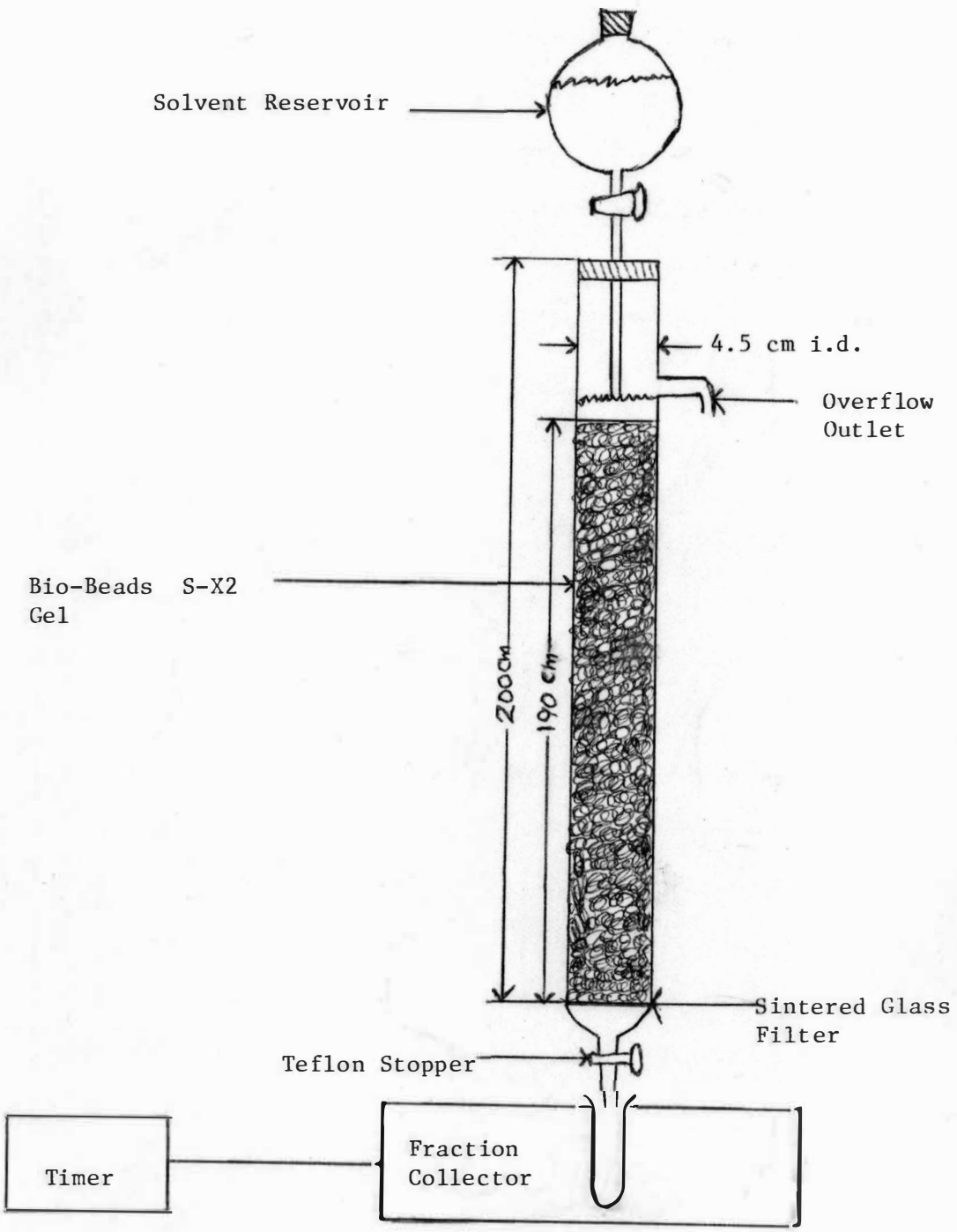


Figure 10. Preparative Column Chromatography

carried out for samples V, VIII, XIII and XIV. The samples which were collected after solvent evaporation were labeled as V_p, $VIII_p$, $XIII_p$, and XIV_p respectively. These samples were analyzed by GPC. Only one peak for each of these samples was obtained with elution volume corresponding to that of the dimer. This indicates that separation between trimer and dimer can be achieved by Preparative Column Chromatography with Bio-Beads S-X2 packing. These samples were used to obtain spectroscopic data that would help determine the structure of the dimer.

Infrared Spectroscopy

Infrared spectra were obtained for the samples of dimers obtained from the preparative column. Films were formed on a sodium chloride plate from a solution of each sample in tetrahydrofuran. The solvent was evaporated by warming the sodium chloride plate on a hot plate. A Beckman Infrared Spectrophotometer Model IR-8 was used to obtain these spectra. Spectra of indane and AMS were also obtained in the similar way. Indane spectrum showed a pattern of bands between 1667 cm^{-1} and 2000 cm^{-1}, characteristic of the ortho disubstitution. Since GPC did not show any presence of trimer or monomer in these samples, the spectra obtained were those of pure dimer. Data of the infrared bands are given in Tables 5, 6, 7, 8 and 9.

The sample V_p may contain some cyclic isomer as indicated by a band at 754 cm^{-1}, but other characteristic bands of cyclic isomer are absent. This sample contains mostly the unsaturated isomer. Since

Table 5
Infrared Spectrum of AMS

Wave Number in cm^{-1}	Strength*	Assignment
3049	M	Stretch due to =C-H
3003	M	Aromatic C-H stretch
2959	S	
2924	M	Asymmetric C-H stretch
2857	S	Symmetric CH_3 stretch
1942	W	Aromatic monosubstitution
1869	W	
1770	W	
1724	M	
1600	M	Isolated C=C band
1493	S	Aromatic Pattern conjugated C=C
1471	M	
1439	S	
1375	M	$-CH_3$ group bending vibration
895	S	Terminal methylene group
752	S	Ortho disubstitution

* S = Strong, M = Medium, W = Weak

Table 6
Infrared Spectrum of Indane

Wave Number in cm^{-1}	Strength*	Assignment
3012	W	Aromatic C-H stretch
2915	M	
1942	W	Ortho disubstitution
1695	S	Pattern
1592	M	Aromatic pattern,
1471	S	Conjugated C=C
1449	S	
1152	M	Aromatic ortho disubstitution pattern
746	S	Ortho Disubstitution

* S = Strong, M = Medium, W = Weak

Table 7
Infrared Spectrum of Sample V_p

Wave Number in cm^{-1}	Strength*	Assignment
3067	M	Stretch due to =C-H
3030	M	
2959	S	Aromatic C-H stretch
2925	S	Assymetric $-CH_3$ stretch
2865	M	Symmetric $-CH_3$ stretch
1957	W	Monosubstitution Pattern
1869	W	
1805	W	
1727	M	
1600	S	Isolated C=C band
1495	S	Aromatic Pattern
1481	M	Conjugated with C=C
1445	S	
1387	M	$-CH_3$ group bending vibration more than one group
1364	M	
1183	W	Indane characteristic bands absent
1156	W	
754	S	Ortho disubstitution
696	S	Monosubstitution

* S = Strong, M = Medium, W = Weak

thermodynamically, the formation of cis isomer is very unlikely, this unsaturated isomer is probably trans. Absence of a strong band at 885-895 cm^{-1} rules out presence of terminal methylene group. Therefore, terminal isomer is absent in the sample V_p.

Sample $VIII_p$ contains cyclic isomer as shown by the presence of bands characteristic to indane structure. Also absence of monosubstitution pattern between 1667 cm^{-1} and 2000 cm^{-1}, and 1600 cm^{-1} band for isolated C=C rules out the presence of unsaturated isomer.

Sample $XIII_p$ may contain some cyclic isomer as indicated by the presence of bands at 1176 cm^{-1} and 752 cm^{-1}, but other characteristic bands of cyclic isomer are absent. This sample may largely contain unsaturated isomer. Absence of a strong band at 885-895 cm^{-1}, rules out the presence of a terminal methylene group. Therefore, terminal isomer is absent. Since thermodynamically, the formation of cis isomer is unlikely, this unsaturated isomer is probably trans.

Sample XIV_p contains a large amount of cyclic isomer as shown by the presence of bands characteristic to indane structure. Also absence of monosubstitution pattern between 1667 cm^{-1} and 2000 cm^{-1}, and 1600 cm^{-1} band for the isolated C=C rules out the presence of unsaturated isomer.

Observations in Table 11 may help to understand the formation of different isomers and their dependence on the concentrations of the reactants.

Table 8
Infrared Spectrum of Sample $VIII_p$

Wave Number in cm^{-1}	Strength*	Assignment
3067 3030	Absent Absent	NO =C-H group
2959	S	Aromatic -C-H stretch
2865	M	Asymmetric $-CH_3$ stretch
1942 1835 1724	W W S	Weak Monosubstitution pattern. The pattern compares with that of Indane.
1600	Absent	No isolated C=C
1592 1493 1439	M M M	Aromatic pattern. No Conjugated C=C.
1361	W	CH_3 group bending vibration
1170 1117	S W	Bands similar to ones for indane
755	S	Ortho disubstitution
697	S	Monosubstitution

* S = Strong, M = Medium, W = Weak

Table 9
Infrared Spectrum of Sample $XIII_p$

Wave Number in cm^{-1}	Strength*	Assignment
3049	M	Stretch due to =C-H
3003	M	Aromatic C-H stretch
2959	S	
2924	M	Asymmetric C-H stretch
2857	S	Symmetric CH_3 stretch
1942	W	Aromatic Monosubstitution
1869	W	
1770	W	
1724	M	
1600	S	Isolated C=C band
1493	S	Aromatic pattern conjugated C=C
1471	M	
1439	S	
1379	M	$-CH_3$ group bending vibration more than one group
1370	M	
1361	M	
1176	M	Indane characteristic band, less intense
752	S	Ortho disubstitution
697	S	Monosubstitution

* S - Strong, M = Medium, W = Weak

Table 10
Infrared Spectrum of Sample XIV_p

Wave Number in cm^{-1}	Strength*	Assignment
3049	V weak	No = C-H group
2941	S	Aromatic C-H stretch
2882	M	Asymmetric $-CH_3$ stretch
1942	W	Ortho Substitution pattern, similar to one for indane
1852	W	
1718	S	
1600	Absent	No isolated C=C
1488	M	Aromatic pattern conjugated C=C bonds
1471	M	
1439	S	
1361	M	More than one CH_3 group Bending vibration
1176	M	Bands similar to those in indane spectrum
1117	W	
755	S	Ortho Disubstitution
697	S	Monosubstitution

* S = Strong, M = Medium, W = Weak

Table 11
Results from Infrared Spectra

SAMPLE	(INITIATOR)/(MONOMER)	PREDOMINANT ISOMER
V_p	0.3	Trans Unsaturated
$XIII_p$	0.5	Trans Unsaturated
XIV_p	0.8	Cyclic
$VIII_p$	1.2	Cyclic

Ultraviolet Spectroscopy

Ultraviolet spectra were obtained for Samples Vp, $VIII_p$, $XIII_p$ and XIV_p. These are the samples of dimers as obtained from the preparative column. Ultraviolet spectra were also obtained for the monomer and indane for comparison purpose. All spectra obtained were dilute solutions of each in methyl alcohol. A Cary-Model 14 Spectrophotometer with hydrogen source was used for this purpose. A matched pair of 10 mm x 10 mm quartz cells were used to obtain these spectra.

Table 12
Data Obtained from Ultraviolet Spectra

SAMPLE	CONCENTRATION g/l	A_{max}	λ_{max} nm	ϵ_{max} * liter $mole^{-1}$ cm^{-1}
V_p	0.0101	0.630	248.65	14000
$VIII_p$	0.0448	0.440	247.35	2500
$XIII_p$	0.0107	0.770	248.00	15000
XIV_p	0.0629	0.650	246.50	2400
Indane	0.1110	0.620	273.53	1300
AMS	0.0114	0.860	253.51	18000

* ϵ = molar absorptivity

The spectra of samples V_p and $XIII_p$ indicated values of ϵ_{max} comparable to that of the monomer. This may be an indication that these samples contain a large amount of unsaturated isomer, 2,4-diphenyl-4-methyl-2-pentene, which has a part of its structure similar to that of the monomer. The spectra of samples $VIII_p$ and XIV_p showed smaller values for ϵ_{max}. These values are higher than that obtained for indane, though the spectra obtained are not similar to those of pure indane or of the cyclic isomer.[23]

Mass Spectroscopy

Mass spectroscopic data were obtained for the samples of dimers

obtained from the preparative column chromatography. A DuPont model 21-490B Mass Spectrometer, with an electron impact of 70 eV, was used for this purpose. The peak obtained at m/e = 86 was chosen as a base peak and relative intensities were calculated for various m/e ratios. Data are given in Tables 13, 14, 15 and 16.

From the data obtained a few observations are significant. For samples V_p and $XIII_p$, more intense peaks are obtained for m/e = 221 and m/e = 76. These are due to loss of $-CH_3$ and a benzene molecule. For samples $VIII_p$ and XIV_p, the intensities for the above m/e are lower, but intensity for m/e = 103 is greater.

The large intensity of the peak at m/e = 76 for samples V_p and $XIII_p$, support the evidence obtained by other analyses that these samples contain a large amount of unsaturated isomer. The unsaturated isomer has two monosubstituted benzene rings as compared to only one for the cyclic isomer. So the possibility for a benzene ring being fragmented is higher for the unsaturated isomer.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic spectra were obtained for the samples of the dimer obtained from the preparative column, monomer and indane. Carbon tetrachloride was used as a solvent. The spectra of samples of dimer were complicated and it was difficult to make group assignment for every peak obtained. The peak for benzene around δ = 7.19 ppm was sharp and characteristic. But a number of peaks were obtained around δ = 3.7 ppm δ = 2.3 ppm δ = 1.9 ppm. This indicates the presence of

Table 13
Partial Mass Spectral Data for Sample V_p

m/e	I %	m/e	I %
236	19.3	118	14.6
222	24.0	117	22.2
221	98.6	116	5.3
191	8.0	115	15.9
186	5.3	114	0.6
179	4.0	106	4.5
178	5.3	105	30.6
165	5.3	104	8.0
159	5.3	103	33.3
144	6.7	102	8.0
143	4.5	101	6.7
135	2.1	93	5.3
132	6.7	92	14.6
131	2.6	91	78.6
130	1.4	89	12.0
129	9.3	88	5.3
128	17.3	87	25.3
127	5.3	86	100.0
121	10.6	85	30.6
120	6.7	79	6.7
119	44.4	78	17.3
		77	28.0
		76	92.0

Table 14
Partial Mass Spectral Data for Sample $VIII_p$

m/e	I %	m/e	I %
236	2.2	115	5.2
222	3.3	114	0.8
221	15.6	106	2.0
191	1.9	105	16.7
186	5.0	104	2.1
179	0.7	103	78.7
178	0.9	102	1.1
165	0.3	101	1.7
159	1.8	93	2.8
144	1.9	92	3.9
143	2.5	91	17.2
135	2.8	89	2.5
134	2.3	88	6.7
132	3.2	87	37.5
121	1.7	86	100.0
130	1.8	85	30.0
129	3.6	84	7.2
128	2.3	83	17.7
127	1.9	82	11.5
121	11.7	81	0.7
120	3.8	79	3.5
119	32.8	78	17.8
118	7.9	77	19.6
116	0.8	76	30.2

Table 15
Partial Mass Spectral Data for Sample $XIII_p$

m/e	I %	m/e	I %
236	8.6	115	13.7
222	11.7	114	3.5
221	58.2	106	4.8
191	4.3	105	37.9
186	8.2	104	5.5
179	3.2	103	18.9
178	3.1	102	5.1
165	3.1	101	7.8
159	3.4	93	7.8
144	3.4	92	7.8
143	24.1	91	37.9
135	3.4	89	8.6
134	1.5	88	17.6
132	6.2	87	98.3
131	3.1	86	100.0
130	2.4	85	81.0
129	6.5	84	7.8
128	8.2	83	25.9
127	3.1	82	10.0
121	18.1	81	2.1
120	10.0	79	5.0
119	39.3	78	34.1
118	15.1	77	39.3
117	39.3	76	99.8

Table 16
Partial Mass Spectral Data for Sample XIV_p

m/e	I %	m/e	I %
236	2.2	115	4.9
222	2.7	114	0.5
221	14.7	106	1.7
191	1.4	105	15.3
186	5.8	104	2.7
179	0.9	103	81.0
178	0.9	102	1.7
165	0.5	101	2.2
159	1.4	93	3.2
144	1.4	92	3.6
143	1.4	91	14.7
135	1.7	89	2.7
134	2.2	88	5.4
132	2.7	87	33.8
131	1.4	86	100.0
130	1.4	85	29.3
129	2.7	84	6.3
128	2.7	83	19.3
127	1.4	82	9.4
121	12.1	81	0.9
120	3.6	79	2.7
119	34.7	78	13.0
117	6.7	77	13.9
116	1.4	76	35.2

three different types of protons -CH, $-CH_2$ and $-CH_3$. From the integration data obtained it was difficult to assign a certain number of protons from each of two predominant isomers.

Gas Chromatography

Attempts were made to separate isomers of the dimer by gas chromatography using SE-30 column. Separation was inadequate for quantitative determinations.

DISCUSSION

Experimental Synthesis

A Lewis acid was chosen rather than a Bronsted acid for polymerization. Unlike the Bronsted acid,[24,12] Lewis acids were not reported to give side products containing oxygen. The oxygen side products were reported to result from the incorporation of the Bronsted acid in the terminating polymer. In particular, stannic chloride was chosen for its low activity [12] relative to other Lewis acids for the purpose of keeping the DP to a minimum.

Within the limits that thermodynamics places on the polymerization process (i.e. equilibrium composition), the solvent can influence the polymerization. The nonpolar solvent carbon tetrachloride was used to restrict the lifespan of the propagating chains. Using a solvent with a high dielectric constant would have only helped to stablize the carbonium ion and thereby increase the lifespan and possibly the DP of the oligomer.

The methods applied were successful as proven by the production of low DP polymers. Considerably more cyclic endgroups were formed when carbon tetrachloride was used as solvent compared to the polymer formed when benzene was used as solvent.[9]

Gel Permeation Chromatography

A soft gel like Bio-Beads S-X2 with average particle size of 75 A and Poragel/60A and Poragel/100 A; which have average pore size of

60A and 100A respectively, in combination offer a good column to separate low molecular weight oligomers of AMS. Best separation was achieved when the sample was passed through 100A gel first then 75A and then 60A gel. Although a complete separation took from seven to eleven hours depending upon the flow rate, it was essential to use low flow rates to prevent the gel from deforming. Long columns are helpful to separate oligomers up to the pentamer. High detector sensitivity was useful in determining small amounts of trimer and the monomer. Those fractions obtained from the preparative column, which do not contain either the trimer or the monomer can be mixed and pure samples of dimer can be obtained.

Infrared Analysis

Infrared analysis is very useful in determining qualitatively the predominant isomer in a given sample. The pattern of bands between 1700 cm^{-1} and 2000 cm^{-1} gives a very good indication of whether the benzene rings are monosubstituted or ortho disubstituted. The pattern in this region gave weak bands at 1957 cm^{-1}, 1869 cm^{-1}, 1805 cm^{-1} and a medium band at 1727 cm^{-1} for monosubstituted benzene. For an ortho disubstituted benzene weak bands at 1942 cm^{-1}, 1852 cm^{-1} and a strong band at 1718 cm^{-1} were observed.

These patterns do not follow exactly the same pattern normally observed for mono and ortho disubstituted benzene.[26] This may be due to the fact that for cyclic isomer one benzene ring is monosubstituted and the second benzene ring is ortho disubstituted. For samples

of dimer containing a large amount of unsaturated isomer with two monosubstituted benzene rings, a small amount of cyclic isomer could alter the pattern considerably. In the region around 1370 cm^{-1} more than one peak indicates presence of more than one methyl group. These methyl groups are less hindered in the unsaturated isomer than in the cyclic isomer. This results in stronger and distinct peaks for the unsaturated isomer around 1370 cm^{-1}.

Ultraviolet Spectroscopic Analysis

Ultraviolet spectra indicated shifts in the wavelength for various samples. The molar absorptivity was higher for two samples of dimer along with that of the monomer. The unsaturated isomer structure has a portion of it similar to the structure of the monomer. This accounts for comparable molar absorptivity for the two samples. The cyclic structure does not have a monomeric structure and therefore has a comparatively low molar absorptivity. In the cyclic isomer the electrons are less delocalized.

These values of molar absorptivities and the wavelengths for peak maxima led to the inference that samples V_p and $XIII_p$ have a large amount of dimer which is unsaturated. Samples $VIII_p$ and XIV_p have the dimer which is predominantly cyclic.

Mass Spectroscopic Analysis

Mass spectroscopic data for samples V_p and $XIII_p$ gave intense peaks for m/e = 221 and m/e = 76. These are due to the loss of

of methyl and benzene groups. These two groups can be relatively easily fragmented from the unsaturated isomer.

The low intensities of such peaks for samples $VIII_p$ and XIV_p indicate less of the unsaturated isomer in these samples.

Nuclear Magnetic Resonance Analysis

Nuclear magnetic resonance spectroscopic data did not give more qualitative information. The mixture of isomers may be the cause for the complicated spectra.

SUGGESTIONS FOR FURTHER STUDY

Pure samples of the dimer can be obtained by using the preparative column packed with Bio-Beads S-X2 gel. Heat of combustion can be determined by using a calorimeter and from the data obtained heat of polymerization can be determined for the dimer of AMS. This value of heat of polymerization will be for a mixture of isomers. It may be possible to obtain a quantitative data on the composition of the isomers by either chemical methods such as hydrogenation or by gas chromatography using a suitable packing material.

Once the composition of isomers is obtained, heat of polymerization obtained can be assigned accurately for a particular isomer. The heats of formation seem to be quite different for the unsaturated isomer and the cyclic isomer due to structural differences.

SUMMARY AND CONCLUSIONS

(1) Using anhydrous stannic chloride as initiator and carbon tetrachloride as solvent, AMS can form a large amount of dimer near ceiling temperature, i.e. 60°C.

(2) The dimer formed under the above conditions predominantly contains the unsaturated isomer at low initiator-to-monomer ratios. The yield of the dimer formed increases with the initial concentration of the monomer.

(3) The sample of the oligomers can be separated by a 4.5 cm X 200 cm preparative column packed with Bio-Beads S-X2 gel, to obtain pure samples of the dimer.

(4) Gel Permeation Chromatography can be used for determining the presence of each of the oligomers. The columns packed with Poragel/100A, Bio-Beads S-X2 (average pore size 75A) and Poragel/60A gels, each of about equal length give the best separation. An ultraviolet detector can be used for this purpose.

(5) A combination of gel permeation chromatography, ultraviolet and infrared spectroscopy can be used to determine the structure of the predominant isomer of the dimer.

REFERENCES

1. Roberts, D.E. and Jessup, R.S., J. Research. Natl. Bur. Standards. 46, 11 (1951).

2. Brown, C.P. and Mathieson, A.R., J. Chem. Soc. 3507 (1958).

3. Cotton, B.J., Cowie, J.M.G. and Bywater, S., Makromol. Chem. 86 116 (1965).

4. Joshi, R.M. and Zwolinski, B.J., Macromolecules, 1, 25 (1968).

5. McCormick, H.M., J. Polym. Sci., 25, 488 (1957).

6. Bergman, E., Taubadel, H. and Weiss, H., Ber., 64, 1493 (1931).

7. Dainton, F.S. and Tomlinson, R.H., J. Chem. Soc. 151 (1953).

8. Petropoulos, J.C. and Fisher, J.J., J. Amer. Chem. Soc., 80, 1938 (1958).

9. Humbert, D.K., Master's Thesis, Western Michigan University, (1972) p. 42.

10. Adams, L.M., Lee, R.J. and Wadsworth, F.T., J. Org. Chem. 24, 1187 (1959).

11. Evans, A.G. and Polanyi, M., Nature, 152, 738 (1943).

12. Ham, G.E., Ed. "Vinyl Polymerization, Part II," Marcel Dekker, New York, (1969), pp. 231-304.

13. Dainton, F.S. "Cationic Polymerization and Related Complexes". Academic Press, New York, (1953), p. 105.

14. Bawn, C.E.H., Ed., "Macromolecular Science, Physical Chemistry, Series One, Volume 8," University Park Press, London, (1972) p. 73.

15. Cheradame, H., Hung, N.A. and Sigwalt, P., Compt. Rend. 268 476, (1969).

16. Branchu, R.E., Cheradame, H. and Sigwalt, P., Compt. Rend. 268 1292 (1969).

17. Bawn, C.E.H., Ed., op. cit. p. 78.

18. Eley, D.D. and Seabrooke, A.J., J. Chem. Soc. 2231 (1964).

19. Humbert, D.K., op. cit., p. 5.

20. Kirkland, J.J., Ed. "Modern Practice of Liquid Chromatography", Wiley-Interscience, New York, (1971), pp. 249-262.

21. Walker, J.Q., Jackson Jr., M.T. and Maynard, J.B., "Chromatographic Systems; Maintainance and Troubleshooting". Academic Press, New York, (1972), pp. 22-46.

22. Perkin-Elmer Corp., "Manual for Liquid Chromatograph Model 1250." Norwalk, Connecticut, (1972).

23. Sadtler Research Laboratories, Catalog of Ultraviolet Spectrums, #21282, Philadelphia, Pennsylvania.

24. Svob, A., Déur-Siftar, D.J. and Jarm, V.J., Chromatogr. 38, 326 (1968).

25. Humbert, D.K., op. cit., p. 24.

26. Dyer, J.R., "Applications of Absorption Spectroscopy of Organic Compounds", Prentice Hall, Inc. (1965), p. 52.