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Heats of Combustion of Alpha-Methylstyrene Oligomers

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HEATS OF COMBUSTION
OF ALPHA-METHYLSTYRENE OLIGOMERS

by

Dale Keith Humbert

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

Western Michigan University
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INTRODUCTION

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

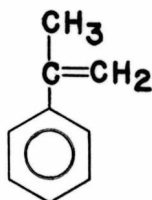


Figure 1. α -Methylstyrene

The first quantitative work was done by Roberts and Jessup.¹ Their values were more positive than those theoretically calculated by Flory² and compared with ΔH_p data of other systems. This was not totally unexpected and could be satisfactorily explained on the basis of steric hindrance and loss of resonance energy of conjugation. This steric hindrance arose from "head-to-tail" polymerization of the 1,1-disubstituted ethylene structure.³ Their data also displayed a ΔH_p dependence on the degree of polymerization (DP). Roberts and Jessup's explanation that the DP was the predominant variable in the functionality of ΔH_p was not completely accepted. Since Roberts and Jessup first published their work in 1951, there have been several reports in the literature with new values for ΔH_p and new explanations for the apparent DP dependence.^{4, 5, 6, 7, 8} There are discrepancies in the more recently reported ΔH_p data and, in general, the differences were not within the range of experimental error. All of these studies were either incomplete, conjectural or included a variety of approximations and corrections.

The original outline for this thesis proposed an experimental method for finding the ΔH_p of oligomeric α -methylstyrene (AMS) without applying major corrections. The plan of attack called for synthesizing very low molecular weight oligomers and analyzing the monodisperse samples. By analyzing only low molecular weight monodisperse polymers, assumptions involving molecular weight distribution and glass transition contributions would be unnecessary. However, the unavailability of a preparative gel permeation chromatography (GPC) instrument for our use prevented separation of the oligomer into the pure monodisperse samples. Therefore, analytical GPC was substituted which dictated that corrections involving the molecular weight distribution would have to be applied to the ΔH_p data.

THEORY

The structure of AMS lends itself admirably to the study of variables affecting the enthalpy and entropy of polymerization. The factors that will affect the entropy are as follows. The monomer unit, a 1,1-disubstituted ethylene, is selective as to where and how the ethylene group may be attacked.³ The steric interference of the methyl and phenyl group severely limit the possible orientations of an attacking ion or radical. This is especially the case if the attacking species is an AMS ion or radical. After the first few monomer units have added, the orientation of subsequent adding monomer units is even more restricted. That is, the monomer unit will have to orient itself specifically to the propagating polymer species. The propagating polymer becomes bulky, rigid and inhibited in its ability to orient itself to the monomer.

The enthalpy will be affected primarily by the stability of the resulting polymer. The AMS polymer is a very strained species. As can be seen by examining space-filling models of the polymer, the possible conformations are limited and those formed have abnormal bond angles or lengths. The steric strain becomes more predominant as the chain grows.

As evidence of the phenomenon described above, it has been suggested that ΔH_p becomes more positive with increasing DP.¹ This would indicate that the longer the chain becomes, the less energetic the propagating reaction is. Roberts and Jessup have also predicted that there is a limiting factor to this process. That is, ΔH_p will reach a limiting value. This is exactly what one would expect on the basis of the preceding argument. At some point in the polymerization the polymer chain will no longer be affected by

additional monomer units. The subsequent additions cannot significantly affect the polymer's ability to rotate or further restrict the number of permissible orientations of the adding monomer unit. The steric strain will also reach a limiting situation.

The preceding argument should be supported by a DP-dependent entropy of polymerization. One purpose of this study is to explore the possibility that the enthalpy of polymerization is also a function of the DP and, in particular, a function of the reciprocal of DP, (fn($1/DP$)).

EXPERIMENTAL

Synthesis of α -Methylstyrene Oligomers

In an attempt to obtain a variety of oligomers with different average molecular weights and molecular weight distributions, the syntheses were carried out with various initiator-to-monomer ratios (varying from 1.5:1 to 0.5:1) and reaction temperatures (5.5-60 °C), but essentially constant dilution factors were maintained (see Table 1).

Carbon tetrachloride was the solvent for reactions at 5.5 and 60 °C, and benzene was the solvent at all other temperatures. Anhydrous stannic chloride was used as an initiator and the reactions were quenched with a dilute hydrochloric acid solution (approximately 0.1 M).

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 distillate was rejected and the last 100 ml of solvent was left in the flask. The solvent was used within one week of its distillation.

Each synthesis was carried out in an integrated distillation-reaction apparatus (IDRA, Figure 2). Except for the ball joints which had little or no lubricant, the ground glass joints of the IDRA were sealed with poly(tetrafluoroethylene) sleeves. A minimum of silicone lubricant was used, because both the AMS and the solvents dissolved it.

Once the IDRA was sealed, it was purged with high purity dry nitrogen for 24 hr before each batch of reactions. A batch was limited to five reactions or five consecutive days. After each batch

Table 1. Conditions for
Synthesis of α -Methylstyrene Oligomers

Sample	Reaction Temp, °C	Monomer Molarity ^a	Reaction time, hrs	$\frac{[\text{Initiator}]}{[\text{Monomer}]}$
II	59.6-60.2	0.84	5.2	1.25
III	59.8-60.2	0.92	6.1	1.00
IV	59.7-60.2	0.93	5.1	0.76
VI	49.6-50.2	0.71	7.0	1.50
VII	49.5-50.0	0.83	5.0	1.25
VIII	49.5-50.5	0.94	5.1	1.00
XII	39.5-40.1	0.87	5.7	1.20
XIV	39.0-40.0	0.98	5.3	0.75
XV	39.0-40.0	1.00	5.1	0.51
XVI	29.5-30.2	0.72	4.7	1.50
XVII	29.5-30.1	0.85	5.6	1.25
XVIII	29.5-30.5	0.96	5.3	1.00
XIX	29.5-30.5	1.02	6.0	0.51
XX	29.8-30.5	0.98	4.5	0.84
XXI	14.9-15.1	0.98	5.3	1.00
XXII	9.9-10.1	0.98	5.4	1.00
XXIII	5.4-5.6	0.99	6.6	1.00
XXIV	19.5-20.5 ^b	0.97	5.3	1.00

^aThe concentrations were calculated for the respective reaction temperature.

^bAt one time the temperature regulator failed and the temperature dropped to 6.5 °C but was immediately returned to 20 °C. Total time lapse involved was 45 minutes to an hour. However, this sample may have an abnormal molecular weight distribution as a result of the temperature fluctuation and will not necessarily have thermodynamic properties that are consistent with the other samples.

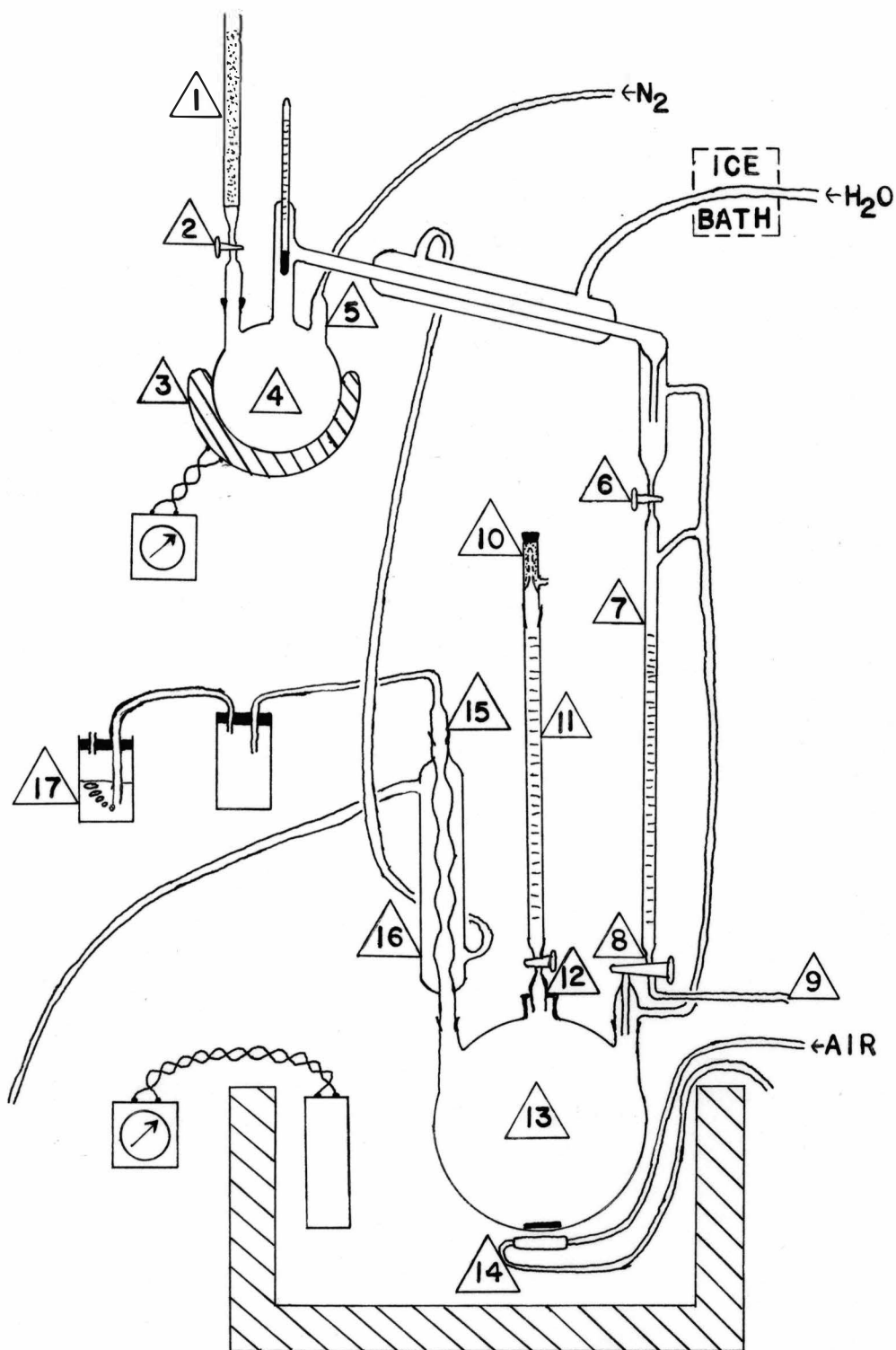


Figure 2. Integrated Distillation-Reaction Apparatus

the IDRA was disassembled and cleaned. Each reaction was performed in a clean two liter, 3-neck flask and reflux condenser ($\triangle 13$ and $\triangle 16$, Figure 2).

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

After the monomer had refluxed in the presence of the amber colored anion for about one hour, it was allowed to distill into the 50 ml graduated buret $\triangle 7$. First the stopcock $\triangle 6$ was opened and the 3-way stopcock $\triangle 8$ was closed. The first 10 ml of AMS was discarded through outlet $\triangle 9$. After the desired amount of AMS was collected in $\triangle 7$, the distillation was discontinued and $\triangle 6$ was closed. Here it was necessary to adjust the nitrogen flow because of temperature changes and, consequently, the pressure changes within the flask $\triangle 4$.

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

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 solution was washed several times with distilled water, until the evolution of gas ceased. The product mixture was allowed to stand over calcium chloride for 18 hr and then filtered through filter paper. The solvent was removed by employing a rotating evaporator with the flask partially immersed in a steam bath. The remaining viscous oil was again filtered with filter paper under a dry nitrogen atmosphere. The final product was then 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 samples.

Analysis of Oligomers

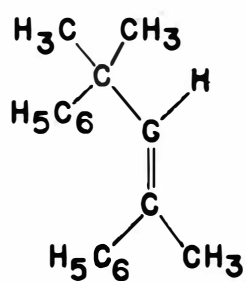
Gas chromatography

Gas chromatography was used to determine the relative isomer concentration of the dimers. The gas chromatograph used in the analysis was an F & M, model 720, dual column, programmed-temperature instrument with a thermal conductivity detector. It was reported by Svob, et. al.⁹ that a gas chromatographic column (Apiezon L, 10 %; Chromasorb W, 80-100 mesh; 1/8 in. by 6 ft column; temperature 200 °C; carrier gas flow rate of 20 ml/min; carrier gas helium; sample size 3-10 μ l) could be used to separate and identify the isomeric forms of the dimer shown in Figure 3.

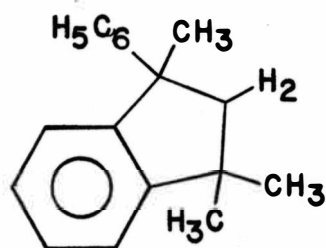
The same column was used to detect any solvent impurities in the final product. For the solvent detection, a column temperature of 100 °C and a gas flow rate of 52 ml/min were maintained. Solutions of pentane and the product were prepared on a Mettler balance. The weight ratios were approximately 1:1. Using the peak areas and equation 1, the percent solvent in the product was estimated.

$$\%SP = \left(\frac{PAS}{PAP} \right) \left(\frac{MP}{MS} \right) 100 \quad (1)$$

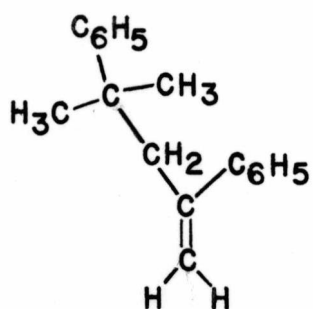
PAS is the peak area of solvent, PAP is the peak area of pentane, MP is the mass of pentane in the solution and MS is the mass of product in the solution. Those samples which were shown to contain any trace of solvent were set aside. A quantitative value for the amount of solvent in a sample could not be obtained for less than 0.01 %. In order to calculate the amount of solvent in the sample,



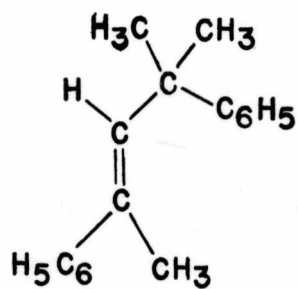
Isomer I
"cis"



Isomer II
"cyclic"



Isomer III
"terminal"



Isomer IV
"trans"

Figure 3. Isomers of Dimeric α -Methylstyrene

the attenuation had to be increased to keep the pentane peak on scale. However, baseline resolution was excellent at very low attenuation and, although in some cases the solvent could be detected, the solvent peak disappeared at high attenuations. All the samples listed in the tables 1, 2, 4, 5, 7 and 8 had no trace of solvent at low attenuation.

In determining the relative isomer concentration, triangles were constructed to approximate the area of the peaks. The peaks were apparently Gaussian in shape which made the triangles isosceles. The areas of the triangles were then calculated. The relative percentage of each isomer is shown in Table 2.

Infrared spectroscopy

A typical infrared (IR) spectrum (sample XVI) is reproduced in Figure 4. Figure 5 shows the characteristic spectra of the substituted phenyl ring. All the peaks can be explained on the basis of a mixture of molecular structures. The isomers II and IV pictured in Figure 3 were assumed to be the principal components of the mixture.

Bromination analysis

Further quantitative data on the degree of unsaturation was desired. To that end, coulometric analysis was employed. Fifteen mg or approximately 6.0×10^{-4} moles of sample was dissolved in a solution containing 15 ml of 10 % aqueous potassium bromide and 65 ml of methanol. With the coulometric technique, the addition reaction with bromine was so slow that any data obtained would be questionable.

Table 2. Estimated Percentage of
Each Isomer in the Dimer

Sample	Isomer I	Isomer II	Isomer III	Isomer IV
II	-	92.3	-	7.7
III	-	93.0	-	7.0
IV	-	93.0	-	7.0
VI	1.2	49.0	2.0	48.0
VII	1.0	34.0	3.3	62.0
VIII	0.6	58.0	-	41.5
XII	0.7	88.0	trace	11.0
XIV	1.0	58.0	trace	41.0
XV	0.8	46.0	-	53.0
XVI	1.6	58.0	-	41.0
XVII	1.0	49.0	-	50.0
XVIII	1.2	44.5	trace	54.3
XIX	0.8	58.7	trace	40.5
XX	0.1	42.9	trace	57.0
XXI	-	55.7	-	44.3
XXII	?	47.2	?	52.7
XXIII	?	80.0	?	20.0
XXIV	0.5	50.0	-	49.0

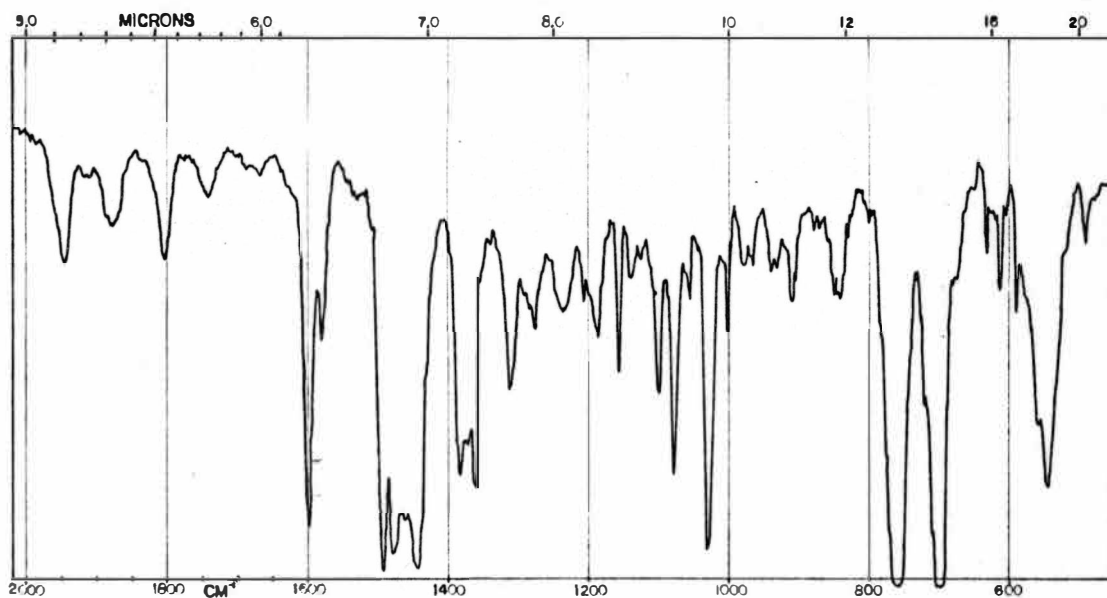
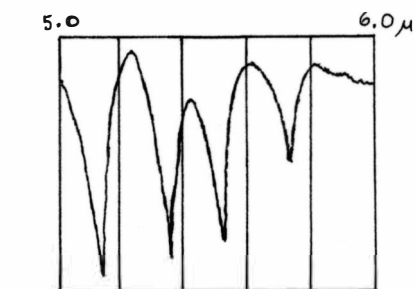
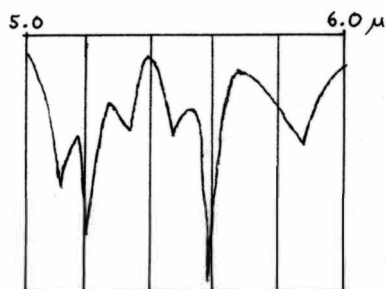


Figure 4. Typical Infrared Spectrum of α -Methylstyrene Oligomer



Mono-Substituted Phenyl



Ortho-Disubstituted Phenyl

Figure 5. Characteristic Infrared Peaks of Monosubstituted and Ortho-Disubstituted Benzene¹⁰

Qualitative brominations of a few samples in ethanol were more successful than the coulometric method. Concentrated solutions were prepared with samples II, IV, XVI, XXII and XXIII. It was found that samples II, IV and XXIII discolored a very small amount of bromine water and samples XVI and XXII discolored considerably more. This experiment was in semi-quantitative agreement with the gas chromatography data.

Vapor phase osmometry

The number average molecular weights (\overline{M}_n) were determined by vapor phase osmometry. A Hitachi Perkin-Elmer model 115 Molecular Weight Apparatus was used. Because of the instrument's extreme sensitivity to radio waves, a Faraday cage was constructed for the instrument. However, the Faraday cage was not effective when radio station WMUK started to broadcast and measurements could be made only when the radio station was not radiating signals.

The procedure for the vapor phase osmometer instrument outlined in the instruction book supplied by Perkin-Elmer¹¹ was followed. In addition to the book's procedures, it was found that a stable zero reading was obtained only if the solvent had been injected no more than 18 hr and no less than 3 hr before the determinations were made. A new zero reading was taken before each determination rather than assuming one value for a given day. The changes in the zero reading were small but, nevertheless, measurable (less than two ΔR divisions). All determinations were run at 41.1 °C.

Four benzil solutions in benzene were used to calibrate the instrument. The benzil was supplied by Perkin-Elmer. The solutions were prepared on a microbalance, thereby allowing the

masses to be determined to the nearest 5.0×10^{-6} g. The calibration data are listed on Table 3.

The least squares values for the slope and intercept, presented in Table 3, were calculated using the origin as an experimental point four times. As previously mentioned, the zero point was determined before each ΔR was measured. It could be argued that the calibration curve should be forced through the origin, primarily because the zero reading (which was the origin on the ΔR versus molality plot) was the best known value. For a curve forced through the origin, the least squares formula was reduced to equation 2.

$$\text{slope} = \frac{\sum x_i y_i}{\sum x_i^2} = \frac{\sum \text{molarity}_i \times \Delta R_i}{\sum (\text{molarity}_i)^2} \quad (2)$$

From equation 2 the calculated value of the slope was 23842.6 ΔR /molality unit. A \bar{M}_n was calculated from both sets of slope and intercept data described above and the average value was reported. The difference in the resulting \bar{M}_n 's was always less than 0.1 molecular weight units (0.03 %).

The oligomer solutions, at least two of each sample, were prepared on a standard Mettler balance and stored in capped containers. In order to partially compensate for the loss of accuracy by not using the microbalance, the total volumes of the oligomer solutions were larger by a factor of two than those of the benzil solutions. The solutions were prepared no longer than 18 hr before their use, agitated whenever possible and allowed to stand overnight to insure homogeneity. There was a small weight loss between the time the solutions were prepared and the time they were used. If the weight loss was attributed entirely to the evaporation of benzene, the \bar{M}_n was changed by no more than an additional two molecular weight units (0.6 % to 0.3 %). The corrected average

Table 3. Calibration Data for
Vapor Phase Osmometer

Solution	ΔR	Molality $\times 10^3$
1	82.0	3.388
3	96.1	4.042
4	116.8	4.922
5	155.5	6.524

Slope = 23826.1 ΔR /molality unit

Intercept = 0.0822 ΔR

$$\sigma_y = 0.5$$

$$\sigma_m = 78.4$$

$$\sigma_b = 0.27$$

\overline{M}_n was 0.2 % different from the uncorrected average \overline{M}_n . From random samples, several aliquots of the same solution were taken for ΔR measurements and no difference in ΔR was found. This was considered adequate evidence for homogeneity.

The greatest discrepancies in any one sample's \overline{M}_n were between different solutions of the same oligomer. The average of the measured \overline{M}_n and standard deviation of the means for each sample are shown in Table 4.

Molecular weights and molecular weight distributions may be studied by fractionation of the polymer in non-solvents. The \overline{M}_n of the fractions may be determined by vapor phase osmometry. Samples II through XXI and XXIV were soluble in methanol which made fractionation difficult. Although fractionation of samples XXII and XXIII was not pursued, they were partially insoluble in ethanol.

Gel permeation chromatography

An effort was made to determine the molecular weight distribution (MWD) of two oligomer samples. Samples IV and XVI were sent to Cellomer Associates, Inc., Webster, N. Y., 14580, for GPC analysis. A two ml aliquot of sample dissolved in chloroform was injected into the GPC instrument. The sample solution had a concentration of 0.2 %. The injections passed through 12 feet of column with 60 Å packing at a chloroform flow rate of 0.30 ml/min. A conventional differential refractometer was used for detection. Three chromatograms of sample IV and two of sample XVI were obtained with different attenuations. The baseline resolution was very good. Each peak was traced on high quality paper. Overlapping peaks were assumed to be Gaussian in shape so that the hidden boundaries of the peaks could be drawn. The peak's shapes

Table 4. Number Average Molecular Weight and Average Degree of Polymerization of Oligomers

Sample	\overline{M}_n	σ_m	\overline{DP}	σ
II	329.7	2.45	2.790	0.021
III	317.9	0.22	2.690	0.002
IV	318.9	1.60	2.698	0.014
VI	331.0	1.93	2.801	0.016
VII	327.2	0.40	2.769	0.003
VIII	327.4	1.34	2.770	0.011
XII	324.1	2.35	2.742	0.020
XIV	333.2	1.73	2.819	0.015
XV	329.2	3.36	2.786	0.028
XVI	355.1	1.82	3.005	0.015
XVII	352.2	0.16	2.980	0.001
XVIII	350.9	2.34	2.969	0.020
XIX	353.6	1.04	2.992	0.009
XX	338.7	1.84	2.866	0.016
XXI	383.9	0.92	3.248	0.008
XXII	410.6	2.36	3.474	0.020
XXIII	508.6	3.47	4.304	0.029
XXIV	362.7	1.33	3.069	0.011

were then cut out and their mass determined on a Mettler balance. In this manner the relative peak areas were determined.

There was one correction that could have been applied to the peak areas involving the detection by differential refractometry. For large molecular weight polymers, the difference in refractive index arising from various chain lengths has been considered negligible. However, for dimer, trimer, etc., the difference of one or two monomer units was significant enough to affect the refractive index. The refractive index-DP least squares equation with DP as the independent variable was determined from the refractive index of each sample except samples II, III, IV and XXIII. An estimate of the refractive index of monodisperse oligomers was calculated from the least squares equation. The calculated refractive indices were 1.5646, 1.5757, 1.5869, 1.5980 and 1.6091 for dimers, trimers, tetramers, pentamers and hexamers, respectively. The refractive index of chloroform, 1.4439,¹² was subtracted from the refractive index of each oligomer listed above. The correction factors were calculated by taking the ratio of the oligomer minus chloroform refractive index difference to the dimer minus chloroform refractive index difference. This ratio was multiplied by the respective peak area. This correction was small and did not change the overall MWD pattern significantly. A calibration of the chromatogram was not carried out because of a lack of authentic samples and so the assignments of peaks were only guesses. The purpose of going through this exercise was to determine if such a correction would change the MWD pattern. The uncorrected relative peak areas and retention times are listed in Table 5. (The largest molecules are eluted first in GPC.)

Table 5. Relative Peak Areas of
Gel Permeation Chromatograms

Retention Time	Percent of Total Peak Area	
	Sample IV	Sample XVI
4 hr 46 min	-	0.78
4 hr 56 min	-	1.91
5 hr 8 min	2.48	7.54
5 hr 25 min	35.66	46.59
5 hr 52 min	53.36	43.17
6 hr 52 min	8.50	-

Heat of Combustion

The heat of combustion (ΔH_c) experiments were performed with a Parr, Series 1230, Model 1115, oxygen bomb calorimeter equipped with a Model 2611 adiabatic control system. The standard procedure for a liquid with a low vapor pressure was followed. Before each combustion the bomb was evacuated to the vapor pressure of water, then pressurized with twenty atmospheres of oxygen. Three to five minutes were allowed for the gases to mix, then the evacuation and pressurization process was repeated. After the final evacuation the volume of water in the bomb was reduced from 1.0 ml to approximately 0.5 ml. Once the system was assembled, it was allowed 10 to 15 minutes to equilibrate before any temperature readings were recorded. After the bucket temperature had stabilized for a 5 minute period of time, temperature readings were taken exactly 4 minutes before ignition, at ignition and 9 minutes after ignition. The change in temperature was taken as the final temperature minus ignition temperature. The uncertainty of the thermometer readings was ± 0.0005 °C and the readings were corrected with the chart supplied with the thermometer by Parr.

The calibration of the calorimeter was made with benzoic acid supplied by Parr and the energy of combustion taken as 6317.8 cal/g. Five samples of benzoic acid were used to determine the energy equivalent of the calorimeter system. The calibration results are listed in Table 6.

Table 6. Energy of Combustion Calibration
with Benzoic Acid

Experiment	Grams of Sample	ΔT , °C	Energy Equivalent, cal/deg
1	0.8735	2.317	2388.814
2	0.9954	2.640	2387.641
3	0.9740	2.5867	2385.534
4	0.9365	2.484	2387.335
22	0.8735	2.321	2385.150

mean = 2386.89 cal/deg

$\sigma_m = 0.68$

DISCUSSION

Discussion of Experimental Synthesis and Analysis

A Lewis acid was chosen rather than a Brønsted acid for a polymerization catalyst. Unlike the Brønsted acid,^{9, 13} Lewis acids were not reported to give side products with oxygen. The oxygen side products were reported to result from the incorporation of the Brønsted acid in the terminating polymer. In particular, stannic chloride was chosen for its low activity¹³ relative to other Lewis acids for the purpose of keeping the DP to a minimum. In addition, stannic chloride-initiated polymers may lose their cocatalyst (water) to form unsaturated and "cyclic" endgroups.¹³

Within the limits that thermodynamics places on the polymerization process (i. e. equilibrium composition), the solvent can influence the polymerization. The nonpolar solvents, benzene and carbon tetrachloride, were used to restrict the life span of the propagating chains. Using a solvent with a high dielectric constant would have only helped to stabilize the carbonium ion and increase its life span, thereby possibly increasing the DP of the oligomer. The methods applied were successful as proven by the production of low DP polymers. Also, the gas chromatograms and the IR spectra showed no trace of oxygen compounds.

There was a marked effect on the percentage of "cyclic" isomers by the two solvents. Considerably more "cyclic" endgroups were formed when carbon tetrachloride was used as solvent. An explanation is difficult because of the solvent's complicated role in cationic polymerization.

When calculating the relative percentage of each isomer from the gas chromatograms, the thermal conductivity of all the isomers was assumed to be equal. This assumption most likely adds to the uncertainty of relative endgroup concentrations.

It should be pointed out that samples II, III, IV and XII were the only ones with crystals while all other samples were viscous oils. These samples had a comparatively high percentage of the dimer with a "cyclic" endgroup (88 % to 93 %). This indicates that the crystals were formed from "cyclic" isomers of the dimer. The melting point range was 34-43 °C for the crystals. The white crystals, immersed in the remaining viscous oil, were sharply defined and in some cases needle-like. However, attempts to completely separate the crystals from the oil were fruitless. The low melting point of the crystals plus the similar solvation properties of the oil and crystal fractions rendered the conventional methods of separation useless, including filtration and recrystallization.

Sample XXIII had 80 % "cyclic" endgroups and no crystals, however, its \bar{M}_n was considerably higher than the other samples (Table 3). The reduced fraction of dimer in XXIII along with the extremely high viscosity would have inhibited any crystallization from taking place.

One very important assumption, derived from the results in Table 2, was that the endgroup configurations of the dimers were representative of the longer chain molecules and that the relative percentage of each configuration was also the same. IR spectroscopy supported this assumption as follows.

The IR spectra of the samples indicated varying percentages of ortho-disubstituted phenyl groups. The peaks between 2000 and 1650 cm^{-1} are characteristic of phenyl group substitutions. The

schematics in Figures 5 are representative spectra of the mono-substituted and the ortho-disubstituted benzene ring. If one considers the oligomers to contain both mono- and disubstituted phenyl groups, the spectrum in Figure 5 for this region looks very reasonable. The relative amount of the disubstituted phenyl group can not be determined precisely from the spectra, but an estimation can be made from the relative heights of the peaks at 5.21, 5.32 and 5.55 μ . The estimates assume all peaks to have identical extinction coefficients and baseline resolution and that there is no shift in any of these lines. It must be taken into consideration when estimating the amount of disubstitution, that only the next to the last phenyl group in the oligomer chain may be disubstituted. All other phenyl groups will be monosubstituted and for higher molecular weight samples the peaks representative of disubstitution will be subdued. Evidence of the trisubstituted alkene is illustrated throughout the spectrum. The IR spectra are therefore in qualitative agreement with the gas chromatography data.

There are several possible explanations for the apparent failure of the bromine coulometric analysis (BCA). These possible explanations include steric hindrance of bromine additions and polar, nonpolar interactions between oligomer and solvent. As evidence of steric interference, it is known that the BCA can be applied to styrene,¹⁴ a less sterically hindered molecule than either AMS or poly-AMS. Another possible inhibiting factor is the polar solvent, such as the solvent in which the reaction took place, which may constrict the relatively nonpolar hydrocarbon chain. The solubility of the oligomer is unknown and the oligomer's state in the polar solvent may approach that of an emulsion rather than that of a solution. The mixture is so dilute (7.5×10^{-3} M) that a dispersed emulsion would be difficult to detect with the naked eye.

The polar solvent hypothesis would also explain why the qualitative bromination succeeded in concentrated solutions with anhydrous ethanol as solvent. It may be possible to find a solvent system with the necessary solvation properties and still be able to conduct an electric charge, however, this would be a significant problem in itself.

Gel permeation chromatography was employed to find the MWD. In order to obtain a definitive interpretation of the GPC chromatograms, a calibration sample of known molecular size (hydrodynamic radius) must be analyzed along with the unknown samples. However, calibration samples of the hydrodynamic radius needed for oligomer analysis were not readily available. Additional GPC chromatograms should be obtained using a gel with a slightly larger pore size. This would enable one to determine the distribution of larger molecular weight fractions in the oligomer as well as the distribution of the smaller molecules obtained with the 60 Å gel.

The prohibitive cost of sending these samples out to be analyzed dictated that only two samples could be analyzed with a single gel.

Attempts to calculate the \bar{M}_n without specific knowledge of the amount of higher molecular weight fractions were fruitless. The calculated value for \bar{M}_n from GPC did not agree with the measured \bar{M}_n from vapor phase osmometry.

Discussion of Thermodynamic Results

The ΔH_c data are listed in Table 7 and computations are described in Appendix A. The enthalpy of polymerization per mole of monomer (ΔH_p) can be calculated from enthalpy of combustion (ΔH_c) data with either equation 3 or 4 (see Appendix B).

$$\Delta H_p = \Delta H_c(M) - \Delta H_c(P) \quad (3)$$

$$\Delta H_p = \frac{\Delta H_f(P) - DP(\Delta H_f(M))}{DP} \quad (4)$$

$\Delta H_c(P)$ is the ΔH_c of oligomeric AMS per monomer mole, $\Delta H_c(M)$ is the ΔH_c of monomeric AMS per mole, $\Delta H_f(P)$ is the ΔH_f of oligomeric AMS per oligomer mole and $\Delta H_f(M)$ is the ΔH_f of liquid AMS per mole. The ΔH_p 's calculated from equations 3 and 4 are exactly equal.

For low DP oligomers the predominant factor affecting the observed enthalpy of polymerization ($\Delta H_p(\text{obs})$) is the contribution from the endgroups. The $\Delta H_p(\text{obs})$ along with the \overline{DP} and percent of oligomers with the "cyclic" endgroup are listed in Table 8. Equation 5 was used in an attempt to correlate the ΔH_p with average degree of polymerization (\overline{DP}) and endgroup contributions.

$$\Delta H_p(\text{obs}) = \Delta H_p(\infty) + A(\text{fn}(1/DP)) + B(FI/DP) + C(FII/DP) + D(FIII/DP) \quad (5)$$

Table 7. Heats of Combustion and Heats of Polymerization
of α -Methylstyrene Oligomers

Sample	$-\Delta H_c$ cal/gm	$-\Delta H_c$ kcal/mole monomer	$-\Delta H_p$ kcal/mole monomer
II	10073.9 10047.4 10064.1 10059.3 mean = 10061.2 $\sigma_m = 5.5$	1189.03 $\sigma = 0.65$	15.84 $\sigma = 0.66$
III	10074.5 10070.6 10016.8 10052.4 mean = 10053.6 $\sigma_m = 13.2$	1188.13 $\sigma = 1.56$	16.74 $\sigma = 1.56$
IV	10095.7 10132.8 10061.0 10061.8 mean = 10087.8 $\sigma_m = 17.0$	1192.18 $\sigma = 2.01$	12.69 $\sigma = 2.01$
VI	10132.6 10036.1 10108.7 mean = 10092.5 $\sigma_m = 29.0$	1192.73 $\sigma = 3.43$	12.14 $\sigma = 3.43$
VII	10106.0 10109.9 10104.8 mean = 10106.9 $\sigma_m = 1.5$	1194.43 $\sigma = 0.18$	10.44 $\sigma = 0.22$

Table 7. Continued

Sample	$-\Delta H_c$ cal/gm	$-\Delta H_c$ kcal/mole monomer	$-\Delta H_p$ kcal/mole
VIII	10097.6 10080.9 10124.8 10119.6 mean = 10105.7 $\sigma_m = 10.2$	1194.29 $\sigma = 1.20$	10.58 $\sigma = 1.21$
XII	10085.5 10077.6 10091.4 mean = 10084.8 $\sigma_m = 4.0$	1191.82 $\sigma = 0.47$	13.05 $\sigma = 0.49$
XIV	10123.2 10056.3 10118.0 mean = 10099.2 $\sigma_m = 21.5$	1193.52 $\sigma = 2.54$	11.35 $\sigma = 2.54$
XV	10103.4 10109.4 10100.5 mean = 10104.5 $\sigma_m = 2.7$	1194.15 $\sigma = 0.32$	10.72 $\sigma = 0.34$
XVI	10101.3 10099.1 10104.4 mean = 10101.6 $\sigma_m = 1.5$	1193.81 $\sigma = 0.18$	11.06 $\sigma = 0.22$

Table 7. Continued

Sample	$-\Delta H_c$ cal/gm	$-\Delta H_c$ kcal/mole monomer	$-\Delta H_p$ kcal/mole
XVII	10106.6 10052.3 10100.4 mean = 10086.4 $\sigma_m = 17.2$	1192.01 $\sigma = 2.03$	12.86 $\sigma = 2.04$
XVIII	10128.2 10105.1 10107.2 mean = 10113.5 $\sigma_m = 7.4$	1195.21 $\sigma = 0.88$	9.66 $\sigma = 0.88$
XIX	10134.0 10108.4 10113.7 mean = 10118.7 $\sigma_m = 7.8$	1195.83 $\sigma = 0.92$	9.04 $\sigma = 0.93$
XX	10092.2 10108.2 10095.3 mean = 10098.6 $\sigma_m = 4.9$	1193.45 $\sigma = 0.56$	11.42 $\sigma = 0.59$
XXI	10071.0 10093.1 10108.0 mean = 10090.7 $\sigma_m = 10.7$	1192.52 $\sigma = 1.26$	12.35 $\sigma = 1.27$

Table 7. Continued

Sample	$-\Delta H_c$ cal/gm	$-\Delta H_c$ kcal/mole monomer	$-\Delta H_p$ kcal/mole
XXII	10108.7		
	10099.3		
	10084.1		
	mean = 10097.4 $\sigma_m = 7.2$	1193.31 $\sigma = 0.85$	11.56 $\sigma = 0.86$
XXIII	9880.2		
	9923.8		
	9929.5		
	mean = 9911.2 $\sigma_m = 15.6$	1171.31 $\sigma = 1.84$	33.56 $\sigma = 1.85$
XXIV	10118.0		
	10060.5		
	10105.4		
	mean = 10094.6 $\sigma_m = 17.5$	1192.98 $\sigma = 2.07$	11.89 $\sigma = 2.07$

Table 8. Correlation of Experimental Data

Sample	$\overline{DP} \pm 2 \sigma$	$-\Delta H_p$ kcal/mole $\pm 2 \sigma$	% Oligomers with Cyclic Endgroups
III	2.690 \pm 0.004	16.74 \pm 3.12	93.0
IV	2.698 \pm 0.027	12.69 \pm 4.02	93.0
XII	2.742 \pm 0.040	13.05 \pm 0.98	88.0
VII	2.769 \pm 0.007	10.44 \pm 0.44	34.0
VIII	2.770 \pm 0.023	10.58 \pm 2.42	58.0
XV	2.786 \pm 0.057	10.72 \pm 0.68	46.0
II	2.790 \pm 0.041	15.84 \pm 1.32	93.3
VI	2.801 \pm 0.033	12.14 \pm 6.86	49.0
XIV	2.819 \pm 0.029	11.35 \pm 5.08	58.0
XX	2.866 \pm 0.031	11.42 \pm 1.18	42.9
XVIII	2.969 \pm 0.040	9.66 \pm 1.76	44.5
XVII	2.980 \pm 0.003	12.86 \pm 4.08	49.0
XIX	2.992 \pm 0.018	9.04 \pm 1.86	58.7
XVI	3.005 \pm 0.031	11.06 \pm 0.44	58.0
XXIV	3.069 \pm 0.022	11.89 \pm 4.14	50.0
XXI	3.248 \pm 0.016	12.35 \pm 2.54	55.7
XXII	3.474 \pm 0.040	11.56 \pm 1.72	47.2
XXIII	4.304 \pm 0.059	33.56 \pm 3.70	80.0

$\Delta H_p(\infty)$ is the limiting ΔH_p for the pure polymer with infinite molecular weight and the "trans" (isomer IV) endgroup. The $A(\ln(1/DP))$ term describes the possible dependence of ΔH_p on some function of the reciprocal of \overline{DP} . Coefficients B, C and D are the heats of isomerization (ΔH_I) of "trans" isomer to "cis" isomer, "cyclic" isomer and "terminal" isomer, respectively, per mole of endgroup. The fractions FI, FII and FIII refer to "cis" isomer, "cyclic" isomer and "terminal" isomer, respectively, and are the fractions of oligomer with the respective endgroup configurations.

There are several additional terms that should be included in equation 5 to make it more general. A heat of mixing term arising from the different endgroups and DP's in the samples could be included. Any attempts to assign a value to the heat of mixing would be an approximation and in any case it would be a small contribution. It has been suggested that the molecules in the glass transition may contribute to the observed ΔH_p from ΔH_c data.⁷ However, the glass transition contribution for liquid low molecular weight samples must be small. These contributions will therefore be considered negligible.

Additional terms including contributions from catalyst and cocatalyst oligomer complexes which remain intact and other possible endgroup configurations could be added to equation 5. However, the gas chromatography and infrared analysis of the samples suggests that terms applying to complexes and additional endgroups are unnecessary.

The values for the ΔH_I may be approximated from the ΔH_c 's of systems with functional groups similar to the dimeric isomer of AMS. Table 9 lists the data from which the following may be calculated.

"trans" isomer → "cis" isomer	$\Delta H = 1.1$ kcal/mole of (6)
	endgroup
"trans" isomer → "cyclic" isomer	$\Delta H = -13.0$ " (7)
"trans" isomer → "terminal" isomer	$\Delta H = 2.6$ " (8)

Table 9.¹⁵ Heat of Combustion Data for Selected Compounds

	$-\Delta H_c$ kcal/mole
trans-2-pentene	804.26
cis-2-pentene	805.34
1-pentene	806.85
trans-2-hexene	961.66
methyl cyclopentane	948.72

The ΔH_I for "trans" isomer → "cyclic" isomer may also be calculated with the group contribution method. Souders'¹⁶ method predicts a value of -5.5 kcal/mole. The range of -5.5 to -13.0 kcal/mole is rather large. The more positive value may be more realistic if the steric strain of the substituted indane structure is significant.

Assuming equation 5 is the appropriate expression for describing the ΔH_p (obs), a regression analysis¹⁷ may be performed. With the data from Tables 2 and 7 and equations 6, 7 and 8 the necessary values for the 3rd, 4th, 5th and ΔH_p (obs) terms in equation 5 may be calculated. The constant, C, contains the most uncertainty and may assume values between -5.5 and -13.0 kcal/mole for comparison. The specific functionality of A(fn(1/DP)) may be found by trial and error with several transformations including A(1/DP) and A(1/DP)².

All the samples were included in the regression analysis except XXIII. Sample XXIII obviously is inconsistent with the other

samples for some unknown reason. The results of the regression analysis, shown in Table 10, are inconclusive and suggest a need for further study. The standard error of A was always larger than the value of A. This was the case regardless of the ΔH_I used for "cyclic" isomer and the function used to describe the DP-dependence. A comparison of the $\Delta H_p(\infty)$ values in Table 10 with 8.96 kcal/mole, the value obtained by Joshi⁷ for high molecular weight poly-AMS, can help to determine which results are the most reasonable. One must also take into consideration the predicted $\Delta H_p(\text{obs})$ for the dimer.

There was, however, little statistical justification for selection of one set of constants for equation 5 over any other calculated from the regression analysis. Although the DP-dependence of ΔH_p is still uncertain, it is believed that equation 5 is a meaningful and representative expression. The precision of the ΔH_c data (0.015 to 0.3 % uncertainty) is very good and would imply that the correlation should be more reliable than what was actually obtained. However, ΔH_p is calculated as the small difference between two large numbers and as a result, ΔH_p has a relatively large propagated error. The uncertainty of ΔH_p plus the uncertainties in the additional data fed into equation 5 probably accounts for the poor correlation results. The fraction of each endgroup isomer must contain a fair amount of uncertainty for two reasons. First, the thermal conductivity of the four isomers may be significantly different and, second, the areas of gas chromatogram peaks are probably not accurately represented by the isosceles triangles constructed around them.

There may also be doubts concerning the average DP used in equation 5. There is the possibility that molecular weight distribution of all the samples do not conform to a single pattern. That is the \bar{M}_n 's are different because of a different type of distribution function and not just because of a shift in a single function. This is

Table 10. Results of Linear Regression Analysis

Variable	ΔH_I (isomer II) kcal/mole		
	- 6.0	-10.0	-13.0
<u>Equation 9a</u>			
$\Delta H_p(\infty)$	- 5.86	- 7.57	- 8.79
A	-14.07	- 6.67	- 1.35
Std. Error	18.08	16.49	15.65
Ave. $\Delta H'_p(\text{obs})$	-10.72	- 9.88	- 9.26
σ_m	1.68	1.51	1.42
<u>Equation 9b</u>			
$\Delta H_p(\infty)$	- 8.02	- 8.53	- 8.88
A	-22.50	-11.24	- 3.13
Std. Error	26.91	24.58	23.36
Ave. $\Delta H'_p(\text{obs})$	-10.72	- 9.88	- 9.25
σ_m	1.68	1.51	1.42

$$\Delta H'_p(\text{obs}) = \Delta H_p(\infty) + A(1/\text{DP}) \quad (9a)$$

$$\Delta H'_p(\text{obs}) = \Delta H_p(\infty) + A(1/\text{DP})^2 \quad (9b)$$

proposed because of the different reaction conditions that each sample experienced. If each sample has a different MWD function, there may be further doubts in the validity of treating the samples as monodisperse polymers with a \overline{DP} derived from the \overline{M}_n .

The regression analysis results must be viewed in light of the limitations described above. It is evident that the importance of the endgroup contribution can not be over emphasized. The endgroup apparently has more influence on the $\Delta H_p(\text{obs})$ than the DP does. For this reason it is essential that all quantitative information relating to the amount and ΔH_I for each isomer be determined accurately before further study on the DP-dependence can be pursued.

Aside from the importance of the MWD relationship to the \overline{DP} , the MWD has a very important relation to the thermodynamics of polymerization. If a complete gel permeation chromatogram were available and the endgroup contributions were known, the ΔH_p as a function of DP could be found explicitly. The mathematical formulation for such a case is derived in Appendix C. The all-important information that can be obtained from the available GPC data (Table 5) is the pattern of the molecular weight distribution. It can be seen that there are fewer moles of the smallest molecule than of the next largest molecule and that there is a considerable quantity of what must be at least tetramers and higher DP oligomers. These points are important because they contradict the predictions from a theoretical model with a single-valued ΔH_p , regardless of the ΔH_p value and single-valued ceiling temperature (T_c), 61 °C. (The T_c is the temperature above which the free energy of polymerization (ΔG_p) is positive.¹⁸) From Markov calculations (see Appendix D) for a DP-independent ΔH_p and T_c , the predicted yield of polymer is less than 10 % regardless of the termination probability (τ) under

the conditions of these syntheses. The yields in all syntheses listed in Table 1 are in excess of 95 %. Moreover, the predicted primary polymer species from Markov calculations would be dimer (in excess of 99 %). Table 5 clearly points out that the concentration of higher DP oligomers may be larger than the concentration of the lowest DP. This is the case of sample XVI where the peak area at 5 hr 26 min is greater than the peak area at 5 hr 56 min. (The larger molecules are eluted first and successively smaller molecules follow.)

If one assumes a DP-dependent ΔG_p in the Markov calculations, it is possible to theoretically synthesize a MWD pattern similar to the one observed for sample XVI.¹⁹ This indicates that either the entropy of polymerization (ΔS_p) or ΔH_p or both must be DP-dependent.

Assuming that ΔS_p and/or ΔH_p are DP-dependent, then T_c may also be DP-dependent as can be seen from equation 10.^{18,20}

$$T_c = \frac{\Delta H_p}{\Delta S_p} \quad (10)$$

Equation 11²⁰ shows that T_c also depends on the equilibrium concentration of monomer.

$$T_c = \frac{\Delta H_p}{\Delta S^0 + R \log_e [m]_{eq}} \quad (11)$$

ΔS^0 is the standard state entropy change (at unit concentration of monomer), R is the universal gas constant and $\log_e [m]_{eq}$ is the natural logarithm of the equilibrium monomer concentration, $[m]_{eq}$.

McCormick⁸ measured the ceiling temperature for the polymerization of AMS. Experimentally he found T_c to be 61 °C. McCormick

calculated the $[m]_{eq}$ from the difference between initial monomer and polymer formed, and from equation 11 found ΔH_p , -6.96 kcal/mole, and ΔS^0 , -24.8 cal/mole deg. For temperatures between 298.2 and 333.2 °K, McCormick's calculated $[m]_{eq}$ ranged from 2.21 to 7.52 moles/liter. (The original publication read 75.2 moles/liter, but this is obviously an error.)

Using McCormick's values for ΔH_p and ΔS^0 , T_c may be calculated for the conditions stated in Table 1. A conservative estimate of the average monomer conversion, 95 %, would leave a $[m]_{eq}$ of about 0.05 moles/liter. The T_c thus calculated is 226 °K. The calculated T_c is considerably lower than the temperatures listed in Table 1.

It can only be concluded that McCormick's ΔH_p and ΔS^0 values are in error and/or do not apply in the low molecular weight range, providing equation 11 applies. Equation 11 applies to an ideal solution. If there is a significant amount of low molecular weight oligomers in his assumed $[m]_{eq}$, the calculated ΔH_p and ΔS^0 would be in error. There could be significant quantities of oligomer in the assumed $[m]_{eq}$ if McCormick collected the polymer by precipitating the reaction product in a non-solvent like methanol.

The preceding calculation of T_c for conditions in Table 1 is important to the argument that ΔS^0 and ΔH_p may be DP-dependent. If it is assumed that $[m]_{eq}$ is the only independent variable in equation 11 for a specified polymer system, the ceiling temperature should drop significantly for more dilute solutions of monomer. This is not the case, however, because reaction at 60 °C can produce significant quantities of oligomers even in dilute solution as documented by this report. This implies that either ΔH_p or ΔS^0 or both are independent variables in equation 11 for any defined polymer system.

It is believed that the data reported and arguments presented in this thesis are strong evidence of a DP-dependent free energy of polymerization which quite possibly involves both the entropy and enthalpy of polymerization.

Suggestions for Further Study

Future experiments that may follow up this study should include a method for the specific synthesis of the respective isomers or isolation of the isomer from a mixture. There are several likely possibilities that may be explored. It has been shown that if carbon tetrachloride is the solvent, the polymerization will produce more of the "cyclic" endgroup than if the solvent is benzene. By regulating the solvent system, it may be possible to optimize the production of one endgroup isomer and exclude the production of other isomers. There is also the possibility that completely different synthesis systems would achieve the same end. In addition to specific isomer synthesis, preparative gas chromatography may be used to collect the isomers from a mixture. With the pure endgroup isomers in hand, a meaningful qualitative and quantitative analysis could be performed including infrared and nuclear magnetic resonance spectroscopy, molecular weight determinations and elemental analysis. Of course, from ΔH_c of these samples, the ΔH_I may be calculated.

A gas chromatography detector system may also be found that would be without the inherent problems of the thermal conductivity detector. If this is possible, the fraction of each dimeric isomer could be found more accurately than the fractions calculated for this report.

The quantitative unsaturation data may be obtained from quantitative hydrogenation. This method does not have the same problems connected to it that BCA has, although it may have some different problems of its own. The purpose of this experiment would be to test the assumption that the total unsaturation of the oligomer sample can be calculated from the unsaturation of the dimer.

As suggested in the discussion, a calibrated and complete analytical GPC chromatogram would be sufficient to find the ΔH_p 's dependence on DP, if the ΔH_I and fraction of endgroup isomers were known accurately.

Perhaps the most desirable experiment would be the collection of individual oligomers with a specific DP. Preparative GPC could possibly be used if enough starting material were available. If samples of this type could be collected it would be possible to test the assumption that the relative endgroup concentrations are the same for oligomers of all DP's. With zone refining in a frozen solvent such as naphthalene it may be possible to separate the endgroup isomers of higher DP than two. Of course, the primary purpose of obtaining monodisperse samples is to collect the ΔH_c data. The ΔH_p dependence on DP would hopefully become more evident if the ΔH_c could be determined for monodisperse oligomers.

Additional information that would eliminate several remaining assumptions would certainly be desirable. The heat of mixing of all combinations of the different endgroups and DP's would be very helpful. It would also be interesting to determine the DP's of oligomers which are in the glass transition at ambient temperatures.

SUMMARY AND CONCLUSIONS

- (1) The ΔH_p for dimers and trimers of AMS is between -9.0 and -16.7 kcal/mole depending on the endgroup formed, and possibly on the DP.
- (2) Oligomerization will proceed above the predicted ceiling temperature for dilute solutions of monomer, if ΔH_p and ΔS^0 are assumed to be constant at previously published values.
- (3) The ceiling temperature and ΔG_p appear to be DP-dependent.
- (4) The data and arguments presented in this thesis are strong evidence for a DP-dependent ΔH_p and ΔS_p , although it is uncertain which term is affected most by the DP and how to describe the dependence quantitatively.
- (5) It is evident that the endgroup influences the ΔH_p of oligomers more than the DP does.

Appendix A. Heat of Combustion Computations

A computer program applying the Washburn corrections was written to analyze all raw combustion data. The outline presented by Hubbard, et. al.,²¹ was modified to fit the conditions stated in the experimental section. Except for the following, the values of the constants used in the program were taken from Hubbard's text. In equations 12 through 22 the capital T stands for degrees Kelvin and the lower case t stands for degrees Celsius.

The heat capacities at constant volumes (C_v) and at constant pressure (C_p) of liquid water were taken to be equal. From the values of C_p at 20 °C (17.994 cal/mole deg), 25 °C (17.978 cal/mole deg) and 30 °C (17.969 cal/mole deg),²² equation 12 was derived.

$$C_p \approx C_v = (31.1684 - 0.085982 T + 0.00014 T^2) \text{ cal/mole deg} \quad (12)$$

C_v for vaporized water (equation 13) was approximated by the C_p of vaporized water²³ minus the universal gas constant, R.

$$C_v = (5.2318 + 2.374 \times 10^{-3} T + 2.67 \times 10^{-7} T^2) \text{ cal/mole deg} \quad (13)$$

The expression for the c_p of liquid oligomeric AMS was approximated in the following manner. The ratio of the heat capacities of AMS and styrene, 0.29534 cal/g deg (300 °K) and 0.28182 cal/g deg (300 °K) respectively,²⁴ was multiplied by the heat capacity equation of polystyrene,²⁵ to obtain equation 14.

$$c_p = (0.2966 + 1.011 \times 10^{-3} t) \text{ cal/g deg} \quad (14)$$

The resulting equation was then converted from Celsius to the Kelvin temperature scale to get equation 15.

$$c_p = (0.02034 + 1.011 \times 10^{-3} T) \text{ cal/g deg} \quad (15)$$

The C_v for solid benzoic acid was approximated by equation 16, the C_p for solid benzoic acid.²⁶

$$c_p = (0.287 + 0.0005 t) \text{ cal/g deg} \quad (16)$$

The equation was converted from Celsius to Kelvin and from grams to moles of benzoic acid to get equation 17.

$$C_v = (18.369 + 0.06106 T) \text{ cal/mole deg} \quad (17)$$

The following C_p expressions were employed for vaporized water (eq. 18), carbon dioxide gas (eq. 19) and for oxygen gas (eq. 20).²³

$$C_p = (7.219 + 2.374 \times 10^{-3} T + 2.67 \times 10^{-7} T^2) \text{ cal/mole deg} \quad (18)$$

$$C_p = (6.369 + 10.10 \times 10^{-3} T - 3.405 \times 10^{-6} T^2) \text{ cal/mole deg} \quad (19)$$

$$C_p = (6.0954 + 3.2533 \times 10^{-3} T - 1.0171 \times 10^{-6} T^2) \text{ cal/mole deg} \quad (20)$$

The C_v expressions found in the literature for carbon dioxide gas²⁷ and oxygen gas²⁸ were converted from Celsius to the Kelvin temperature scale. The C_v expressions for carbon dioxide and oxygen are shown as equation 21 and 22, respectively.

$$C_v = (4.92 + 6.28 \times 10^{-3} T - 2.73 \times 10^{-6} T^2 + 4.7 \times 10^{-10} T^3) \text{ cal/mole deg} \quad (21)$$

$$C_v = (4.93 + 1.95 \times 10^{-4} T + 5.5 \times 10^{-8} T^2) \text{ cal/mole deg} \quad (22)$$

The computations for calculating heat of combustion followed the thermodynamic cycle shown in Figure 6.

The following are calculations for ΔH_c using the data in Table 11.

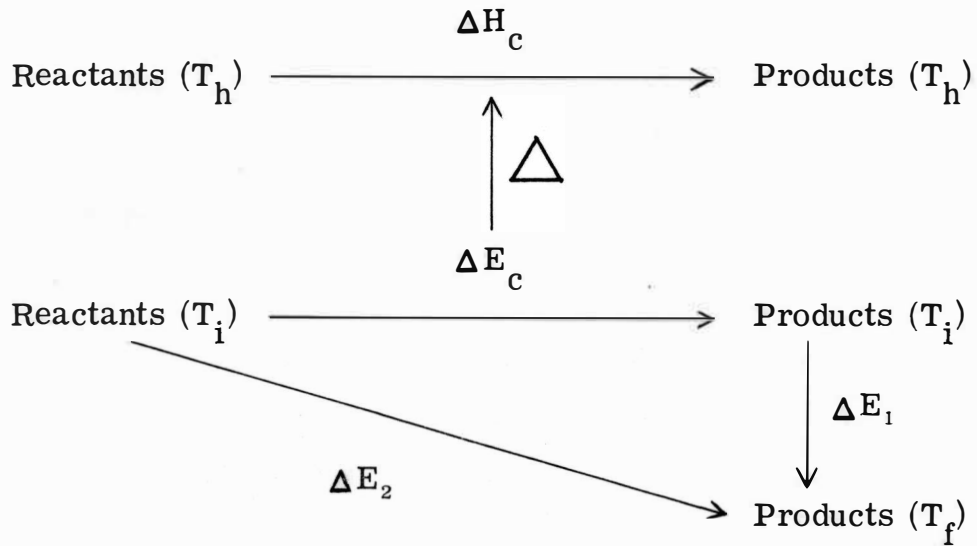
Table 11. Experimental Data for Sample XVI

Experiment	T_i	T_f	Sample mass, g	Sample volume, ml	Burned fuse mass, g
	°C				
18	24.725	26.988	0.5345	0.56	0.0078
33	24.559	26.518	0.4619	0.49	0.0132
47	24.336	26.721	0.5624	0.59	0.0136

The uncorrected energy of combustion, ΔE_2 , may be calculated using equation 23.

$$\Delta E_2 = \frac{\Delta T \times (\text{Energy Equivalent}) - (\text{mass of fuse} \times (-1400 \text{ cal/g}))}{\text{number of moles of oligomer}} \quad (23)$$

For experiments 18, 33 and 47 the respective ΔE_2 's are 3581.31 kcal/mole, 3580.56 kcal/mole and 3582.39 kcal/mole. Computer program I applies the corrections and conversions outlined in Figure 6 to arrive at the following ΔH_c values, 10101.3 cal/g, 10099.1 cal/g and 10104.4 cal/g for experiments 18, 33 and 47 respectively. The mean value was 10101.6 cal/g with a σ_m of 1.5.



T_i = initial temperature

T_f = final temperature

T_h = reference temperature, 25 °C

ΔE_1 = internal energy change of product going from

$$T_i \text{ to } T_f = n \int_{T_i}^{T_f} C_{vdT}$$

ΔE_2 = total energy change in combustion process, including appropriate corrections

Δ = temperature corrections from T_i to T_h and conversion from ΔE_c to ΔH_c

$$= \Delta PV + \int_{T_i}^{T_h} \Delta C_{pdT}$$

ΔE_c = $\Delta E_2 - \Delta E_1$, hypothetical isothermal energy of combustion at T_i

ΔH_c = isothermal enthalpy of combustion at the reference temperature

Figure 6. Heat of Combustion Thermodynamic Cycle

Computer Program I: FORTRAN IV Program for Calculating Heat
of Combustion With Standard State Corrections

```

        DIMENSION X(5,5), XY(5)
        REAL MAS, MOWS, NST, MAF, MHTI, NHTI, NHVI, NHLI,
        2NGI, KOI, NODI, NOTI, NFB, KOF, NOTF, KCO, K2CO,
        3K2O, NODF, NCOD, NHLF, MHLF, NCOT, NOGF, NGTF,
        4NHVF, NCGF
1       WRITE (5,10)
10      FORMAT (' VOL OF SAMPLE MASS OF SAMPLE' /)
        READ (5,50) VS, MAS
50      FORMAT (F13.6,2X,F14.5)
        IF (VS .EQ. 0.0) CALL EXIT
        WRITE (5,15)
15      FORMAT (' VOL OF BOMB VOL H2O IN BOMB' /)
        READ (5,55) VB, VH2O
55      FORMAT (F11.6,2X,F15.7)
        PI = 20.0
        WRITE (5,13)
13      FORMAT (' # OF EACH KIND OF ATOM IN MOLECULE',/,
        2' CARBON HYDROGEN OXYGEN' /)
        READ (5,53) C, H, O
53      FORMAT (F6.2, 2X, F8.2, 2X, F6.2)
        IF (C .EQ. 0.0) GO TO 150
        GO TO 155
150     WRITE (5,14)
14      FORMAT (' # AVE MOLE WT' /)
        READ (5,54) MOWS
54      FORMAT (F13.3)
        DP = MOWS/118.18
        C = DP * 9.
        H = DP * 10.
        GO TO 185
155     CM = 12.011
        HM = 1.008
        OM = 15.999
        MOWS = C * CM + H * HM + O * OM
185     NST = MAS/MOWS
        WRITE (5,17)
17      FORMAT (' INITIAL TEMP FINAL TEMP' /)
        READ (5,57) TI, TF
57      FORMAT (F12.6,2X,F11.6)
        TH = 25.0
        WRITE (5,20)

```

```

20  FORMAT (' MASS OF FUSE BURNED  CAL/GM FOR FUSE' /)
    READ (5,60) MAF, ECF
60  FORMAT (F15.6, 6X, F15.5)
    IF (ECF .EQ. 0.0) ECF = -1400.0
    DHI = 0.9982 - (TI - 20.) * 0.00012
    MHTI = VH2O * DHI * 1000.
    NHTI = MHTI / 18.016
    VGI = VB - VH2O - VS
    CO = .01009 - .000272*TI + .0000316*TI*TI
111 ALPO = (TI - 20.) * (0.000004) + 0.00006
    NHVI = (CO + ALPO * PI) * VGI / 18.016
    NHLI = NHTI - NHVI
    NGI = PI * VGI / (24.4685 * (1.0 - 0.0006075 * PI))
    KOI = 0.00133 - (TI - 20.) * 0.000026
    PHVI = 0.02 + (TI - 20.) * 0.002
    NODI = 0.01807 * KOI * NHLI * (PI - PHVI)
    NOTI = NODI + NGI - NHVI
    NFB = MAF / 55.847
    NOTF = NOTI - (C + (H/4.) - (0/2.)) * NST - (3./2.) * NFB
    NHLF = NHTI + (H/2.) * NST - NHVI
    MHLF = 18.016 * NHLF
    VHLF = MHLF / (1000. * (0.9982 - (TF - 20.) * 0.00012))
    VGF = VB - VHLF
    NCOT = C * NST
    XCO = 0.05
    PF = 19.0
    KCO = .0641 - .001462*TF + .0000104*TF*TF
    KOF = .001398 - (TF - 20.) * .0000276
776 X(1,1) = 0.908
    X(1,2) = 0.914
    X(1,3) = 0.920
    X(2,1) = 0.894
    X(2,2) = 0.900
    X(2,3) = 0.908
    X(3,1) = 0.880
    X(3,2) = 0.887
    X(3,3) = 0.896
    K = 0
777 IF (XCO .LT. 0.1) I = 1
    IF (XCO .GE. 0.1) I = 2
    IF (TF .LT. 25.) J = 1
    IF (TF .GE. 25.) J = 2
    TDL = TF - 20.
    IF (TDL .GE. 5.0) TDL = TDL - 5.0
    X2CO = XCO

```



```

IF (XCO .GE. 0.1) X2CO = XCO - 0.1
Y = X(I,J+1) - X(I,J)
Z = X(I+1,J+1) - X(I+1,J)
DC1 = X(I,J) + (Y * TDL)/ 5.0
DC2 = X(I+1,J) + (Z * TDL)/5.0
DDW = (X2CO * (DC1 - DC2)) / 0.1
DCO = DC1 - DDW
IF (K .NE. 0) GO TO 377
XY(1) = 0.0040
XY(2) = 0.0045
XY(3) = 0.0050
DWX=((XY(1+I)-XY(I))*X2CO/0.1)+XY(I)
IF (DWX .EQ. 0.0) DWX = XY(I)
DCO = DCO + (20. - PF) * DWX
K2CO = DCO * KCO
NCOD = 24.4685 * NCOT * VHLF * K2CO / VGF
NCOD = NCOD/(1.0 + K2CO * (VHLF/VGF) * 24.4685)
NCGF = NCOT - NCOD
K = 1
X(1,1) = 0.949
X(1,2) = 0.951
X(1,3) = 0.954
X(2,1) = 0.945
X(2,2) = 0.947
X(2,3) = 0.951
X(3,1) = 0.941
X(3,2) = 0.944
X(3,3) = 0.947
GO TO 777
377 DO = DCO + (20. - PF) * 0.0025
K2O = KOF * DO
NODF = 24.4685 * NOTF * VHLF * K2O / VGF
NODF = NODF/(1.0 + (24.4685 * K2O * VHLF/ VGF))
NOGF = NOTF - NODF
NGTF = NOGF + NCOT + NHVI
X3CO = NCGF / NGTF
L = 0
A = ABS(X3CO - XCO)
IF (A .GT. 0.005) L = 1
XCO = X3CO
UGF = 0.0006075 * (1. + 3.21 * XCO *(1. + 1.33*XCO))
P2F = 1./(VGF/(24.4685 * NGTF) + UGF)
B = ABS(P2F - PF)
PF = P2F
IF (B .GT. 0.005) GO TO 776

```

```

IF (L .NE. O) GO TO 776
ALPC = 0.0004 + (TF + 20.)*0.000016
ALPO = (TF-20.)*0.000004+0.00006
NHVF = ((CO+(ALPO+(ALPC-ALPO)*XCO)*PF)*VGF)/18.016
EHVI = (9973.-10.2 * (TI - 20.)) * NHVI
EHVF = (9973.-10.2 * (TF - 20.)) * NHVF
E = EHVI + EHVF
EPHI = (-0.0335 +(25. - TI) * 0.00135) * NHLI*(PI - 1.)
EPHF = (-0.0335 + (25. - TF) * 0.00135) * NHLF*(-PF)
ESOI = (-3400. + (TI - 20.) * 40.) * NODI
ESOF = -(-3400. + (TF - 20.) * 40.) * NODF
E = E + EPHI + EPHF + ESOI + ESOF
EPOI = (-1.605 + 0.0062 * (TI - 20.)) * PI * NGI
EP = -1.605 + 0.0062 * (TF - 20.)
EPGF = -EP*(1. + 1.69 * XCO * (1. + XCO)) * PF * NGTF
ESC = -(-4050 + (TF -25.) * 4.3) * NCOD
E = E + EPOI + EPGF + ESC
TIA = TI + 273.15
TFA = TF + 273.15
THA = TH + 273.15
CUIL = (31.684*(TF-TI)-0.042991*(TFA**2-TIA**2)
2 +0.000046666*(TFA**3-TIA**3))*(NHLF-NHLI)
IF ((NHVF-NHVI) .LE. 0.0) GO TO 800
CVIV = 5.2318*(TF-TI)+1.187*(TFA**2-TIA**2)*0.001 +
2 0.89 * (TFA**3-TIA**3)*0.0000001
CVIV = CVIV * (NHVF - NHVI)
800 CVIC = (4.923*(TF-TI)+0.00314*(TFA**2-TIA**2)-
2 0.0001*(0.00909*(TFA**3-TIA**3)) +
3 0.00001*(0.00001175*(TFA**4-TIA**4))) * NCOT
ECV = CVIL + CVIC + CVIV
EF = MAF * ECF
CPIC = 6.369*(THA-TIA)+5.05*(THA**2-TIA**2)
2 *0.001-0.1135*(THA**3-TIA**3)*0.00001
CPIC = CPIC * C
CPIO = 6.0954*(THA-TIA)+1.6266*(THA**2-TIA**2)*0.001
2 -3.39*(THA**3-TIA**3)*0.0000001
CPIO = CPIO * (C + (H/4.) - (O/2.))
CPIH = (31.1684*(TH-TI)-0.042991*(THA**2-TIA**2)
2 +0.000046666*(THA**3-TIA**3))*(H/2.)
WRITE (5,30)
30 FORMAT (' IF ENTHALPY OF COB IS TO BE CALCULATED
2 ENTER ENERGY EQUIVALENT',/, ' NOT ENTHALPY
3 EQUIV OF CALORIMETER. IF ENERGY EQUIV IS TO BE
4 CALC',/, ' WITH BENZOIC ACID, LEAVE BLANK.'//)
WRITE (5,33)

```

```

33  FORMAT (' ENERGY EQUIV.'//)
    READ (5,63) EEQ
63  FORMAT (F12.2)
    IF (EEQ .EQ. 0.0) GO TO 810
    EWTMI = (EEQ*(TI-TF))-EF)/MAS
    ESTI= (EEQ*(TI-TF)+E-EF-ECV)/NST
    VBR = VB - VH2O
    HSTI = (ESTI + (VBR*PF-VBR*PI)/(NST*0.041292))/1000.
    IF (0 .NE. 0.0) GO TO 940
    CPIS = MOWS*(.020345*(TH-TI)+0.00050564*(THA**2-TIA**2))
    GO TO 950
940  CPIS = 18.369*(TH-TI)+0.03053*(THA**2-TIA**2)
950  HSTH = (CPIC + CPH - CPIO - CPIS)/1000. + HSTI
    HSG = (HSTH / MOWS) * 1000.
    WRITE (5,35) HSTH,HSG,EWTMI
35  FORMAT (' ENTHALPY COMB = ' F10.4, ' KCAL/MOLE' ,/,
2  '          "          " = ' F10.2, ' CAL/GRAM' ,/,
3  ' ENERGY COMB = ' F10.3, ' CAL/GRAM' ,//)
    GO TO 2
810  CVIB = 18.369*(TI-TH)+0.03053*(TIA**2-THA**2)
    CVIC = C*(4.923*(TI-TH)+0.00314*(TIA**2-THA**2)
2  -0.909*(0.000001*(TIA**3-THA**3))
3  +0.00001175*(0.00001*(TIA**4-THA**4)))
    CVIH = -CPH
    CVIO = 4.927*(TI-TH) +0.0000975*(TIA**2-THA**2)
2  + 0.183*(0.0000001*(TIA**3-THA**3))
    CVIO = CVIO * (C + (H/4.) - (0/2.))
    EBTI = -6317.8+(CVIC + CVIH -CVIO -CVIB)/122.12
    EEQ = (EBTI*MAS +ECV -E + EA + EF)/(TI -TF)
    WRITE (5,42) EEQ
42  FORMAT (' ENERGY EQUIV. = ' F10.4, ' CAL/DEG' //)
2  WRITE (5,45)
45  FORMAT (5(' * * * * * '))//)
    GO TO 1
END

```

Explanation of Symbols in Computer Program I

The following is a complete list with corresponding explanations of all symbols appearing in the computer program. Hubbard's abbreviations were used in many cases to facilitate comparison of the computer program with Hubbard's text.²¹ Chemical symbols for compounds are used throughout the explanation.

VS	volume of sample
MAS	mass of sample
VB	volume of bomb
VH ₂ O	volume of H ₂ O initially in bomb
PI	initial pressure in bomb, 20 atmospheres
C	number of carbon atoms in one molecule of the sample
H	number of hydrogen atoms in one molecule of the sample
O	number of oxygen atoms in one molecule of the sample
MOWS	number average molecular weight of AMS oligomer
DP	average degree of polymerization
CM	atomic mass of carbon
HM	atomic mass of hydrogen
OM	atomic mass of oxygen
NST	number of moles of sample
TI	ignition temperature, Celcius scale
TF	final temperature, Celcius scale
TH	reference temperature, 25.0 °C
MAF	mass of fuse wire burned
ECF	energy of combustion of fuse wire, cal/g
DHI	density of water initially in bomb
MHTI	mass of H ₂ O initially in bomb
NHTI	number of moles of H ₂ O initially in bomb
VGI	volume of gas initially
CO	} intermediate variables for calculating number of moles
ALPO	
NHVI	number of moles of H ₂ O in vapor phase
NHLI	number of moles of H ₂ O in liquid phase
NGI	total number of moles in gas phase, initially
KOI	intermediate variable for calculating O ₂ dissolved in liquid H ₂ O
PHVI	vapor pressure of H ₂ O, initially
NODI	number of moles of O ₂ dissolved in H ₂ O initially

NOTI	total number of O ₂ moles initially
NFB	estimated number of moles of fuse wire burned
NOTF	number of O ₂ moles after ignition
NHLF	number of moles of H ₂ O in liquid phase after ignition
MHLF	mass of liquid H ₂ O after ignition
VGf	volume of gas after ignition
NCOT	number of moles of CO ₂ produced by combustion
XCO	estimated mole fraction of CO ₂ in combustion products
PF	estimated pressure after combustion
KCO	K(CO ₂)
DCO	D(CO ₂)
K2CO	K*(CO ₂) (K*(CO ₂) = (D(CO ₂))(K(CO ₂)))
X(I, J)	(1st list) table of values of D(CO ₂)
TDL	} intermediate variables used to interpolate D(CO ₂) table of values if K = 0 or D(O ₂) table if K = 1
X2CO	
Y	
Z	
DC1	
DC2	
DDW	
XY(I)	table of values to correct D(CO ₂) for pressure changes
DWX	interpolation values from XY(I) table
NCOD	number of moles of CO ₂ dissolved in H ₂ O after combustion
NCGF	number of moles of CO ₂ in gas phase
KOF	K(O ₂)
DO	D(O ₂)
K2O	K*(O ₂)
X(I, J)	(2nd list) table of values of D(O ₂)
NODF	number of moles of O ₂ dissolved in H ₂ O after combustion
NOGF	number of moles of O ₂ gas after combustion
NGTF	total number of moles in gas phase after combustion
X3CC	calculated value of mole fraction of CO ₂ gas
A	comparison of X3CO and XCO
UGF	intermediate variable for calculating final pressure
P2F	calculated final pressure in bomb
B	comparison of PF and P2F
ALPC }	} intermediate variables for calculating NHVF
ALPO }	
NHVF	number of moles of H ₂ O vapor after combustion
EHVI	$\Delta E^i_{\text{vap H}_2\text{O}}$
EHVF	$-\Delta E^f_{\text{vap H}_2\text{O}}$
EPHI	$\Delta E^i(\text{H}_2\text{O}) \Big _1^{P_i}$

EPHF	$-\Delta E^f(\text{H}_2\text{O}) \Big _{P_f}^1$
ESOI	$\Delta E^i_{\text{solu}}(\text{O}_2)$
ESOF	$-\Delta E^f_{\text{solu}}(\text{O}_2)$
EPOI	$\Delta E^i(\text{O}_2) \Big _0^{P_i}$
EP	$(\partial E / \partial P)_{T_f}(\text{O}_2)$
EPGF	$\Delta E^f(\text{gases}) \Big _{P_f}^0$
ESC	$\Delta E_{\text{solu}}(\text{CO}_2)$
E	sum of Washburn corrections
TIA	initial temperature, Kelvin scale
TFA	final temperature, Kelvin scale
THA	reference temperature, Kelvin scale
CVIL	integrated expression of C_v for liquid H_2O
CVIV	integrated expression of C_v for H_2O vapor
CVIC	integrated expression of C_v for CO_2 gas
ECV	total internal energy change of products going from T_i to T_f
EF	energy of combustion from fuse wire
CPIO	integrated expression of C_p for O_2 gas
CPIC	integrated expression of C_p for CO_2 gas
CPIH	integrated expression of C_p for H_2O liquid
CPIS	integrated expression of C_p for poly-AMS
EEQ	energy equivalent of calorimeter, cal/deg, $^{\circ}\text{C}$
EWMI	uncorrected energy of combustion of sample
ESTI	corrected isothermal energy of combustion at T_i
VBR	volume of reaction
HSTI	isothermal enthalpy of combustion at T_i , kcal/mole
HSTH	isothermal enthalpy of combustion at 25°C , kcal/mole
HSG	isothermal enthalpy of combustion at 25°C , kcal/g
CVIB	integrated expression of C_v for benzoic acid
CVIC	integrated expression of C_v for CO_2 gas
CVIH	integrated expression of C_v for H_2O liquid
CVIO	integrated expression of C_v for O_2 gas
EBTI	theoretical energy of combustion of benzoic acid at T_i

Appendix B. Heat of Polymerization Computations

A computer program was written to calculate and print out the ΔH_c kcal/monomer mole, ΔH_p kcal/mole and degree of polymerization with their respective uncertainties. The program computed ΔH_p with both equations 3 and 4 which were presented in the discussion of thermodynamic results.

For liquid water at 25 °C, the ΔH_f° was taken as -68.3174 kcal/mole and for carbon dioxide gas at 25 °C, a ΔH_f° value of -94.0518 kcal/mole was used.²⁹

The ΔH_c for liquid AMS at 25 °C was taken as -1204.87 ± 0.13 kcal/mole,¹ giving it a ΔH_f° of 16.8168 kcal/mole.

Computer Program II: FORTRAN IV Program for Calculating Heats of Polymerization

```
REAL MOWS
1  WRITE (5,5)
5  FORMAT (' H COMB CAL/GM  STD HC' /)
  READ(5,50) HCG, STHG
50  FORMAT (2G)
  WRITE (5, 15)
15  FORMAT (' #AVE MOLE WT  STD MN' /)
  READ (5, 55) MOWS, STMN
55  FORMAT (2G)
  IF (HCG .EQ. 0.0) CALL EXIT
  SHCM = STHG * 0.11818
  HCM = HCG*(0.11818)
  STHP = SQRT ((SHCM**2)+0.0169)
  HCO = HCG * MOWS / 1000.
  DP = MOWS / 118.18
  STDP = STMN/118.18
  C = DP * 9.0
  H = DP * 10.0
  HF = -HCO - C*94.0518 - (H/2.) * 68.3174
```

```
HPF = (HF - DP*16.8168)/DP
HPC = -HCG * 0.11818 - 1204.87
WRITE (5, 7) HCM, SHCM, HPC, STHP, HPF, DP, STDP
7  FORMAT (' HEAT OF COMB = 'F9.3,' KCAL/MOLE OF
2  MONO',/, ' STD DEV = 'F5.3,/,
3  ' HEAT OF POLY (COMB) = 'F7.3, ' KCAL/MOLE',/,
4  ' STD DEV = 'F5.3,/,
5  ' HEAT OF POLY (FORM) = 'F7.3,' KCAL/MOLE',/,
6  ' DEG OF POLY = 'F7.5,/,
8  ' STD DEV = 'F7.5,/,
7  5(' * * * * * ')/)
GO TO 1
END
```


Explanation of Symbols in Computer Program II

The following is a complete list with corresponding explanations of all symbols appearing in the computer program.

HCG	average ΔH_c in cal/g for a AMS oligomer sample
STHG	σ_m of ΔH_c
MOWS	\bar{M}_n of AMS oligomer sample
STMN	σ_m of \bar{M}_n
SHCM	propagated error of ΔH_c in kcal/mole of monomer
HCM	ΔH_c , kcal/mole of monomer
STHP	propagated error in ΔH_p (from equation 3)
HCO	ΔH_c , kcal/mole of oligomer
DP	average DP
STDP	propagated error of DP
C	number of carbon atoms in an average molecule of poly-AMS
H	number of hydrogen atoms in an average molecule of poly-AMS
HF	ΔH_f , kcal/mole of oligomer
HPF	ΔH_p , kcal/mole of monomer, from ΔH_f (equation 4)
HPC	ΔH_p , kcal/mole of monomer, from ΔH_c (equation 3)

Appendix C. Calculation of the Observed Heat of Polymerization with Gel Permeation Chromatography Data

The mole fraction of each specific oligomer of known DP can be calculated from GPC chromatograms. The mole fraction of dimer, trimer, tetramer, ..., (i)-mer, ..., (n)-mer is b_2 , b_3 , b_4 , ..., b_i , ..., b_n , respectively. The integer n is the DP of the largest oligomer that can be detected by GPC. The fraction b_{i+n} for DP's larger than n can be estimated if the MWD pattern can be described with a specific mathematical function. The equations developed here will assume b_n is the last fraction in the series.

The average DP is given by equation 24.

$$\overline{DP} = \sum_{i=2}^n i(b_i) \quad (24)$$

Equation 25 describes one step in the series of reactions which take place in the formation of an oligomer, exclusive of the initiation reaction.



M is one monomer unit and $O_{(i-1)}$ is the propagating oligomer with a DP equal to (i-1). The resulting oligomer, O_i , has a DP of i. The integer i may assume values between two and n.

The number of monomer-monomer bonds that produce dimers only is B_2 . In each oligomer molecule, the first reaction step is the formation of a dimer or a monomer-monomer bond and is included in B_2 (which makes B_2 equal to the total number of oligomer chains).

In other words, B_2 is the number of times the reaction described by equation 25 takes place with $i = 2$. The number of $(i-1)$ -mer-monomer bonds is B_i . The factor B_i is the number of unit-unit bond formations that result in (i) -mers exclusive of those unit-unit bonds which are included in the $(i-1)$ -mers. Each oligomer molecule with a DP of i or more has one $(i-1)$ -mer-monomer bond.

The factor B_i' in equation 26 calculated from b_i is equivalent to B_i .

$$B_2' = \sum_{i=2}^n b_i = 1.00 \quad (26a)$$

$$B_3' = \sum_{i=3}^n b_i \quad (26b)$$

$$B_4' = \sum_{i=4}^n b_i \quad (26c)$$

•
•
•

$$B_n' = b_n \quad (26d)$$

$$B_j' = \sum_{i=j}^n b_i \quad (26)$$

The total number of unit-unit bonds, T , in the sample from which the GPC chromatogram is taken, is described by equation 27.

$$T' = \sum_{i=2}^n \quad B'_i = \sum_{i=0}^{n-2} (n-i-1) b_{(n-i)} \quad (27)$$

The sum T' is also related to the total number of monomer moles in the oligomer sample. A unit-unit bond represents the addition of one monomer unit. It follows that T' is the total number of monomers added to the chain exclusive of the first monomer in each chain. Therefore, the total number of monomer units in the sample is equal to T plus the number of chains, B_2 .

Assuming the ΔH_p is a function of DP, the ΔH_p of a monomer-monomer bond, ΔH_{p_2} , will be different than the ΔH_p of an $(i-1)$ -mer-monomer bond, ΔH_{pi} . The equation for calculating the ΔH_{pi} for i equal 2 to n , will be similar to equation 5 in the discussion. The ΔH_p for each oligomer of a specific DP will be given by equation 28.

$$\Delta H_{pi} = \Delta H(\infty) + A \ln(1/i) + B(FI/i) + C (FII/i) + D (FIII/i) \quad (28)$$

Before equation 28 can be used in this method, the values of B , C , D and FI , FII and $FIII$ must be known accurately.

With successive approximations for the value of $\Delta H(\infty)$ in conjunction with various $A \ln(1/i)$ transformations, the $\Delta H_p(\text{obs})$ may be calculated from equation 29.

$$\Delta H_p(\text{obs}) = \frac{\Delta H_{p_2} + \sum_{j=3}^n \left[\Delta H_{pj} \left(\sum_{i=j}^n b_i \right) \right]}{\left[\sum_{i=0}^{n-2} (n-i-1) b_{(n-i)} \right] + 1} \quad (29)$$

The numerator of equation 29 is the total enthalpy contributed from all unit-unit bonds and the denominator is the total number of monomer units.

Appendix D. Theoretical Molecular Weight Distributions

A computer program was composed for calculating the theoretical DP distributions in terminated reversible polymerization. The basic format was discussed by Lowry.³⁰

Computer Program III: FORTRAN IV Program for Molecular Weight Distributions

```
DIMENSION V(201), VP(201), W(201)
REAL MOLAM, MCON
5  WRITE (5, 50)
50  FORMAT (' HEAT POL CEI TEM' /)
    READ (5, 10) HPOL, CTEM
10  FORMAT (F8.1, 2X, F7.3)
    WRITE (5, 52)
52  FORMAT (' VOL AMS TOT VOL REA TEMP' /)
    READ (5, 12) VAMS, TVOL, TEMP
12  FORMAT (3(F7.2, 2X))
    IF (VAMS .EQ. 0.0) CALL EXIT
    TVOL = TVOL/1000.
    TEMP = TEMP + 273.15
    MOLAM = (0.9088 * VAMS)/(118.18)
    MCON = MOLAM/TVOL
    E = EXP((HPOL/1.9872) * (1.0/TEMP - 1.0/CTEM))
    PI = 1.0/(1.0 + (7.38992/MCON) * E)
    WRITE (5, 55) PI
55  FORMAT (' PI =' F10.8 /)
    WRITE (5, 60)
60  FORMAT (' TAU' /)
    READ (5, 15) TAU
15  FORMAT (F8.6)
    P = (1.0 - TAU) * PI
    D = (1.0-TAU) * (1.0 - PI)
    DO 102 I = 1, 103
        W(I) = 0.0
102  V(I) = 0.0
        V(1) = TAU
    DO 105 K = 1, 200
```

```

      KK = K + 1
      IF (KK .LE. 102) GO TO 110
      KK = 102
110    TEM1 = D * (V(1) + V(2))
      DO 104 I = 2, KK
      TEM2 = P * V(I-1) + D * V(I+1)
      V(I-1) = TEM1
      W(I-1) = W(I-1) + V(I-1)
104    TEM1 = TEM2
      V(I) = TEM1
      W(I) = W(I) + V(I)
105    CONTINUE
      VTWM = 0.0
      VTLM = 0.0
      DO 115 I = 2, 200
      VTWM = W(I-1) + VTWM
115    VTLM = W(I) + VTLM
      DO 120 I = 2, 200
      W(I-1) = W(I-1)/VTWM
120    VP(I) = W(I)/VTLM
      WRITE (5, 65) (W(I), I = 1, 20)
65    FORMAT (' VALUES OF W(I) FROM 1 TO 20 INCLUDING
      2 MONOMER ' /4(2X, 5(F10.8, 2X)/))
      VTLM = 0.0
      DO 140 I = 2, 200
140    VTLM = VTLM + W(I)
      WRITE (5, 70) VTLM
70    FORMAT (' SUM OF ELEMENTS LESS MONOMER ' F10.8/)
      WRITE (5, 75) (VP(I), I = 2, 20)
75    FORMAT (' VALUES OF VP(I) FROM 2 TO 20 EXCLUDING
      2 MONOMER ' /4(2X, 5(F10.8, 2X)/))
      DP1 = 0.0
      DP2 = 0.0
      DO 130 I = 2, 200
      A = I
      DP1 = DP1 + W(I-1) * (A-1) * 118.18
130    DP2 = VP(I) * A * 118.18 + DP2
      WRITE (5, 80) DP1, DP2
80    FORMAT (' #AVE MOLE WT WITH MONOMER = ' F10.1, /
      2, ' #AVE MOLE WT WITHOUT MONOMER = ' F10.1///)
      WRITE (5, 85)
85    FORMAT (10(' * * * '))//)
      GO TO 5
      END

```

Explanation of Computer Program III

The following is a complete list with corresponding explanations of all symbols appearing in the computer program.

HPOL	ΔH_p , kcal/mole of monomer
CTEM	ceiling temperatures, Kelvin scale
VAMS	volume of AMS in reaction vessel
TVOL	total volume of reaction mixture at TEMP
TEMP	temperature of reaction, Celcius scale
MOLAM	number of moles of AMS
MCON	monomer concentration, moles/liter
E	intermediate variable used to calculate PI
PI	π , probability of propagations for ion
TAU	τ , probability of termination
P	elements and temporary elements of vector which describes DP distribution
D	
W(I)	
V(I)	
TEM1	
TEM2	
VTWM	sum of elements of DP vector with monomer included
VTLM	sum of elements of DP vector less monomer
VP(I)	elements of vector which are fractions of each DP in polymer
DP1	number average molecular weight with monomer included
DP2	number average molecular weight less monomer

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