# Heat of Polymerization of Alpha-Methylstyrene from Heats of Combustion of Monomer and Four Polymer Fractions

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Measurements have been made with a bomb calorimeter of the heats of combustion $(-\Delta Hc^\circ)$ at 25° C to form gaseous carbon dioxide and liquid water, of liquid alpha-methylstyrene (1-methyl-1-phenylethylene) and four fractions of its solid polymer having number average molecular weights of (I) 5,400, (II) 3,750, (III) 2,200, and (IV) 1,300. The values of heat of combustion are: monomer, 1204.87 kcal/mole; fraction I, 1196.04; fraction II, 1195.83; fraction III, 1195.50; and fraction IV, 1194.74 kcal/C_9H_{10} unit. Values of heats of polymerization $(-\Delta Hp^\circ)$ at 25° C of liquid alpha-methylstyrene to its solid polymers have been calculated from the heats of combustion. The values of heat of polymerization are: fraction I, 8.83; fraction II, 9.04; fraction III, 9.37; and fraction IV, 10.13 kcal/mole of monomer. The standard deviations of the mean for heat of combustion are not more than 0.30 kcal/mole, and for heat of polymerization, not more than 0.26 kcal/mole. The decrease in heat of polymerization with increasing molecular weight is discussed. The low values of heats of polymerization are ascribed in part to steric interference between the substituent groups of the polymer chain.

I. Introduction

This project was undertaken in connection with a general investigation of molecular properties of high polymers, and as a sequel to the work on heat of polymerization of styrene [1].[1] The purpose was to determine the effect of the alpha-methyl group on heats of combustion and polymerization. It was known that alpha-methylstyrene (1-methyl-1-phenylethylene) does not polymerize readily (in absence of catalyst) [2,3] and it was suspected that the steric interference between the substituent groups of the polymer chain might be partly responsible. A Fisher-Hirschfelder-Taylor molecular model of the polymer was made with the monomer units arranged head-to-tail, and alternating d and l units, that is, with Me and Ph groups interchanged, as follows:

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    H   Me   H   Ph   H   Me   H   Ph
----C---C----C---C----C---C----C---C----
    H   Ph   H   Me   H   Ph   H   Me
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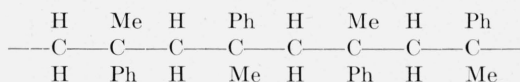
This model indicated that the molecule was so closely packed that it permitted only limited flexing or vibration and very little, if any, rotation. All models having other configurations (all head-to-tail) showed even higher degrees of interference. As a result of this steric effect, a low heat of polymerization was anticipated [4]. A second purpose of this work was to investigate the effect of molecular weight on the heat of polymerization.

II. Methods and Apparatus

The methods and bomb-calorimetric apparatus used in this work were the same as those described previously [1, 5, 6 to 10]. The observed value of heat of combustion in the bomb process, $-\Delta U_B$, in each experiment was reduced to the value of $-\Delta Uc^\circ$, the decrease in intrinsic energy accompanying the

combustion reaction

$$C_9H_{10}(l \text{ or } s) + \frac{23}{2} O_2(g) \rightarrow 9CO_2(g) + 5H_2O(l),$$
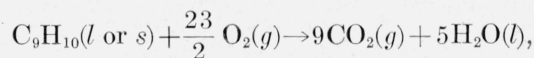
with each of the reactants and products in its thermodynamic standard state. The standard state for C_9H_{10} in this equation is that of the liquid monomer or solid polymer. The procedure described by Washburn [11] for calculating the above reduction was modified so as to apply to 30° C and to the energy content of the gases at zero pressure.

The values of heat of combustion are based on the amount of the combustion reaction, obtained from the mass of carbon dioxide formed (molecular weight 44.010). No corrections were applied for unburned carbon in the crucible. In the few experiments in which carbon remained, it was found to be negligible in amount. Frequent tests, using a method described by Shepherd [12], revealed no carbon monoxide in the gaseous products of combustion.

The calorimetric system was calibrated with NBS Standard Sample 39f of benzoic acid, using the value for the heat of combustion of this sample under the conditions of the standard bomb process, $Q_B = 26433.8$ abs j/g at 25° C, obtained from the value reported previously [8, 13].

The energy unit used is the absolute joule. Conversion to the conventional thermochemical calorie was made by use of the relation [14] 1 cal = 4.1840 abs j.

III. Materials

The alpha-methylstyrene monomer and polymer were obtained from the Dow Chemical Co. through the courtesy of D. R. Stull. The monomer was stored in a closed bottle in a refrigerator at about 11° C until it was introduced into glass bulbs preparatory to the combustion experiments. It contained no inhibitor of polymerization.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Analysis of alpha-methylstyrene by the Mass Spectrometry Section[2] of this Bureau gave the following results:

Alpha-methylstyrene_____99.6 mole percent
Styrene_____ 0.4

The values given for heat of combustion of alpha-methylstyrene in table 2 have been corrected for the presence of this amount of styrene, using the value previously found [1] for the heat of combustion of styrene.

The polymer used was formed during distillation of the monomer in the plant finishing still. No catalyst could be detected, although very minute amounts of some oxidation product in the iron still may have been present. The maximum temperature to which the material was subjected was about 50° to 60° C. After receipt at this Bureau, the sample of polymer was fractionated[3] and reprecipitated, the final product being four fractions consisting of fine noncrystalline powders. In the fractionation process, the raw polymer was dissolved in distilled toluene to make a 1-percent solution and filtered. The solution was placed in a 20-liter spherical flask in a constant-temperature (30° C) water bath. Methanol was added dropwise with stirring, and fractions were removed when the methanol concentration reached 40 percent (Fraction I), 60 percent (II), and 80 percent (III). The precipitates were allowed to settle for 1 to 3 days and took the form of a viscous liquid phase at the bottom of the flask. Fraction IV was obtained by evaporation of the remaining solution. Fractions I, II, and III were diluted to 1-percent solution with a mixture of toluene and a small amount of methyl ethyl ketone to prevent phase separation from absorbed water. The polymer fractions were reprecipitated from these solutions, by adding each solution dropwise to excess methanol in the approximate ratio of 1 to 20. Fraction IV was diluted to 4-percent solution and precipitated in the ratio of 1 to 10. The fractions were decanted, washed eight times with methanol and dried at 30° C and 0.001 mm of mercury for about 1 month. The above treatment of the polymers was such that monomer and lowest molecular weight polymer probably were removed.

The largest portion of the polymer yield was fraction II, lesser amounts were obtained for fractions III and IV, and fraction I was quite small.

The vacuum pump system used for drying the polymer fractions contained a trap immersed in liquid air located in the line between the pump and the vacuum chamber, where the polymer powders were placed. By means of this trap, removal of condensible material from the polymer was continued during periods when the pump was shut off (at night and on week ends). After evacuation had continued for about a month, the liquid air was removed from the trap, which was then pumped out to a pressure less than 10^{-4} mm of mercury. After this the stopcock between the pump and the trap

was shut off, and observations of the pressure in the system were made with a McLeod gage over a period of about 3 weeks. The rise in pressure during this time corresponded to the evaporation of a few hundredths of a milligram per week of material, assumed to be methanol, from about 10 to 15 g of polymer.

After completion of the above treatment, the polymers were exposed to the atmosphere for about 3 months. A sample of about 3.85 g of Fraction III was then evacuated for 2 days at 50° to 65° C and weighed immediately after removal from the vacuum chamber. It was found to have lost about 2.0 mg, all of which was regained upon exposure to the atmosphere for 6 days. It was concluded that all solvent and methanol probably had been removed from the polymer powders. Residual moisture would not affect the heat of combustion, as the results are calculated from the mass of CO_2 formed by burning the sample.

The results of determinations of molecular weight, intrinsic viscosity, and oxygen content of the poly-alpha-methylstyrene fractions are

Fraction	Molecular weight	Intrinsic viscosity	Oxygen content
	$\overline{M}_n$	$[\eta] = dl/g$	Avg. wt. % O_2
I_____	5, 400	0. 102	0. 039
II_____	3, 750	. 065	. 047
III_____	2, 200	. 039	. 085
IV_____	1, 300	. 036	. 050

The molecular weights[4] were determined by both cryoscopic and isothermal distillation methods [15] for each fraction. Good agreement between the results of the two methods was obtained. In the cryoscopic method 0.5- to 0.7-percent solutions in spectroscopic grade cyclohexane were used, and the lowering of the melting point was about 0.02° to 0.1° C. For the isothermal distillation, 5- to 15-percent solutions in toluene were made and suspended by a glass dish in the vapor of the solvent at 30° C. A modified method of measurement was used, in which the rate at which the solution gains weight is compared to the rate when a material of known molecular weight is in solution. These methods give approximate number average molecular weights. They correspond to average degrees of polymerization of 45.7 to 11.0, which are not very large. Differences in heats of combustion per monomer unit for polymers having given differences in molecular weights are more likely to be measurable if the molecular weights are small. The low molecular weights of the polymer used here may be partly a result of the fact that the alpha-methylstyrene was polymerized at raised temperatures. Previous workers [2] have found it difficult to obtain polymers of alpha-methylstyrene of high molecular weight, except at very low temperatures.

The measurements of intrinsic viscosity[5] were made by means of the Ubbelohde viscometer at

about 30° C, with concentrations in distilled toluene ranging from about 0.5 to 2 g/100 ml. These viscosity values are included only for relative comparison.

The oxygen contents [6] of the purified polymer fractions were determined by a direct method developed at this Bureau [16]. In the procedure for oxygen analysis, adsorbed water and air were removed by sweeping the sample for 2 hours at 30° to 50° C with pure helium.

The effect of the oxygen content of the polymer samples on the values of heat of combustion and heat of polymerization will depend on whether the oxygen is present in some inert impurity or is chemically combined with the polymer molecules. In the former case the effect of the oxygen would be negligible. If the oxygen is chemically combined with the polymer, the values of heat of combustion will be too low, and the values of heat of polymerization will be correspondingly too high. From the oxygen contents of the polymer samples given above, it is estimated that if all the oxygen is combined with the polymer the effect would not be greater than 0.03 percent in heat of combustion, or about 4 percent in heat of polymerization.

Since it is not known whether any of the oxygen is chemically combined with the polymer, the results have not been corrected for combined oxygen. The presence of the oxygen in the polymer samples introduces some uncertainty into the results, in addition to that resulting from other causes. Allowance for this has been made in calculating the estimated over-all standard deviations.[7]

IV. Results

The results of the calibration experiments are given in table 1. Two series of calibration experiments were required because of repairs to the bomb. The results of heat of combustion measurements on

[6] Measured by F. W. McCulloch and W. H. Smith.

[7] Standard deviation of the mean as used in tables 1 and 2 is defined as $[(\Sigma d^2)/n(n-1)]^{1/2}$, where d is the difference between a single observation and the mean, and n is the number of observations. In the case of the final values of heat of combustion given in table 3, the values of standard deviation include the effects of estimated systematic errors, as well as accidental errors. These values were calculated from the relation

$$s = Q[(s_E/E)^2 + (s_Q/Q)^2 + B^2 + R^2]^{1/2},$$

where s_E is the standard deviation of the mean of the experiments with benzoic acid to determine E, the energy equivalent of the calorimetric system; s_Q is the standard deviation of the mean of the results of the experiments to determine Q, the heat of combustion of the sample; B is an allowance of 5×10^{-5} for the standard deviation of the value used for the heat of combustion of benzoic acid; and R is an allowance of 2×10^{-4} in the case of the polymer or 5×10^{-5} for the monomer calculations, and takes account of systematic errors associated with the impurities in the polymer samples and the determination of the amount of the combustion reaction from the mass of carbon dioxide. The expression used in connection with the values in table 4 was

$$s' = [(s_m)^2 + (s_p)^2]^{1/2}.$$

In this expression s_m and s_p were calculated from the data of the heat of combustion measurements on monomer and polymer, respectively, by means of expressions of the form

$$s_m = Q[(s_E/E)^2 + (s_Q/Q)^2]^{1/2}$$

$$s_p = Q[(s_E/E)^2 + (s_Q/Q)^2 + R^2]^{1/2}$$

As used here R is an allowance of 15×10^{-5} for the errors associated with impurities in the polymers. It is assumed that systematic errors in the value used for the heat of combustion of benzoic acid and in the method of determining the amount of the combustion reaction will cancel in taking the difference between the heats of combustion of polymer and monomer.

the polymer and monomer for each experiment were calculated by using the appropriate mean of calibration series A or B, depending on whether the combustion experiment was performed before or after the alteration of the bomb.

TABLE 1. *Calibration of calorimeter with benzoic acid*

Observed energy equivalent (E) at 28.5°C		
	Series A	Series B
	abs j/°C	abs j/°C
	13793.2	13780.6
	13792.6	13783.8
	13794.4	13782.8
	13792.0	13781.6
	13791.7	13783.6
	13792.7	13788.0
	13789.8	13786.4
	13791.5	13785.1
		13783.0
		13787.4
		13786.6
Mean	13792.2	13784.4
Standard deviation of mean [a], s_E	0.5	0.7

[a] See footnote 7.

The results of heat of combustion measurements are given in table 2, where $-\Delta U_B$ is the observed heat of combustion under the conditions of the bomb process: the temperature (30° C) to which the reaction is referred, the mass (1g) of water placed in the bomb before each experiment, the internal volume of the bomb (377 ml), and the conditions specified in columns 1 and 2 of the table. The quantity $-\Delta U c^\circ$ is the reduced value, as explained in section II.

The values obtained for the mass of carbon dioxide formed in combustion are lower than the corresponding values calculated stoichiometrically from the masses of samples burned, assuming that the composition of the samples is represented by $(C_9H_{10})_x$. The average differences between observed and calculated masses of carbon dioxide are, for alpha-methylstyrene 0.052 percent, and for poly-alpha-methylstyrene fractions: I, 0.110 percent; II, 0.106 percent; III, 0.188 percent; IV, 0.082 percent. Frequent measurements of the carbon dioxide formed in combustion of Standard Sample 39f of benzoic acid yielded results in agreement with calculated values within about 0.016 percent. The observed deficiency of carbon dioxide in the case of alpha-methylstyrene can probably be attributed to air or moisture dissolved in the liquid. The deficiency in the case of the samples of poly-alpha-methylstyrene is probably due to the presence of nonhydrocarbon material in the samples as an impurity.

In table 3 are given values of $-\Delta U c^\circ$ per mole of C_9H_{10} (or per monomer unit) derived from the mean values given in table 2 by taking 9 moles of carbon dioxide as equivalent to 1 mole of monomer, or the C_9H_{10} unit of the polymer. There are also given in table 3 values of $-\Delta H c^\circ$, the decrease in heat content in the combustion reaction, with all reactants and products in their standard states.

TABLE 2. *Bomb-calorimetric measurements on poly-alpha-methylstyrene and alpha-methylstyrene*

Mass of sample	Initial O₂ pressure at 30° C	Mass of CO₂	Heat of combustion at 30° C $-\Delta U_B$	Heat of combustion at 30° C $-\Delta U_c°$
g	*atm*	*g*	*abs j/g* CO_2	*abs j/g* CO_2
POLY-ALPHA-METHYLSTYRENE, FRACTION I				
0.89655	36.2	3.00141	12628.3	12621.7
.95498	36.5	3.19689	12625.3	12618.4
.91254	37.2	3.05418	12620.7	12613.7
.96967	33.9	3.24617	12620.5	12613.9
.93899	33.2	3.14361	12616.8	12610.3
.98114	33.2	3.28476	12620.2	12613.7
Mean				12615.3
Standard deviation of mean [a], s_Q				1.7
POLY-ALPHA-METHYLSTYRENE, FRACTION II				
0.92370	35.9	3.09308	12620.5	12613.7
.95762	36.1	3.20656	12620.5	12613.6
.95526	36.7	3.19895	12619.4	12612.5
.98681	36.7	3.30407	12617.5	12610.5
.94285	36.5	3.15585	12623.3	12616.4
.96934	37.2	3.24607	12618.8	12611.8
Mean				12613.1
Standard deviation of mean [a], s_Q				0.8
POLY-ALPHA-METHYLSTYRENE, FRACTION III				
0.92886	32.6	3.10661	12616.5	12610.2
.93525	32.4	3.12905	12616.1	12609.8
.93816	32.5	3.13786	12620.5	12614.2
.96117	32.5	3.21605	12613.5	12607.1
.97595	32.7	3.26540	12615.5	12609.1
.94137	32.4	3.15006	12613.2	12606.9
Mean				12609.6
Standard deviation of mean [a], s_Q				1.1
POLY-ALPHA-METHYLSTYRENE, FRACTION IV				
1.02726	32.9	3.44043	12610.7	12604.2
0.94887	33.0	3.17777	12608.1	12601.7
.98428	33.2	3.29671	12607.1	12600.6
.93562	32.9	3.13345	12607.6	12601.2
.95606	32.5	3.20232	12608.6	12602.2
.94128	32.5	3.15200	12605.9	12599.6
Mean				12601.6
Standard deviation of mean [a], s_Q				0.6
ALPHA-METHYLSTYRENE, MONOMER				
0.89208	32.7	2.98873	12710.2	12710.4
.80943	32.6	2.71183	12708.4	12708.7
.79325	32.6	2.65744	12709.4	12709.7
.74323	32.4	2.48983	12705.7	12706.2
.90776	32.2	3.04109	12710.9	12711.2
.90256	32.3	3.02352	12709.3	12709.5
Mean				12709.3
Standard deviation of mean [a], s_Q				0.7

[a] See footnote 7.

For reducing the values at 30° to corresponding values at 25° C, the heat capacity of alpha-methylstyrene was derived from unpublished data obtained at the Bureau on the heat capacity of styrene [17], and an estimate of the increase in $\bar{C}_p$ accompanying the addition of a CH₂ group; the heat capacity of poly-alpha-methylstyrene was obtained from that of the monomer by use of the ratio of heat capacities [17], polystyrene: styrene.

Values of heat of polymerization of alpha-methylstyrene to give the four polymer fractions are shown in table 4. These values were obtained by taking the difference between the value of $-\Delta Hc°$ (25° C) (table 3) for the monomer, and the value for each of the polymer fractions.

TABLE 4. *Values of heat of polymerization*

| Fraction	$-\Delta H_p°$ (25° C)	Standard deviation of mean [a], s'
	kcal/mole	
I	8.83	0.26
II	9.04	.22
III	9.37	.23
IV	10.13	.22

[a] See footnote 7.

V. Discussion

The values of heat of polymerization given in table 4 are lower than the value ($-\Delta Hp°=16.7$ kcal/monomer unit) previously reported for styrene [1], and are also lower than any value previously reported for a vinyl compound [18]. It has been suggested by Flory [19] and by Evans and Tyrrall [4] that low values of heat of polymerization of 1,1-disubstituted ethylenes are to be attributed to steric interference between the substituent groups. There are other effects that may be partly responsible for the low heat of polymerization, such as the effects of side groups on bond energies in the monomer as compared with those in the polymer, and the lack of a large "end effect", which in ethylene arises from the nearness of the double bond to the ends of the monomer molecule [18]. It is believed, however, that the magnitude of the latter two effects is not sufficient to account for the very low values of $-\Delta Hp°$ for alpha-methylstyrene, but that steric interference must be an important factor.

TABLE 3. *Values of heat of combustion*

| Quantity	Fraction I abs kj/C₉H₁₀ unit	Fraction I kcal/C₉H₁₀ unit	Fraction II abs kj/C₉H₁₀ unit	Fraction II kcal/C₉H₁₀ unit	Fraction III abs kj/C₉H₁₀ unit	Fraction III kcal/C₉H₁₀ unit	Fraction IV abs kj/C₉H₁₀ unit	Fraction IV kcal/C₉H₁₀ unit	Alpha-methylstyrene (liquid) abs kj/mole	Alpha-methylstyrene (liquid) kcal/mole
$-\Delta Uc°$ (30° C)	4996.80	---	4995.93	---	4994.54	---	4991.37	---	5034.03	---
$-\Delta Hc°$ (30° C)	5003.10	---	5002.23	---	5000.84	---	4997.67	---	5040.33	---
$-\Delta Hc°$ (25° C)	5004.24	1196.04	5003.37	1195.83	5001.98	1195.50	4998.81	1194.74	5041.17	1204.87
Standard deviation of mean [a], s	1.24	0.30	1.10	0.26	1.15	0.27	1.09	0.26	0.53	0.13

[a] See footnote 7.

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In general, it is found that molecular models of polymers of 1,1-disubstituted ethylenes indicate that steric interference is quite pronounced if the monomer units are joined head-to-tail but is much less for the head-to-head and tail-to-tail arrangement. The low values of $-\Delta Hp^\circ$ for alpha-methylstyrene are therefore consistent with other evidence [20, 21] that polymers of 1,1-disubstituted ethylenes are formed by head-to-tail addition.

It will also be seen from table 4 that the values of heat of polymerization of alpha-methylstyrene decrease systematically with increasing molecular weight of the polymer. This was not expected, and it seems worth while to examine other pertinent information to see whether it is consistent with the observed variation of heat of polymerization with molecular weight of polymer.

It is well known [22] that the heats of formation of an homologous series of hydrocarbons, either liquid or gaseous, can be represented by a linear function of the number of carbon atoms in the normal alkyl radical, provided this number is fairly large, but that this relation does not hold for the first few members of the series. It may be inferred that the heat of formation of a straight-chain polymer molecule will be a linear function of the number of monomer groups in the molecule, provided this number is sufficiently large, but that this relation may not hold for a molecule containing only two or three monomer units. Then the heat of addition of a mole of liquid (or gaseous) monomer to a mole of straight-chain liquid or noncrystalline solid (or gaseous) polymer according to the reaction

$$m_{n-1} + m = m_n, \tag{1}$$
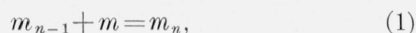
will be a constant, q, independent of n if $n > r$, where r is some small integer. If $n \leqq r$ the heat of reaction will, in general, differ from q. Let $(q + \Delta_i)$ represent the heat of the reaction

$$m_{i-1} + m = m_i \qquad (i \leqq r). \tag{2}$$
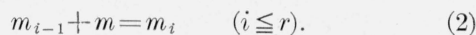
Then the heat of the reaction

$$n m = m_n, \tag{3}$$
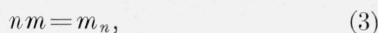
with $n > r$ will be given by

$$-\Delta H^\circ = (n-1)q + \sum_{i=2}^{r} \Delta_i \tag{4}$$

and the heat of polymerization per mole of monomer will be

$$-\Delta Hp^\circ = -\Delta H^\circ / n = q + \frac{\sum_{i=2}^{r}\Delta_i - q}{n}. \tag{5}$$

If M_0 and M represent the molecular weights of monomer and polymer, respectively, then eq 5 may be written in the form

$$-\Delta Hp^\circ = q + \frac{M_0\left[\sum_{i=2}^{r}\Delta_i - q\right]}{M}. \tag{6}$$

From eq 6 it is evident that if $\sum_{i=2}^{r}\Delta_i < q$, $-\Delta Hp^\circ$ will increase with increasing M, as has been shown to be true in the case of ethylene [23]. In order that $-\Delta Hp^\circ$ shall decrease with increasing M it is necessary that $\sum_{i=2}^{r}\Delta_i > q$.

The equation

$$-\Delta Hp^\circ = 8.424 + \frac{2194}{M}, \tag{7}$$

was derived by the method of least squares from the experimental values of $-\Delta Hp^\circ$ and M for the four fractions of alpha-methylstyrene polymer. The observed values of $-\Delta Hp^\circ$ and values calculated from eq 7 are compared in the following tabulation.

	$-\Delta Hp^\circ$		
M	Observed	Calculated	Observed − Calculated
	kcal/monomer unit	kcal/monomer unit	kcal/monomer unit
5400	8. 83	8. 83	0. 00
3750	9. 04	9. 01	−. 03
2200	9. 37	9. 42	+. 05
1300	10. 13	10. 11	−. 02

The maximum difference between observed and calculated values is seen to be 0.05 kcal, which corresponds to about 0.004 percent of the heat of combustion. The standard deviation for q is 0.05, and for $M_0(\sum_{i=2}^{r}\Delta_i - q)$ is 97. According to eq 7, $q = 8.4$ kcal and $(\sum_{i=2}^{r}\Delta_i - q) = 18.6$ kcal, so that $\sum_{i=2}^{r}\Delta_i = 27.0$ kcal.

As indicated in the derivation, eq 5 and 6 are valid only for $n \geqq r$, that is, for values of n such that heat of formation per mole of polymer is a linear function of n. The good agreement between the observed and calculated values of $-\Delta Hp^\circ$ therefore indicates that heat of formation (or combustion) of poly-alpha-methylstyrene per mole of polymer is a linear function of n, the number of monomer units in the

molecule,[8] at least for $n \geqq 11$, and it seems probable that this relation would hold for $n > 3$ or 4.

It may be noted that in the derivation of eq 5 and 6 it was tacitly assumed that n and M are constants for any given sample of material, that is, that all of the polymer molecules in a given sample are of the same length. When these equations are applied to polymers containing molecules of various lengths, it can be shown that the proper values of M and n to be used are the number averages, which were actually used in the derivation of eq 7.

The only 1,1-disubstituted ethylene for which data are available on which a reasonable estimate of $\sum_{i=2}^{r} \Delta_i$ for that compound can be based is isobutene. Chemical and X-ray evidence [20, 21], as well as a low heat of polymerization, indicate that the monomer units in the polyisobutene molecule are joined head-to-tail. Evans and Tyrrall [4] have reported for the heat of polymerization of liquid isobutene to liquid polymer the value 12.6 kcal per mole of monomer, and for the heat of dimerization of gaseous monomer to gaseous head-to-tail dimer (2,4,4-trimethyl-1-pentene) the value 19.9 kcal per mole of dimer. These values indicate that for isobutene $q = 12.6$ kcal and $\Delta_2 = 7.3$ kcal, if the difference between heats of vaporization of polymer and monomer is neglected.

The heat of dimerization of alpha-methylstyrene is not known. If it is assumed to be about the same as that of isobutene, that is, about 20 kcal per mole of dimer, and if q is about 8 kcal as indicated by eq 7, then Δ_2 would be about 12 kcal. It would be expected from the fact that steric interference is quite small in a head-to-tail dimer, but is pronounced in the trimer and in polymers of higher molecular weight [4], that $(\Delta_3 + \Delta_4 + \ldots \Delta_r)$ would be small in comparison with Δ_2, and might even be negative, so that it is unlikely that the value of $\sum_{i=2}^{r} \Delta_i$ based on the above assumptions would be much more than half of the value 27.0 kcal derived from eq 7. However, the fact that the above value of Δ_2, 12 kcal, is greater than the value 8 kcal derived from eq 7 for q, suggests that the above assumptions are consistent with a decrease in heat of polymerization with increasing molecular weight of polymer, although they do not lead to quantitative agreement with the observed variation of heat of polymerization with molecular weight. In this connection, it should be emphasized

that some of the assumptions made in comparing alpha-methylstyrene with isobutene are subject to considerable uncertainty.

The estimated effect of the oxygen contents of the polymer fractions on heat of combustion is too small to account for the observed decrease in heat of polymerization with increasing molecular weight.

Although the low values of heat of polymerization of alpha-methylstyrene indicate that the monomer units in the polymer molecule are joined head-to-tail for the most part, there is some reason for conjecturing that the first step in the formation of the polymer molecule may be the tail-to-tail
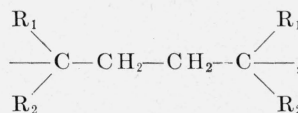
combination of two monomer units, and that the subsequent growth of the molecule is by head-to-tail addition. As stated previously, a model of a polymer molecule with monomer units joined head-to-tail indicates a considerable amount of steric hindrance. A model of a polymer molecule in which two units are joined tail-to-tail, and the others are joined head-to-tail to one of the first two indicates only a little steric hindrance in the first three groups. It would therefore be expected that for such a molecule both Δ_2 and Δ_3 would have fairly large positive values, possibly large enough to bring $\sum_{i=2}^{r} \Delta_i$ into quantitative agreement with the value derived from eq 7.

In regard to whether the initial step in the formation of a 1,1-disubstituted ethylene polymer molecule could be the tail-to-tail combination of two monomer units, it may be noted that Evans and Polanyi [25] have concluded from calculated heats of reaction that in the first step, tail-to-tail addition of isobutene is more probable than head-to-tail addition, and that the latter is more probable than head-to-head addition.

It is believed that the heat of polymerization of alpha-methylstyrene decreases with increasing molecular weight of polymer, as is indicated by the experimental data reported herein. The magnitude of the observed decrease is greater than would be expected from the data on isobutene. The foregoing discussion shows, nevertheless, that the observed change in heat of polymerization with molecular weight is consistent with certain plausible assumptions regarding the structure of the polymer molecule and the heats of the first few steps of the polymerization reaction.

VI. Previous Work

Auwers, Roth, and Eisenlohr [26] reported for the heat of combustion of alpha-methylstyrene monomer the experimental values 10,183 and 10,194, mean 10,189 cal/g. By applying appropriate corrections for the value used for heat of combustion of benzoic acid, and by applying the Washburn correction, calculating for weight in vacuum, and correcting to the

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[8] It has been pointed out [24] that this fact can be shown more directly by representing the heat of combustion per mole of polymer as a linear function of n:

$$-\Delta Hc^\circ \text{ (25°C) (solid alpha-methylstyrene polymer)} = A + Bn,$$

or heat of combustion per monomer unit by the equivalent relation

$$-\frac{\Delta Hc^\circ}{n} \text{ (25°C) (solid alpha-methylstyrene polymer)} = \frac{A}{n} + B.$$

(A determination of the constants in the latter equation by the method of least squares yielded the values $A = -18.56$, $B = 1196.447$). Combination of the above equation with the value for the heat of combustion of alpha-methylstyrene monomer, designated by the symbol C, yields the relation

$$-\Delta Hp^\circ = C - \frac{A}{n} - B,$$

which is of the same form as eq 5. However, it is not immediately evident from this derivation how the constant A is related to $q = (C - B)$ and to the end effects, $\Delta_1, \Delta_2, \ldots$ This relation is given explicitly by the derivation in the text.

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reaction at constant pressure at 25° C, the mean of the above results may be reduced to a comparable basis with the present work. After these corrections, the above value for heat of combustion becomes 1202.8 kcal/mole.

Approximate corrections applied to the value reported by Lemoult [27] give 1209.4 kcal/mole for heat of combustion of the monomer.

Previous measurements at this Bureau [28] give the value for heat of combustion of liquid alpha-methylstyrene $-\Delta Hc°$ (25° C) $=1204.3$ kcal/mole, with an uncertainty of ± 0.4 kcal/mole.

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