U. S. Department of Commerce
National Bureau of Standards

Research Paper RP2073
Volume 44, March 1950

Part of the Journal of Research of the National Bureau of Standards

Heats of Polymerization. A Summary of Published Values and Their Relation to Structure

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This paper contains a table showing values of heats of polymerization assembled from a survey of the literature. There are 42 substituted vinyl compounds arranged as follows: vinyl alkyls, vinyl aryls, other vinyls, vinyl acids and esters, dienes and copolymers. Values reported by different authors are given for each compound, with corresponding states of monomers and ploymers and a notation on the methods used in obtaining the values. A second table gives structural formulas of monomers.

Some values of heats of polymerization to hypothetical polymers having no steric hindrance are calculated from published values of heats of formation of hydrocarbons, making certain assumptions regarding branch groups. The method of calculation is explained. Heat of polymerization is arbitrarily assigned to four energy effects: (1) the reaction $\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$; (2) the effect of side groups on bond energies when there is no interaction between the groups; (3) the effect of steric hindrance between side groups; and (4) the "end effect" arising from the nearness of the double bond to the end of the monomer molecule.

Values of heats of polymerization are compared, and their relation to structure is examined, with particular emphasis on the effect of steric hindrance. Etyhlene has the highest and alpha-methylstyrene the lowest heat of polymerization; isobutene and the methacrylates also are low. Disubstitution on the same vinyl carbon is a frequent cause of steric interference, with consequent reduction in heat of polymerization. Large branched substituents may cause steric interference. The substitution of chlorine on the aromatic ring of styrene has little effect on heat of polymerization. Steric interference may prevent polymerization above the dimer. The heat of copolymerization of butadiene and styrene lies between the values for the separate monomers. Heat of copolymerization of other monomer pairs may be higher or lower than the value for the separate components. Heat of polymerization depends somewhat on the ratio of 1,2- and 1,4-addition, and on the amount of crystallinity of the polymers.

I. Introduction

Values of the heats of polymerization of various materials are recorded in many journal articles, but there is no recent systematic compilation and comparison of these values. Flory [1] [1] calculated a number of values in 1937 before there were many experimental observations available, and Roth and Rist-Schumacher [2] published in 1942 a summary of values almost entirely obtained from German sources. Since then a large number of experimental observations have been made, and many interesting comparisons are now possible. This paper has been written to collect the scattered data and list them in a convenient form for reference so that useful values of heats of polymerization can readily be obtained without extensive searching. A second purpose is to permit comparison of the data for different compounds, so that systematic trends and anomalies can be recognized. The discussion that follows calls attention to some of the relations between the

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

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heats of polymerization and the structures of the monomers and polymers. The reader may wish to make further comparisons of the types illustrated.

II. Description and Use of Tables

The table of values of heats of polymerization (table 1) is arranged for convenience according to substituent groups as follows: vinyl alkyls, vinyl aryls, other vinyls, and vinyl acids and esters; these are followed by dienes and copolymers. Within each class, the compounds are arranged according to increasing size and molecular weight of the monomer. The values reported by the several authors are arranged chronologically for each compound.

TABLE 1. *Heats of polymerization*

Compound	$-\Delta Hp$ [a]	States of monomer and polymer	Experimental (E) or Calculated (C) [b]	Method and comment
VINYL ALKYLS				
Ethylene [b]	*kcal/mole of monomer*			*Polymer is 55 to75% crystalline* [36, 37].
Flory [1] (1937)	23.1	gas→gas	C	Heats of formation.
Jessup [15] (1948)	[c] 12.4*	do	C	Do.
Do	[d] 22.3	do	C	Limit value for ∞ chain, no steric hindrance between side groups. $\Delta Hv=2.4$, $\Delta Hm=1.2$.
Do	24.7	Gas→liquid	C	
Do	25.9	Gas→solid	C	
Jessup (Roberts) [15] (1948); Prosen & Rossini [8] (1946)	25.4	do	E	Heats of combustion.
Propylene				
Flory [1] (1937)	22.8	Gas→gas	C	Heats of formation.
Roberts [e] (1949)	20.5	do	C	Do.
Fontana & Kidder [42] (1948)	16.5 (−74.5°C)	Liquid→solid	E	Equilibrium constants.
1-Butene				
Flory [1] (1937)	23.4	Gas→gas	C	Heats of formation.
Roberts [e] (1949)	20.9	do	C	Do.
Isobutene				
Flory [1] (1937)	23.0	do	C	Do.
Roberts [e] (1949)	19.2	do	C	Do.
Thomas, et al [43] (1940)	10 (−78°C)	Liquid→solid [g]	E	
Kazanskii & Rozengart [44] (1942)	10.2* (130° to 295°C)	Gas→gas [g]	E	Equilibrium constants; dimerized with catalyst, product is mixed isomers
Evans & Polanyi [3] (1943)	12.8	Solution in hexane	E	Calorimetric.
Evans & Tyrrall [4] (1947)	9.9*	Gas→gas	C	Heats of formation; dimer is 2,4,4-trimethyl-1-pentene.
Do	19.2 (20.3)	do	C	Heats of formation, head-tail, no steric hindrance between side groups.
Do	12.6	Liquid→liquid	E	Heats of formation and combustion, with steric hindrance.
cis-2-Butene				
Flory [1] (1937)	23.2	Gas→gas	C	Heats of formation.
Roberts [e] (1949)	19.4	do	C	Do.
trans-2-Butene				
Flory [1] (1937)	22.3	do	C	Do.
Roberts [e] (1949)	18.4	do	C	Do.
2-Methyl-1-butene				
Flory [1] (1937)	23.6	do	C	Do.
Roberts [e] (1949)	18.7	do	C	Do.
cis-2-Pentene				
Flory [1] (1937)	23.1	do	C	Do.
Roberts [e] (1949)	19.2	do	C	Do.
trans-2-Pentene				
Flory [1] (1937)	23.1	do	C	Do
Roberts [e] (1949)	18.1	do	C	Do.

See footnotes at end of table.

TABLE 1. *Heats of polymerization*—Continued

Compound	$-\Delta Hp$ [a]	States of monomer and polymer	Experimental (E) or Calculated (C) [b]	Method and comment
VINYL ALKYLS—Continued				
2,3-Dimethyl-1-butene	*kcal/mole of monomer*			
Flory [1] (1937)	23.1	Gas→gas	C	Heats of formation.
Roberts [e] (1949)	18.4	do	C	Do.
1-Heptene				
Flory [1] (1937)	23.6	do	C	Do.
Roberts [e] (1949)	20.5	do	C	Do.
VINYL ARYLS				
Styrene				
Flory [1] (1937)	20	Gas→gas	C	Heats of formation.
Roberts [e] (1949)	19	do	C	Three kcal less than for ethylene [1].
Luschinsky [45] (1938)	13.8	Liquid→solid	E	Heats of combustion, fractionated polymer.
Roth & Rist-Schumacher [2] (1942)	20.2*	Liquid→liquid	E	Heats of combustion. Perhaps the value is per mole of dimer.
Votinov, et al [46] (1942)	21.9	Liquid→solid [g]	E	Heats of combustion.
Goldfinger, et al [47] (1943)	15.0 (70° to 140° C)	Liquid→solution (35 to 85%) in monomer.	E	Adiabatic calorimeter.
Ferguson, et al [48] (1945)	17.2	Liquid→solution (12%) in monomer.	E	Do.
Tong & Kenyon [49] (1947)	16.3 to 18.0 (76.8° C)	Liquid→solid	E	Isothermal calorimeter.
Do	16.1 (76.8° C)	do	E	Extrapolated to zero catalyst.
Roberts, et al [50] (1947)	16.7	do	E	Heats of combustion.
Do	17.5	Liquid→solution (7%) in monomer.	E	Heat of solution ($-\Delta Hs$=0.86).
Indene				
Roth & Rist-Schumacher [2] (1942)	16.9*	Liquid→solid	E	Heats of combustion. Perhaps the value is per mole of dimer.
alpha-Methylstyrene				
Roberts & Jessup [17] (1948)	8.8 to 10.1	do	E	Heats of combustion; fractionated polymer, average D. P. 15 to 7.5, respectively.
para-Ethylstyrene				
Tong & Kenyon [49] (1947)	16.4 to 16.9 (76.8° C)	do	E	Isothermal calorimeter.
Do	16.3 (76.8° C)	do	E	Extrapolated to zero catalyst.
ortho-Chlorostyrene				
Tong & Kenyon [49] (1947)	16.5 to 17.6 (76.8° C)	do	E	Isothermal calorimeter.
Do	16.4 (76.8° C)	do	E	Extrapolated to zero catalyst.
para-Chlorostyrene				
Tong & Kenyon [49] (1947)	16.2 to 17.5 (76.8° C)	do	E	Isothermal calorimeter.
Do	16.0 (76.8° C)	do	E	Extrapolated to zero catalyst.
2, 5-Dichlorostyrene				
Tong & Kenyon [49] (1947)	16.8 to 18.0 (76.8° C)	do	E	Isothermal calorimeter.
Do	16.5 (76.8° C)	do	E	Extrapolated to zero catalyst.
Anethole				
Staudinger & Schläpfer [51] (1939)	13.8	do [g]	E	Heats of combustion.
OTHER VINYLS				
Ethylene oxide [h]				*Polymer may be crystalline.*
Staudinger & Schläpfer [51] (1939)	22.6	Liquid→solid	E	Heats of combustion.
Acrylonitrile [h]				*Polymer may be crystalline.*
Tong & Kenyon [41] (1947)	17.3 (76.8° C)	do	E	Isothermal calorimeter; extrapolated to zero catalyst.
Vinyl acetate				
Tong & Kenyon [41] (1947)	21.3 (76.8° C)	do	E	Isothermal calorimeter; not dependent on catalyst concentration.

See footnotes at end of table.

TABLE 1. *Heats of polymerization*—Continued

Compound	$-\Delta Hp$ [a]	States of monomer and polymer	Experimental (E) or Calculated (C) [b]	Method and comment
OTHER VINYLS—Continued				
Vinylidene chloride [h]	*kcal/mole of monomer*			*Polymer is largely crystalline* [39, 40].
Tong & Kenyon [41] (1947)	14.4 (76.8° C)	Liquid→solid	E	Isothermal calorimeter; extrapolated to zero catalyst.
Vinyl butyl ether [h]				
Shostakovskii & Bogdanov [52] (1942)	14.4 (40° to 60° C)	Liquid→liquid [g]	E	Polymerized with alcoholic $FeCl_3$.
VINYL ACIDS AND ESTERS				
Acrylic acid				
Staudinger & Schläpfer [51] (1939)	15.0	Liquid→solid [g]	E	Heats of combustion.
Evans & Tyrrall [4] (1947)	18.5	Solution 5 ml in 100 ml H_2O.	E	Calorimetric.
Methacrylic acid				
Evans & Tyrrall [4] (1947)	15.8	Solution 10 ml in 100 ml H_2O.	E	Do.
Methyl acrylate				
Evans & Tyrrall [4] (1947)	20.2	Solution 50 ml in 50 ml EtOH.	E	Do.
Tong & Kenyon [41] (1947)	18.7 (76.8° C)	Liquid→solid	E	Isothermal calorimeter; not corrected for unreacted monomer; 0.01% benzoyl peroxide.
Methyl methacrylate				
Iwai [53] (1946)	16.3	do [g]	E	Heats of combustion.
Tong & Kenyon [54, 55] (1945–46)	13.0 (76.8° to 110° C)	do	E	Isothermal calorimeter.
Tong & Kenyon [54] (1945)	13.1 (76.8° C)	Solution (51%) in CCl_4	E	Do.
Do	13.6 (76.8° C)	Solution 26 to 32% H_2O, 26 to 32% MeOH.	E	Isothermal calorimeter; polymer insoluble in MeOH–H_2O.
Kunst & Magat [56] (1947)	10 to 13		E	
Evans & Tyrall [4] (1947)	12.9	Emulsion 25 ml in 100 ml H_2O.	E	Calorimetric.
Do	20	Gas→gas	C	Estimated from isobutene, head-tail, no steric hindrance between side groups.
Ethyl methacrylate				
Iwai [53] (1946)	14.1	Liquid→solid [g]	E	Heats of combustion.
normal-Butyl methacrylate				
Tong & Kenyon [55] (1946)	13.5 (76.8° C)	do	E	Isothermal calorimeter.
Phenyl methacrylate				
Tong & Kenyon [55] (1946)	12.3 (76.8° C)	do	E	Do.
Cyclohexyl methacrylate				
Tong & Kenyon [55] (1946)	12.2 (76.8° C)	do	E	Do.
Benzyl methacrylate				
Tong & Kenyon [55] (1946)	13.4 (76.8° C)	do	E	Do.
DIENES				
1,3-Butadiene				
Lebedev, et al [31] (1935)	18.1 to 38.4	Gas→solid	E	Heats of combustion; several polymers, formed in different ways.
Do	12.2 to 32.5	Liquid→solid	E	
Flory [1] (1937)	19.9	Gas→gas	C	Heats of formation, 1,2-polymerization.
Roberts [e] (1949)	17.4	do	C	Heats of formation, 1,2-polymerization.
Flory [1] (1937)	20.4	do	C	Heats of formation, 1,4-polymerization.
Roberts [e] (1949)	18.7	do	C	Heats of formation, 1,4-polymerization.
Roberts & Jessup [57] (1948); Prosen & Rossini [5] (1945)	23 (preliminary)	Gas→solid	E	Heats of combustion.
Do	18 (preliminary)	Liquid→solid	E	Do.
1,3-Cyclopentadiene				
Baur & Frater [58] (1941)	8.7* (149° to 185° C)	Gas→gas [g]	E	Equilibrium constant, dissociation at constant volume. Cyclic dimer.
1,4-Pentadiene				
Flory [1] (1937)	24.1	do	C	Heats of formation, 1,2-polymerization.
Roberts [e] (1949)	20.7	do	C	Heats of formation, 1,2-polymerization.

See footnotes at end of table.

TABLE 1. *Heats of polymerization*—Continued

Compound	$-\Delta Hp$ [a]	States of monomer and polymer	Experimental (E) or Calculated (C) [b]	Method and comment
DIENES—Continued				
Isoprene	*kcal/mole of monomer*			
Jessup [59] (1938)	24.1	Gas→solid	E	Heats of combustion; polymer is purified natural rubber.
Do	17.9	Liquid→solid		
Staudinger & Schläpfer [51] (1939)	21.6	do [g]	E	Heats of combustion.
Evans & Tyrrall [4] (1947)	16.1 (16.9)	Gas→gas	C	Heats of formation, no steric hindrance between side groups.
Roberts [f] (1949)	16.9 (17.7)	do	C	Heats of formation, no steric hindrance between side groups.
COPOLYMERS				
Butadiene-styrene				
Jessup [60] (1944)	17 to 18	Liquid, liquid→solid	E	Heats of combustion, 23% (wt) styrene.
Roberts & Jessup [50,61] (1947, 1944); Prosen & Rossini [5] (1945)	17.9	do	E	Heats of combustion, 25.5% (wt) styrene.
Vinyl acetate-maleic anhydride				
Tong & Kenyon [29] (1948)	20.2 (76.8° C)	Solution of monomers→solid.	E	Isothermal calorimeter; 1:1 copolymer insoluble in the system.
Isopropenyl acetate-maleic anhydride				
Tong & Kenyon [29] (1948)	17.8 (76.8° C)	do	E	Isothermal calorimeter; 1:1 copolymer insoluble in system.
Vinyl acetate-diethyl maleate				
Tong & Kenyon [29] (1948)	20.0 (76.8° C)	do	E	Isothermal calorimeter; 1:1 copolymer.
Vinyl acetate-diethyl fumarate				
Tong & Kenyon [29] (1948)	18.6 (76.8° C)	do	E	Isothermal calorimeter; 1:1 copolymer.

[a] At or near 25° C unless otherwise indicated.

[b] The calculated values (except those for ethylene and dimerization if isobutene) are not the actual heats of polymerization which would be obtained experimentally, but apply only to hypothetical ploymers that are free from steric interference between substituent groups attached to the polymer chain.

[c] *denotes heat of dimerization.

[d] Recalculation of Flory's values by the author was done in the same manner and gives this same value.

[e] Recalculated by the author following Flory [1] (see Section III).

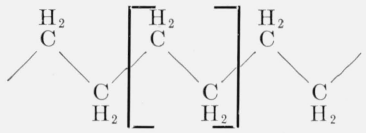
[f] Reference [62] gives a value for the heat of formation of isoprene, supposed to be the "best value" to date. It was obtained by applying certain corrections to the data of Jessup [59] (which was used unchanged by Evans and Tyrrall), and combining this result with calculations by Prosen and Rossini. Using this value for isoprene, calculations like those of Evans and Tyrrall give the values shown for $-\Delta Hp$.

[g] Probable states.

[h] See comments in last column.

A table of structural formulas (table 2) is included so that the reader can readily compare the structural features of the polymers. The arrangement of this table is the same as that of table 1. The monomers are shown with the vinyl or diolefin group as the principal portion with substituent groups to the side. The polymer chain would be formed by joining these vinyl or diolefin groups. Since the diagrams in table 2 represent only one view of the molecule, they do not show the zig-zag nature of the polymer chain, which is shown here in idealized form:

Polyethylene



Polybutadiene (*cis*-1,4-polymerization)

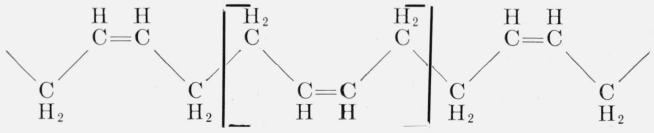


TABLE 2. *Formulas and molecular weights*

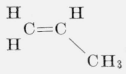
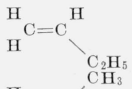
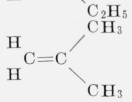
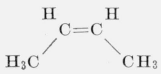
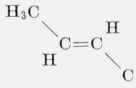
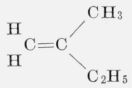
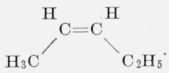
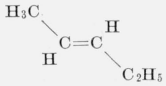
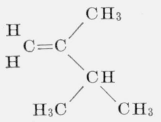
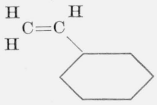
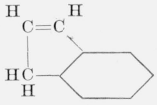
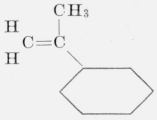
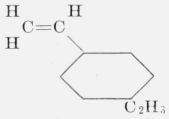
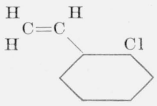
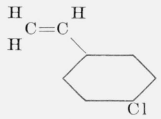
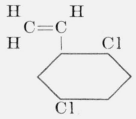
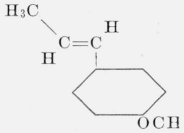
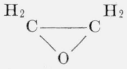
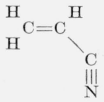
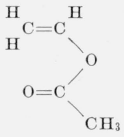
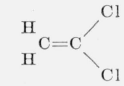
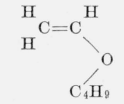
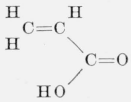
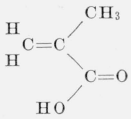
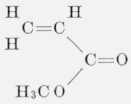
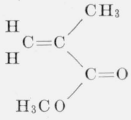
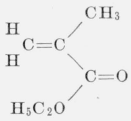
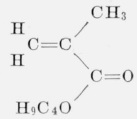
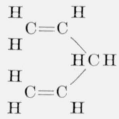
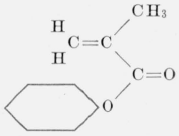
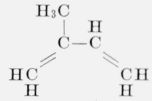
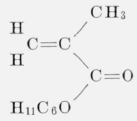
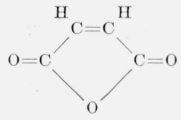
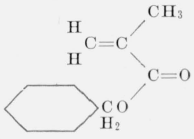
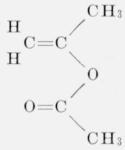
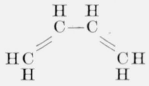
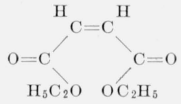
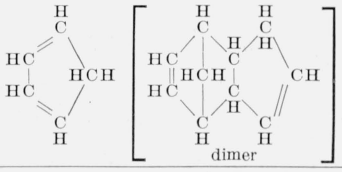
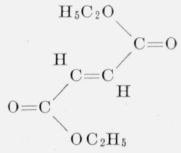
Ethylene		28.052
Propylene		42.078
1-Butene		56.104
Isobutene		56.104
cis-2-Butene		56.104
trans-2-Butene		56.104
2-Methyl-1-butene		70.130
cis-2-Pentene		70.130
trans-2-Pentene		70.130
2, 3 - Dimethyl-1-butene		84.156
1-Heptene		98.182
Styrene		104.144
Indene		116.154
alpha - Methylstyrene		118.170
para-Ethylstyrene		132.196
ortho - Chlorostyrene		138.593
para-Chlorostyrene		138.593
2,5-Dichlorostyrene		173,042
Anethole		148.196
Ethylene oxide		44.052
Acrylonitrile		53.062
Vinyl acetate		86.088
Vinylidene chloride		96.950
Vinyl butyl ether		100.156
Acrylic acid		72.062
Methacrylic acid		86.088
Methyl acrylate		86.088
Methyl methacrylate		100.114
Ethyl methacrylate		114.140

TABLE 2. *Formulas and molecular weights*—Continued

normal-Butyl methacrylate		142.192	1,4-Pentadiene (1,2-polymerization).		68.114
Phenyl methacrylate.		162.180	Isoprene		68.114
Cyclohexyl methacrylate.		168.228	Maleic anhydride		98.056
Benzyl methacrylate.		176.206	Isopropenyl acetate		100.114
1,3-Butadiene		54.088	Diethyl maleate		172.176
1,3-Cyclopentadiene	 dimer	66.098	Diethyl fumarate		172.176

Some values of heat of polymerization that can be found in the literature have not been included in the table for one of three reasons: (1) the compounds are not closely related to those listed here (e. g., tricyano compounds) and involve a different type of reaction; condensation reactions also are excluded; (2) the values reported appear to be in serious error, e. g., because of oxidation of the material; (3) values have been superseded by later values by the same authors. Early values reported by other authors have been included for completeness, although some of these values may be regarded as obsolete. Heats of polymerization can be calculated not only from heats of combustion and formation, but also from activation energies and equilibrium constants. There are many data in the literature other than those listed in this paper, from which heats of polymerization could be calculated if desired, although in some cases the uncertainty of such values will be large.

The states of monomer and polymer and the corresponding values of heats of polymerization given in table 1 are those reported by the several authors, and no corrections have been applied. The values have been rounded to the nearest 0.1 kcal in some cases, since uncertainties in general may amount to the order of 0.5 kcal. Values of heat capacities, and of heats of fusion, vaporization, and solution are known only for a few monomers and polymers, so it is not often possible to convert values of heats of polymerization to correspond to temperatures and states other than those in which the measurements were made. It can sometimes be assumed [3, 4] that the heats of fusion, vaporization and solution for the polymer are not very different from those for the monomer because of the chemical similarity with the monomer.

In making comparisons of heats of polymerization, values for equivalent states should be used, otherwise the included heats of vaporization, fusion, and solution may result in misleading values, especially if these heats are unusually large, as in styrene [5]. For polymers that are noncrystalline or have a second-order transition with no heat of fusion, as in polystyrene [6], the solid

state is equivalent to the liquid state for purposes of comparison. Strictly, comparisons of heats of polymerization should be made only when the monomers and polymers are all referred to the same state. In converting values of heats of polymerization to other states, heats of vaporization, fusion, and solution should be used which are for the same temperature as that which applies to the heat of polymerization. The possibility of dependence of heat of solution upon concentration should also be considered.

III. Recalculation of Flory's Values

The author of this paper has recalculated the values given by Flory [1] for heats of ploymerization to hypothetical head-to-tail polymers having no steric hindrance between branch groups attached to the polymer chain. The method of calculation was essentially the same as Flory's except that a later expression for heats of formation of hydrocarbons [7] was used in calculating heats of formation of polymers, and the heats of formation of the monomers were obtained directly from [8], or for 1,4-pentadiene from [9], instead of calculating them. The estimated corrections for branching in the polymer were obtained by comparing the heats of formation of the octanes [7] (see also [4]). These were chosen from the available data as being more likely than shorter molecules to give the best approximations.

The recalculated values are 1 to 5 kcal lower than those given by Flory, varying between 18 and 21 kcal/mole of monomer; there are also greater differences among the recalculated values. The calculated values for the diolefins are not appreciably lower than those for the monolefins. Hypothetical polymers without steric hindrance having double-branch structures have lower heats of polymerization (18.1 to 19.4 kcal/mole of monomer) than do those with single-branch structures (20.5 to 20.9); polymers with *trans* structure have heats of polymerization about 1 kcal less than those with *cis* structure. The calculated value for 1,2-polymerization of 1,3-butadiene (17.4) is much lower than that for 1,4-pentadiene (20.7). The hypothetical value for polymerization of styrene (19 kcal), obtained by use of the calculations of Kharasch [10] as was done by Flory, falls about 1.5 kcal lower than that for the single-branch structures.

The above relations are due partly to the assumption of certain values for branch corrections and apply to polymers having no steric interference between side groups. The calculations were performed as follows:

The expression for heat of formation per mole of a long normal saturated hydrocarbon, C_nH_{2n+2} ($n>5$,gas) [7] is:

$$\Delta Hf^\circ_{298} = -10.408 - 4.926n \text{ kcal/mole,}$$

$$= -4.926n \text{ as } n \text{ approaches } \infty .$$

If the chain is sufficiently long, any part of it will have a heat of formation proportional to the length of that part. The heat of formation of a structural unit of the hypothetical polymer is then $\Delta Hf^\circ(\text{unit}) = -4.926n + \Delta_b$ kcal/unit where Δ_b is the correction for the bond effect of branches on the unit. The heat of polymerization is obtained by taking the difference in heats of formation in the gas state of the polymer unit and the monomer, $\Delta Hf^\circ(m)$ [8,9]: $\Delta Hp^\circ = -4.926n + \Delta_b - \Delta Hf^\circ(m)$ kcal/mole of monomer. The unsaturated group at the end of the polymer chain is neglected. Since the above calculations apply to saturated polymers, a correction must be applied for diolefins in which an unsaturated group remains. The same values of heats of hydrogenation may be used as in Flory's calculations: +29.95 kcal for $-HC{=}CH_2$ and +27.80 kcal for $-HC{=}CH-$. These values were obtained as the mean of those given in [11,12] for mono- and 1,2-disubstituted ethylenes and reduced to 298° C by the correction −0.25 kcal.

In calculating corrections for branching, the heat of formation [7] of *n*-octane was compared with that of 4-methylheptane for the correction where there is a single branch per polymer unit, 3,3-dimethylhexane where there are two branches on one of the carbons of the polymer unit, and 3,4-dimethylhexane where there are adjacent single branches in the polymer unit. The following assumptions were made in applying the branch corrections for hypothetical polymers:

1. Length of a normal alkyl substituent makes little difference in bond effect. (This is supported by data of Kistiakowsky and coworkers [12] on heats of hydrogenation.)

2. Branches in the octanes mentioned are far enough removed from the end carbon atoms to

avoid end effects, so that a suitable value for the branch effect is obtained by comparing these octanes.

3. The application of branch corrections to the hypothetical polymer unit is appropriate when those corrections were obtained from correspondingly branched octanes. This neglects the small bond effect of having substituents on nearby C atoms of the polymer chain, which are not present in the octanes. Although certain objections can be raised to the use of these branching corrections, it is felt that they afford a better approximation than those available at the time of Flory's calculations, and they were obtained from the best data available at the present time.

IV. Comparison of Values and Steric Effects

The heat of polymerization of vinyl compounds can be arbitrarily assigned to four energy effects, which are not entirely separable, the second and third being negative with respect to the first and fourth. These energy effects are: (1) the reaction $\begin{array}{c}|\quad|\\ C{=}C\\ |\quad|\end{array} \longrightarrow \begin{array}{c}|\quad|\\ -C-C-\\ |\quad|\end{array}$; (2) the effect of side groups on bond energies when such side groups are so spaced that there is no interaction between them; (3) the effect of steric hindrance between side groups attached to the polymer chain; (4) the "end effect" arising from the nearness of the double bond to the end of the monomer molecule [13].

The first and fourth effects are represented by the polymerization of ethylene, whose polymer has no side groups and therefore no bond effect nor steric hindrance from such groups. The second effect arises from the fact that the bonds to the substituents and the chain bonds in the monomer have different effects on each other from those they exert in the polymer. The value of the third effect can be obtained by the difference between the calculated values of heats of polymerization, which include effects (1), (2), and (4), for the hypothetical polymers, and the experimental values, which include all effects. Both calculated and experimental values are available in only a few cases; isobutene may be used as an example. The difference between 19.2 calculated and 12.8 observed is −6.4 kcal/mole of monomer, attributable to steric hindrance between side groups.

The end effect will be different for each monomer and can generally be neglected in polymers. The value of this effect is given by the deviations from linearity with number of carbon atoms of the heats of formation of the lower members of the homologous series and is known at present for only a few monomers, as follows [14]:

Ethylene	+2. 76 kcal,
Propylene	0. 7,
1-Butene	0. 39,
1-Heptene	0. 00.

For the others, it is estimated to be of the order of 0.5 kcal or less. This effect will make a small difference in the values obtained in comparison of heats of polymerization, depending on the difference in the end effects of the monomers to be compared. The true value of effect (1) above is 19.59 kcal, obtained by deducting the end effect in ethylene from the value 22.35 kcal [15].

Substituent groups of larger sizes may cause greater amounts of steric interference, resulting in lower experimental heats of polymerization. Length of the *n*-alkyl substituents makes little difference, although branched substituents may cause steric hindrance [12]. The substitution of chlorine on the aromatic ring of styrene has little effect on the heat of polymerization, since the substituent is well removed from the polymerizing bonds and is not likely to interfere with other branch groups. In ethylene whose polymer has no steric hindrance between side groups, the experimental and calculated values of heat of polymerization agree within experimental error (the calculated values for ethylene were derived from experimental data on hydrocarbons), whereas isobutene, alpha-methylstyrene, and the methacrylates have values of heat of polymerization about two-thirds of what would be expected if there were no steric hindrance between side groups. Ethylene has the highest and alpha-methylstyrene the lowest heat of polymerization among the compounds listed.

A frequent cause of steric interference between side groups is the presence of two substituents on the same vinyl carbon atom, especially if one or more of the substituents is a methyl group. This

can be seen by comparing the experimental values of heat of polymerization for styrene (16.7 kcal) and alpha-methylstyrene (8.8 to 10.1 kcal). If the latter values are increased by an allowance of 2.2 kcal for the bond effect of the methyl group, they become 11.0 to 12.3 kcal, respectively. (The value 2.2 kcal is obtained by taking the difference between the calculated values for 1-butene and 2-methyl-1-butene in table 1.) Effect (4) above cancels in this comparison. A substituent phenyl group may be able to rotate so that its plane is perpendicular to the direction of the polymer chain thus making the steric interference less than might be expected [3]. Another example of the effect of disubstitution can be seen by comparing methyl acrylate (18.7 kcal) and methyl methacrylate (13.0+2.2=15.2 kcal).

Steric hindrance becomes so great in some molecules that polymerization becomes impossible, although in some cases a dimer may be formed [3, 16]. There is generally no steric interference between side groups in dimers, but it becomes noticeable in the trimers and higher polymers in those polymers that show that property [4]. For actual polymers, in the absence of steric hindrance between side groups, heat of polymerization per mole of monomer should increase as the polymer chain becomes longer, because of the factor $(1-1/n)$, which takes account of the fact that there is one less bond reacting than there are monomer units, as shown in Jessup's calculations for ethylene [15]. (The expression for heat of polymerization of ethylene [13, 14, 15] may be written $\Delta Hp^{\circ}=-19.59\ (1-1/n)-\delta$, where δ is the end effect in ethylene, 2.76 kcal.) If steric hindrance occurs in the polymer, its effect should increase rapidly at first as more units are added to the chain, and after the first three units the heat of polymerization per monomer unit should either increase more slowly or decrease, and the steric energy per unit added should approach a constant value as the chain lengthens. The data for alpha-methylstyrene [17] show some of these effects; here the heat of polymerization per mole of monomer decreases as the molecular weight increases.

Ethylene oxide appears to be a somewhat different monomer from the others listed. The reaction, which differs from vinyl polymerization in being a stepwise addition process rather than a free radical mechanism [18, 19, 20] involves the net difference of the breaking of one C—O bond and the forming of another C—O bond in the chain:

This simple C—O bond rearrangement in itself cannot account for the heat of polymerization. The chain is terminated by —OH groups: HO—H_2C $(H_2C—O—CH_2)_nCH_2$—OH, but if the average molecular weight is large, the contribution to the heat of polymerization from the addition of H—OH would then be very small. The explanation for the heat of polymerization is to be found in the following consideration. The three-member ring of ethylene oxide has been regarded as a strained structure [21] but Walsh [22, 23] (see also [24, 25, 26, 27]) believes it advantageous to translate much of the old idea of strain in ethylene, cyclopropane, ethylene oxide, and other similar molecules into terms of hybridization. He has suggested that ethylene oxide contains overlapping orbitals and carbon atoms that are more nearly trigonal (ethylenic) than tetrahedral. When this molecule is converted to a straight-chain polymer structure containing ordinary tetrahedral C atoms, energy will be evolved, as with ethylene.

The effect of the esterification of the acrylic acids is confusing. In the case of acrylic acid, esterification increases the heat of polymerization, whereas the opposite effect occurs with methacrylic acid.

The heat of copolymerization of the butadiene-styrene mixture lies between the values for the separate monomers. Copolymers having different monomer ratios from those given will of course have different heats of polymerization. The heats of copolymerization of vinyl acetate with maleic anhydride, diethyl maleate, and diethyl fumarate are lower than the heat of polymerization of vinyl acetate alone. In some cases, however, the effect of steric hindrance between side groups in copolymers may be diminished by 1 : 1 alternation of the units. Tong and Kenyon [28] have observed that with methyl acrylate and methyl methacrylate the heat of copolymerization is higher than the sum of the heats of polymerization of the components alone. These authors [29] point out that with the diethyl fumarate and maleate copolymers with vinyl acetate, the difference in their heats of copolymerization is less

than half of the heat of isomerization of maleic to fumaric esters, suggesting that different stereoisomers are produced. A discussion of heat of copolymerization appears in reference [30].

Polymers having different structure, although derived from the same monomer (see butadiene [31]) may have different heats of polymerization. In a polymer or copolymer containing a diene, there is the possibility that there will be present a mixture of 1,2- and 1,4-addition (or 3,4- in isoprene), and the value of heat of polymerization will vary according to the ratio [32, 33, 34, 35]. The 1,2-addition may lead to cross-linking. The 1,4-polymers may be partly *cis* and partly *trans* structure.

Ethylene [36, 37, 38] and vinylidene chloride [39, 40] both form polymers that are rather highly crystalline. The polymers of ethylene oxide and acrylonitrile also are probably crystalline. The apparent heat of polymerization to solid polymer must then include a small quantity representing the heat of crystallization, depending on the percentage of crystallinity. If we use the value for heat of fusion of polyvinylidene chloride (0.3 kcal) given by Reinhardt [39], then the heat of polymerization in the liquid states would be reduced from 14.4 [41] to 14.1 kcal/mole of monomer at 76.8° C.

The author expresses his appreciation for helpful comments offered by Raymond F. Boyer, D. R. Stull, L. K. J. Tong and W. O. Kenyon, Ralph S. Jessup, Edward J. Prosen, and Leo A. Wall.

It has been brought to our attention that there is no reported value for the heat of polymerization of vinyl chloride. An estimate of the value can be made by considering its structure and comparing with other values in the table. Not enough data are available for an accurate prediction, but at least a rough idea can be obtained. Assuming that the end effects are negligible in all cases, and that the heats of vaporization are the same for the monomers as for their polymers, vinyl chloride should be between ethylene (19.6 kcal/mole, no end effect, gas-gas) and vinylidene chloride (at 25°, about 14.0 kcal/mole, liquid-liquid), and somewhere near propylene since the bond and steric effects of Cl are similar to those for CH_3. To obtain an estimate from the data of Fontana and Kidder for propylene, their value may be adapted by subtracting 0.7 kcal for heat of fusion of the polypropylene (same as for the monomer), and adding a few tenths of a kilocalorie for raising the temperature from —75° to 25° C. The value then becomes about 16 kcal/mole for liquid-liquid at 25° C. The second estimate, obtained from ethylene and vinylidene chloride, should be somewhat above the midpoint of the difference between 19.6 and 14.0, since substitution of a second chlorine causes a greater steric effect than that of the first. The final estimate for vinyl chloride might then be placed at about 17 kcal/mole (liquid-liquid or gas-gas, 25° C).

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WASHINGTON, October 6, 1949.