Heats of Combustion Studies on Polymers[1a]

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ABSTRACT: Heats of combustion of eleven well-characterized, high molecular weight polymers have been measured in an isothermal jacketed, static bomb calorimeter with a platinum resistance thermometer, a G-II Mueller bridge, and a Keithley electronic null detector as the temperature measuring device. The precision of measurement was 0.01% or better. The heats of combustion $-\Delta H_c^\circ$ in kilocalories per mole are poly(ethylene), high-density linear polymer, 311.11; isotactic poly(propylene), 467.08; isotactic poly(1-butene), 624.78; poly(styrene), isotactic and 39% crystalline, 1032.76; poly(styrene), isotactic and amorphous, 1033.66; poly(styrene), atactic, 1033.94; poly(α-methylstyrene), mol wt 10^6, 1195.91; poly(acenaphthylene), 1429.00; poly(2,6-dimethylphenylene ether), PPO (General Electric), 993.79; poly(4,4′-dioxydiphenyl-2,2-propane carbonate), Lexan (General Electric), 1879.76. Enthalpies of formation (gas phase) show excellent agreement with the predictions of current bond-energy procedures. Calculated enthalpies and Gibbs energies of vinyl polymerization are consistent with molecular structural features such as ring strain counteracting resonance (acenaphthylene) and steric hindrance in polymer (α-methylstyrene). The heat of crystallization of isotactic polystyrene was found to be 1.60 kcal/mol by taking into consideration the glass enthalpy of the amorphous portion of the partly crystalline samples subjected to combustion.

In principle, standard thermochemical data such as the enthalpy of formation (ΔH_f°) of polymers should be a valuable adjunct for a better understanding of newer aspects of polymer structure such as tacticity, crystallinity, and steric hindrance. Furthermore, the data will be most valuable for obtaining heats of polymerization in exact physical states, for kinetic interpretations of the polymerization reaction, and for judging the thermodynamic feasibility of new routes to polymer synthesis. In this study heats of combustion on six new, well-characterized, high molecular weight polymers have been measured in an isothermal jacketed, static bomb calorimeter, and previous data on a few others confirmed. Enthalpies of formation of polymers and enthalpies and Gibbs energies of polymerization were evaluated. The polymers selected for study have several features of interest. Thermochemical measurements were carried out in order to verify predictions of some bond-energy schemes for hydrocarbons as extended to polyolefins. Measurements were also made evaluating the exact energies associated with stereoregularity and crystallinity in polystyrenes. Poly(α-methylstyrene) was investigated to measure large steric hindrance in the polymer chain. Finally, poly(acenaphthylene) was studied to evaluate the contribution of ring strain to the heat of polymerization and to verify earlier estimates of this contribution.

Experimental Section

Apparatus and Procedure. The isothermal jacketed, static bomb calorimeter and the associated procedures used in the present investigation were the same as described by Browne and Rossini.[2] Modifications made to improve the performance and precision of the calorimeter are described below.

1. An abnormal variation in the stirring energy (apparatus constant, *u*) of a factor of 10–50 was corrected by a realignment of the stirrer, by redesigning the stirring gland, and by a rigid positioning of the calorimeter inside the jacket in accordance with constructional details of more recent custom-built calorimeters. Both of the important apparatus constants, *k* and *u*, were remarkably constant over a period of 6 months.

2. To improve the procedures for recording the time–temperature data, the deflection of the galvanometer was read and interpolated at fixed time intervals. In the fast reaction period, the Mueller bridge dials had to be manipulated unduly fast to keep pace with the zero-crossing (null) of the galvanometer spot. In our null-procedure, time, and not the interpolated bridge reading, was the precisely recorded observation at the null point for various fixed settings of the bridge covering an entire range of the experimental temperature rise with sufficiently close and numerous set points. The galvanometer was replaced by a Keithley 147 nanovolt null detector which was used as null detector in the fore and after periods and as linear microvoltmeter in the reaction period. A full-scale deflection of the meter was obtained just before firing the bomb by setting the bridge at almost the expected final temperature. When the bomb was fired, the firing time was simultaneously recorded by a punched mark on a running paper strip chronograph and the microvoltmeter deflection slowly decreased toward the null as the calorimeter temperature rose. The movement of the meter needle was key punched on the chronograph at several scale readings for which the corresponding exact resistance value on the bridge was calculated.

The energy equivalent of the calorimeter system was determined by calibrations with NBS standard benzoic acid sample 39h to a precision of 0.01% or better. The ignition energy was measured from blank calorimetric runs (without sample) at the temperature of equilibrium between jacket and calorimeter (θ_∞) and was found to be 8.2 ± 0.3 cal. The isothermal bomb energies, ΔE_b° (25°), given in Table I were based on weights *in vacuo* of the polymer samples.

The time–temperature readings, covering the fore, reaction, and after periods, together with other data pertaining to a combustion run, were fed to the IBM-7094 digital computer which was programmed to compute ΔE_b° (25°), the energy of the idealized bomb process with Washburn corrections made by a standard procedure. The starting temperature of the combustion reaction was made exactly 25° by firing the bomb at the calculated instant when this temperature was

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(1) (a) Paper presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) National Chemical Laboratory, Poona 8, India.

(2) C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 1960).

TABLE I

ENERGIES OF THE IDEALIZED COMBUSTION REACTION AT 25° OF POLYMERS

Polymer, type, crystallinity, %	Formula	Approx DP	No. of combustions	$-\Delta E_b°$ (25°), cal/g	$-\Delta E_c°$ (25°), kcal/monomol
1. Poly(ethylene), linear, high density, 72%	$(C_2H_4)_n$	≈3,000	9	11071.5 ± 2.0[b]	310.51
2. Poly(propylene), isotactic, 58%	$(C_3H_6)_n$	≈4,000	9	11080.5 ± 2.2	466.18
3. Poly(1-butene),[a] isotactic, 34%	$(C_4H_8)_n$	≈800	6	11109.4 ± 0.5	623.59
4. Poly(styrene), isotactic, 40%	$(C_8H_8)_n$	≈1,000	6	9909.9 ± 3.1	1031.57
5. Poly(styrene), isotactic, amorph	$(C_8H_8)_n$	≈1,000	5	9918.5 ± 2.4	1032.47
6. Poly(styrene), atactic, amorph	$(C_8H_8)_n$	≈1,000	5	9921.2 ± 1.4	1032.75
7. Poly(α-methyl styrene), anionic, amorph	$(C_9H_{10})_n$	≈34,000	5	10111.9 ± 2.6	1194.42
8. Poly(α-methyl styrene), anionic, amorph	$(C_9H_{10})_n$	≈13,000	5	10111.7 ± 2.9	1194.44
9. Poly(acenaphthylene), amorphous	$(C_{12}H_8)_n$	≈600	6	9388.0 ± 2.0	1427.81
10. Poly(2,6-dimethylphenylene ether) (PPO), polymer, ~20%	$(C_8H_8O)_n$	≈300	4	8273.2 ± 1.4	993.49
11. Poly(4,4′-dioxydiphenyl-2,2-propane carbonate) (Lexan), polymer, ~20%	$(C_{16}H_{14}O_3)_n$	≈150	3	7392.9 ± 1.4	1878.57

[a] Experimental work, C. W. Hayes, M.S. Dissertation, Texas A&M University, 1966. [b] Standard deviation, $\sigma = \pm[\Sigma(x_i - \bar{x})^2/n - 1]^{1/2}$; F. D. Rossini, "Experimental Thermochemistry," Part I, Interscience Publishers, Inc., New York, N. Y., 1956, pp 297–320; $\Delta E_b°$ = isothermal bomb energy.

attained by the calorimeter. This step simplifies the Washburn correction procedure considerably. All data are based on the 1961 International Atomic Weights, the new Fundamental Constants (1963), and the thermochemical calorie, 4.184 J (exactly).

Samples Used for Combustion. 1. Polyethylene. The material was a commercial Ziegler-polymerized ethylene homopolymer received from the Monsanto Co., Texas City, Texas. Low molecular weight end (about 30%) was removed by sand column elution fractionation technique using *p*-xylene as solvent and ethylene glycol monoethyl ether (Cellosolve) as a nonsolvent. It was expected that during the elution operation the original degree of crystallinity of this linear high density polyethylene would be essentially unaltered and perhaps slightly improved. Infrared analysis indicated negligible amounts of vinylidene and internal unsaturation and of the CH_3 groups. Vinyl unsaturation was determined by infrared spectroscopy to be 0.0095 wt % and the ensuing correction to the heat of combustion was negligibly small. Total inorganic residue was less than 50 ppm as determined by X-ray fluorescent scattering at the Monsanto laboratory. The polymer was dried for more than 24 hr under high vacuum of 10^{-6} torr or better. The degree of polymerization was about 3000 by a viscosity method.

2. Polypropylene. The commercial, pelletized sample of isotactic polypropylene was received from the Union Carbide Co., South Charleston, W. Va. The polymer was freed from antioxidants, plasticizers, if any, and other extraneous matter by heating with 20 volumes of *n*-pentane for a few hours at about 120° in a bomb under nitrogen atmosphere. On cooling, the polymer precipitated to a fine, white, granular powder leaving the impurities of additives together with some low molecular weight and atactic polymer in the pentane solution. This technique[3] was repeated with fresh pentane a few times and then the finally washed precipitate was dried under high vacuum at 50° and pelletized for combustion. The degree of polymerization was about 4000 by a viscosity method.

3. Poly(1-butene) and several higher poly(α-olefin) samples were supplied by Phillips Petroleum Co., Bartlesville, Okla. The polymer was purified by continuous Soxhlet extraction with ethyl ether for over 200 hr and was dried under high vacuum for a prolonged period. The ash content of the sample was negligible for applying any correction to the heat of combustion. The degree of polymerization was about 800 by a viscosity method.

4. Polystyrenes. Three polystyrene samples were studied, namely, isotactic polystyrene, with fully developed crystallinity (about 40%) through annealing, isotactic polystyrene rendered amorphous by quenching from melt, and the atactic polystyrene. These samples were all supplied by the General Electric Laboratory, Schenectady, N. Y. The degree of polymerization was about 1000 by a viscosity method.

5. Poly(α-methylstyrene). In the earlier work on this monomer–polymer system, the polymer fractions used were all of very low molecular weight, therefore involving relatively large error from the end groups. These fractions were recovered from stillage of a monomer distillation plant and hence were of inadequate purity for combustion–calorimetry standards. With the advent of anionic polymerization technique, high polymers from this monomer have now become available. Such polymer fractions used in the present combustion work were supplied by the National Research Council, Canada, and had the molecular weights of 4×10^6 and 1.6×10^6. These were rendered into a fine granular form through repeated precipitations in methanol and finally dried under high vacuum at a low temperature of 40°. The infrared spectrum showed no impurity of any kind.

6. Poly(acenaphthylene) was prepared by thermal polymerization at 95–100° of highly purified acenaphthylene from the Borden Chemical Co., resulting in a high molecular weight polymer of the order of 10^5. The polymer was purified by several precipitations of benzene solution into hot methanol and was dried under high vacuum at 80–100°. The intrinsic viscosity of the polymer in benzene was about 1.0, giving the degree of polymerization of about 600.

7. Poly(2,6-dimethylphenylene ether) and poly(4,4′-dioxydiphenyl-2,2-propane carbonate) are products of General Electric Co. and are known by the respective trade names of PPO and Lexan. Both samples had the crystallinity estimated at about 20% and both were purified by a few precipitations and then exhaustively vacuum dried. The degrees of polymerization were about 300 and 150, respectively, by a viscosity method.

Results

The combustion data on eleven polymer samples and the derived thermal data on polymers together with literature data on the corresponding monomers are presented in Tables I and II, respectively. The calculated enthalpies of polymerization for the appropriate standard state of the monomer and polymer are given in the last column of Table II. Ancillary

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(3) R. M. Joshi, *J. Appl. Polymer Sci.*, **10**, 1806 (1966).

TABLE II

THERMAL DATA FOR THE POLYMER REPEAT UNIT AND THE MONOMER AT 25° AND HEATS OF POLYMERIZATION AS DERIVED FROM THE COMBUSTION DATA

	Polymer		Monomer	Heat of polymerization
Polymer	$-\Delta H_c°$ kcal/monomol	$\Delta H_f°$ (c or c′), kcal/monomol	$\Delta H_f°$ (X),[a] kcal/mol	$-\Delta H_p$ (XY),[a] kcal/mol
1. $(C_2H_4)_n$	311.11 ± 0.03[b]	−13.62 ± 0.06[c]	12.50 (g)	26.12 (gc′)
2. $(C_3H_6)_n$	467.08 ± 0.05	−20.02 ± 0.10	4.88 (g)	24.90 (gc′)
3. $(C_4H_8)_n$	624.78 ± 0.05	−24.68 ± 0.10	−0.03 (g)	24.65 (gc′)
4. $(C_4H_8)_n$ (isobutylene)[d]	...	−21.24	−4.04 (g)	17.20 (gc)
5. $(C_8H_8)_n$				
isotactic, cryst	1032.76 ± 0.15	7.09 ± 0.30	24.91 (l)	17.82 (lc′)
isotactic, amorph	1033.66 ± 0.15	7.99 ± 0.30	24.91 (l)	16.92 (lc)
atactic, amorph	1033.94 ± 0.10	8.27 ± 0.20	24.91 (l)	16.64 (lc)
6. $(C_9H_{10})_n$	1195.91 ± 0.18	7.88 ± 0.36	16.84 (l)	8.96 (lc)
7. $(C_{12}H_8)_n$	1429.00 ± 0.18	27.13 ± 0.36	44.7 (c′)	17.57 (c′c)
8. $(C_8H_80)_n$	993.79 ± 0.13	−31.88 ± 0.26	Condensation-type polymer, a polyether	
9. $(C_{16}H_{14}O_3)_n$	1879.76 ± 0.30	−103.26 ± 0.60	Condensation-type polymer, a polyester	

[a] X, Y = physical states: g = gas, l = liquid, c = condensed, essentially amorphous "liquid" or glass, c′ = condensed (partly) crystalline solid. [b] Standard deviation of the mean; $s = \pm[\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, combined for the sample and the calibration. See Table I, footnote *b*. [c] "Uncertainty interval" equal to twice the final over-all standard deviation of the mean. [d] Data of Parks and Mosher[10] quoted for comparison with polymer 3.

TABLE III[a]

APPLICATION OF SEMIEMPIRICAL BOND-ENERGY CORRELATION PROCEDURES FOR DERIVING THE HEATS OF FORMATION IN STANDARD IDEAL GASEOUS PHASE AT 25° AND COMPARISON WITH THE EXPERIMENTAL DATA

Polymer	ΔH_v (monomer), kcal/mol obsd	ΔH_m or ΔH_{gl} (polymer), kcal/mol obsd	ΔH_v (polymer), kcal/mol calcd[b]	$\Delta H_f°$(g) (polymer), kcal/mol exptl	$\Delta H_f°$(g) (polymer), kcal/mol predicted Cox scheme[f]	$\Delta H_f°$(g) (polymer), kcal/mol predicted S-Z scheme[g]
1. $(C_2H_4)_n$	...	1.37	2.36	−9.89	−9.8	−9.84
2. $(C_3H_6)_n$	...	1.18	3.29	−15.55	−16.2	−15.98
3. $(C_4H_8)_n$	...	0.55	4.63	−19.50	−21.1	−20.34
4. $(C_4H_8)_n$ (isobutylene)[c]	...	0.0	3.96	−17.11	−24.5	−17.32
5. $(C_8H_8)_n$	10.6	−0.65	10.0	17.4	16.1	...
6. $(C_9H_{10})_n$	11.8	−1.3	10.9	17.5	7.9	...
7. $(C_{12}H_8)_n$	17.0 (subl)	−2.3	16.5	41.3	43.2	...
8. $(C_8H_8O)_n$	...	0.47[d]	10.1	−21.3	−22.2	...
9. $(C_{16}H_{14}O_3)_n$	...	1.41[e]	19.6	−82.4	−82.6	...

[a] Abbreviations: ΔH_v = enthalpy of vaporization; ΔH_m = enthalpy of fusion; ΔH_{gl} = glass enthalpy (with negative signs); $\Delta H_f°$ = standard enthalpy of formation. [b] Calculated by methods of R. M. Joshi, B. J. Zwolinski, and C. W. Hayes, *Macromolecules*, **1**, 30 (1968). [c] See footnote *d* in Table II. [d] Differential scanning calorimetry: F. E. Karasz and J. M. O'Reilly, *J. Polymer Sci.*, **B3**, 561 (1965). [e] Low-temperature specific heat measurements: J. M. O'Reilly, F. E. Karasz, and H. E. Bair, *ibid.*, **C6**, 109 (1964). [f] See ref 14. [g] See ref 13.

data, such as heats of fusion, glass enthalpy for polymers, and heats of vaporization of monomers, have been taken from standard compilations such as the API Research Project 44 tables and from recently published literature on polymers.[4–8] For enthalpy of vaporization of a polymer segment, it is reasonable to assume a corresponding value of the saturated monomer molecule or of a structurally equivalent compound with the same number of carbon atoms. For the olefin polymers, the heats of vaporization have been derived from the bond-energy scheme of Tatevskii, *et al.*[9] All these auxiliary data necessary for converting the heats of formation of polymers into the ideal gas phase are shown in Table III. This table also contains a comparison of the "experimental" heats of formation in gas phase with those calculated (predicted) with the help of bond-energy schemes. For the monomer–polymer systems, Table IV gives the calculated Gibbs energy data which represent an index

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(4) G. V. Schulz, K. von Grunner, and H. Gerrens, *Z. Physik. Chem.* (Frankfurt), **4**, 192 (1955).

(5) (a) S. Bywater, *Makromol. Chem.*, **52**, 120 (1962); B. J. Cottam, J. M. G. Cowie, and S. Bywater, *ibid.*, **86**, 116 (1965); (b) J. Brandrup and E. H. Immergut, "Polymer Handbook," Interscience Publishers, Inc., New York, N. Y., 1966.

(6) J. Boor, Jr., and E. A. Youngman, *J. Polymer Sci.*, **A4**, 1861 (1966).

(7) F. E. Karasz, H. E. Bair, and J. M. O'Reilly, *J. Phys. Chem.*, **69**, 2657 (1965).

(8) I. Abu-Isa and M. Dole, *ibid.*, **69**, 2668 (1965).

(9) V. M. Tatevskii, V. A. Benderskii, and S. S. Yarovoi, "Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons," Pergamon Press Ltd., London, 1961.

Table IV
Standard Gibbs Energies of Vinyl Polymerization in the Ideal Gas Phase at 25° at Unit Monomer Concentration

Monomer	$-\Delta H_p°$(gg), kcal mol^{-1}	$-\Delta S_p$(gg),^{a} cal deg^{-1} mol^{-1}	$\Delta G_p°$(gg), kcal mol^{-1}
1. Ethylene	22.2	34.0	−12.1
2. Propylene	20.7	39.9	−8.8
3. 1-Butene	19.1	39.8	−7.2
4. Styrene	18.1	35.5	−7.5
5. Acenaphthylene	20.4	45^b	−7.0
6. α-Methylstyrene	8.1	35^b	+2.3

[a] Taken from ref 19. [b] Calculated from observed ceiling temperatures; ~300° for acenaphthylene and 62° for α-methylstyrene in liquid phases.

of thermodynamic polymerizability of vinyl monomers. The last two polymers in Tables I, II, and III are condensation type and hence are not included in Table IV.

Discussion

The mean heat of combustion of our polyethylene is about 10 cal/g lower than that reported for a similar high-density polyethylene, Marlex-50, in a recent work of Parks and Mosher.[10] This fact perhaps indicates a different degree of crystallinity in our sample. All precautions were taken to minimize oxidation of samples except for the unavoidable exposure to oxygen in the bomb prior to ignition. Normal temperature drifts in the fore period as also infrared analyses failed to detect any appreciable oxidation. It is also noteworthy to observe that in the work of Parks and Mosher, polymethylene, a highly crystalline linear hydrocarbon chain, gave a heat of combustion about 16 cal/g lower than that of Marlex-50. Correction was made for the presence of 0.2% antioxidant, the heat of combustion of which was assigned as 5 cal/g lower than that of polymethylene. We evaluated the exact extent of crystallinity in our sample by measuring directly the heat of fusion by a Perkin-Elmer differential scanning calorimeter at the General Electric laboratory. The value thus obtained was 49 cal/g (1.37 kcal/mol) which was determined equivalent to about 72% crystallinity by using the well-established mean value of 1.90 kcal/mol selected by Flory and Vrij[11] for 100% crystalline linear polymer. The heat of formation, $\Delta H_f°$(g), for $1/n(C_2H_4)_n$ is derived using the experimentally observed heat of fusion and the (hypothetical) heat of vaporization per C_2H_4 segment. The latter is calculated from the bond-contribution scheme of Tatevskii, *et al.*,[9] which has successfully correlated properties of many normal and branched alkanes.[12] Our value of $\Delta H_f°$(g) of −9.89 kcal/monomol is 0.05 kcal more negative than twice the standard incremental value for the enthalpy of formation of the methylene group used in the API 44 tables, −9.852 kcal/mol. A close agreement of this experimental value with those calculated from bond-energy procedures indicates that there is little or no "extra" steric hindrance due basically to long chain formation for this polymer.

The heat of combustion of the isotactic polypropylene is in excellent agreement with the previous work of Parks and Mosher. The calculated $\Delta H_f°$(g) shows a small deviation of about 0.4 kcal/mol from the value predicted by the bond-energy scheme of Somayajulu and Zwolinski[13] which is a more precise procedure for branched alkanes than the scheme of Cox.[14] The former scheme does not consider specifically interactions between atoms four or more bonds removed; thus it is capable of predicting only approximately the heat of formation of a syndiotactic polymer segment where the steric hindrance would be the least. The more positive heat of formation of the isotactic polypropylene, by about 0.4 kcal, may perhaps signify the energy difference due to stereospecificity of the two forms. A more definite elucidation of this factor must await measurements on the syndiotactic polypropylene which has become available recently.

As a next higher member of polypropylene in the poly(α-olefin) series, the heat of formation of poly(1-butene) was of interest for deriving its standard heat of polymerization with the help of the earlier precise measurement of the heat of formation of the monomer. The heat of polymerization of 1-butene was found to be only slightly lower than that of propylene, indicating no appreciable steric hindrance of a longer side chain when attached singly on every alternate carbon in contrast to the 1,1 disubstitution of polyisobutylene.

In the polymerization of the α-olefin series, it is seen from the enthalpies and Gibbs energies of polymerization given in Table IV that both of these reaction potential terms diminish gradually and asymptotically to a minimum which is high enough to account for their ready polymerizability. Polymers of branched side chains, such as those of 3-methyl-1-butene and 4-methyl-1-pentene, which are currently under study may be expected to show some characteristic features in their enthalpies of formation. The enthalpy of formation of the isotactic poly(1-butene) shows a higher steric energy of the isotactic placement over the predicted value for the syndiotactic polymer through the Somayajulu–Zwolinski scheme.

The polystyrenes in our work have already been a subject of an exhaustive, low-temperature calorimetric study of the specific heat–temperature relationship by Karasz, *et al.*,[7] and have shown characteristic specific heat differences. The object of our combustion study was to measure, if possible, the subtle energy differences due to tacticity (stereoisomerism in polymers) and to crystallinity. The crystallinity in polymers is generally partial unless they are single crystals. In the case of the isotactic polystyrene in this work, it is rather low, only about 40%, and the rest of the polymer is amorphous, stoichiometrically. Thus in calculating the enthalpy of crystallization of polystyrene, the observed difference in the heat of combustion of about 8.6

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(10) G. S. Parks and H. P. Mosher, *J. Polymer Sci.*, **A1**, 1979 (1963).

(11) P. J. Flory and A. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).

(12) H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 264 (1963).

(13) G. R. Somayajulu and B. J. Zwolinski, *Trans. Faraday Soc.*, **62**, 2327 (1966).

(14) J. D. Cox, *Tetrahedron*, **18**, 1337 (1962); **19**, 1175 (1963).

cal/g between the isotactic–crystalline and the isotactic–amorphous is a combined effect of both the enthalpy of crystallization and the glass enthalpy. Schulz, *et al.*,[4] have shown that a polymer below its glass transition is in a higher state of energy than the true, liquidlike state to which crystallinity is referred and that the magnitude of this energy, *i.e.*, the glass enthalpy, is the integral $\int_{25}^{T_g} \Delta C_p dT$, where $\Delta C_p = C_p$(liquid) − C_p(glass) for the glass at 25°. Such integrations on several available specific heat–temperature data on polystyrene agree unanimously on a value of about 0.65 ± 0.02 kcal/mol, as the glass enthalpy at 25° shown in Table III. Subtracting this value from the observed enthalpy of the transition, crystal → glass (=2.25 kcal/mol, 8.6 cal/g for a 40% transition), we derive the true value of the heat of fusion (crystal → "liquid") as 1.60 kcal/mol. The difference between the isotactic and the atactic (syndiotactic, by contrast) polystyrenes, both in the amorphous state, was found to be only about 2 cal/g, which is within the standard deviation of the mean combustion values and cannot be definitely ascribed to the configurational enthalpy of stereoisomerism. Such an inference will also be questionable because of the incidence of differing glass enthalpies in the two amorphous polymers. On the contrary, we have grounds to believe that the configurational enthalpy ($\Delta H_f°$(l)) of the two isomers is essentially the same as are the glass transition temperatures and the specific heat–temperature behavior of the two.[8] This point has been thoroughly discussed in a recent publication.[15] The heat of combustion of the atactic, free-radical polystyrene in this work based on weight of sample, $\Delta H_c° = -1033.94 \pm 0.10$ kcal/monomol, showed a very gratifying agreement with the previous work of Roberts, Walton, and Jessup[16] based on CO_2 assay of the combustion products, namely, $\Delta H_c° = -1033.9 \pm 0.10$ kcal/monomol.

Our results on poly(α-methylstyrene) show that the earlier inference by Roberts and Jessup[17,18] of a systematic dependence of the heat polymerization on the degree of polymerization in the very low DP region does not seem to hold. Our high molecular weight polymer failed to show the expected higher (by at least 5 cal/g) heat of combustion value required by Jessup's extrapolated heat of polymerization of 8.4 kcal/mol for the high DP polymer.[17] On the contrary, our derived value of the heat of polymerization comes close to his highest molecular weight fraction then available. We conclude that the standard ΔH_p(lc) at 25° is 8.96 kcal/mol by the differential combustion method. When comparing this value with that derived from anionic equilibrium, due consideration must be given to include a small glass enthalpy contribution arising from the higher energy vitreous state of the polymer at 25°, since the glass transition temperature T_g is 170–190°. The low heat of polymerization of this monomer is consistent with the established concept that the 1,1-disubstituted ethylenic polymers are sterically highly hindered as amply demonstrated by the case of polyisobutylene.

The heat of formation of poly(acenaphthylene) in the hypothetical gas phase agrees closely with that calculated from the bond-energy scheme of Cox and thus reveals no steric hindrance in the polymer chain in spite of the bulky substitution of the naphthalene moiety. This is in accord with the view that the 1,2 disubstitution in ethylene does not create steric hindrance in the final state, although it undoubtedly affects the transition state of vinyl polymerization thus preventing such polymerizations as that of 2-butene. The heat of polymerization in the corresponding appropriate states of the monomer and polymer [ΔH_p(c′c)] was found to be 2 kcal/mol lower than the value obtained by Dainton, *et al.*,[19] by direct reaction calorimetry. Their exceptionally high value of about 24 kcal/mol (in solution) had led these authors to suggest that the monomer ring was highly strained and that some of the strain was relieved during the process of polymerization, through change in the hybridization of the ethylenic carbons. This view point of strain relief in the polymer is not supported by the recent combustion work of Boyd, *et al.*,[20] on the monomer and its saturated analog, acenaphthene, or by our *normal* value of the heat of polymerization in gas phase. The former authors have shown that the bridging strain in acenaphthylene is nearly balanced by the stabilizing, delocalization interaction of a double bond with the aromatic nucleus, with a net strain of only about 2 kcal/mol. On the other hand, the acenaphthene-type bridging in the polymer segment is much more strained, to the extent of 6–7 kcal/mol. By combining the appropriate quantities (calculated or measured) for the enthalpies of fusion, glass enthalpy, and enthalpies of vaporization for the monomer and polymer segment with the heat of combustion of the polymer, the enthalpy of polymerization in gas phase, ΔH_p(gg), is calculated to be 20.4 kcal/mol. This is a very *normal*, basic value for ethylenic polymerization apparently without much contribution from strain relief.

Accurate data on heats of fusion by differential scanning calorimeter and low-temperature specific heat data were available on PPO and Lexan, the two commercial polymers of importance. To this fund of basic thermal data on industrially important materials, the heats of formation have been contributed. As seen from Table III, the values of $\Delta H_f°$(g) of these polymers derived by using some auxiliary thermal data agree remarkably well with the simple bond-energy scheme of Cox, proving its wide applicability. The new $\Delta H_f°$(g) data are valuable to derive enthalpies and Gibbs energies of the main polymer-forming reactions involved in their industrial production.

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Correlation Procedures for Estimating the Enthalpies of Vaporization, Formation, and Polymerization and Certain Physical Properties of α-Olefin Polymers

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ABSTRACT: The Somayajulu–Zwolinski generalized bond-energy scheme developed for low molecular weight isomeric alkanes has been extended to 15 olefinic polymer structures for estimating their enthalpies of formation and enthalpies of polymerization. The agreement with available experimental data is quite satisfactory, provided that due allowance is made for the structural energy differences arising from tacticity of the α-olefin polymers. The Tatevskii procedure, which successfully correlates several physical properties of hydrocarbons, was also applied to the olefin polymers for calculating the molal volume (densities), molal refraction (and refractive indices), and enthalpy of vaporization of a polymer repeat unit. The predicted densities, while internally consistent, are generally 1–7% high, whereas the sparse experimental values vary among themselves by 1–10%. The usefulness of these estimated molal volumes in calculating volume changes in polymerizations and for predicting effects of pressure for certain polymeric systems is noted. The calculated refractive indices show better agreement within 2%. The Greenshields–Rossini bond-energy procedure, although very precise for lower isomeric alkanes, was found to be inapplicable for estimating physicochemical properties of long-chain branched polyolefins.

In recent years empirical and semiempirical bond-energy schemes have proved quite successful[1] in predicting physical and thermodynamic properties such as molal refraction, density, boiling point, enthalpies of vaporization and of formation, etc., of paraffinic hydrocarbons, within a precision attainable experimentally. To our knowledge no systematic application of these procedures has been made for predicting similar properties for the hydrocarbon polymers except for a few occasional calculations[2] such as the enthalpy of polymerization. Poly(α-olefins) offer an excellent class of polymers to test the applicability and effectiveness of the various bond-energy and group-contribution procedures for predicting their physical and thermodynamic properties. The experimental data on the properties of these hydrocarbon polymers are rather meager at present; however, it is very rapidly accumulating and these relatively simple polymers offer an ideal testing ground for determining the effectiveness of correlation procedures in evaluating, correlating, and extending experimental data.

The enthalpy of formation and the enthalpy of vaporization (hypothetical) of a polymer segment are important thermodynamic quantities often required in interpretations of polymolecular phenomena such as intermolecular entanglement,[3] chain stiffness,[4] glass transition,[4,5] cohesive energy density,[6] etc. The enthalpy of vaporization of a polymer segment is not an experimentally measurable quantity, for obvious reasons, and only an estimated value is possible. The enthalpies of formation for the condensed phase can be accurately determined from precise heats of combustion measured in bomb calorimetry and such a program for obtaining the standard enthalpies of formation of certain classes of polymers including the α-olefin polymers has been initiated in our laboratory.[7] For these thermal data to be truly useful, it is necessary to define the condensed phase of the polymer more rigorously and at the same time to reduce the enthalpy of formation data to the standard ideal gas phase at 25°. Only then are we in a position to correlate energies with the structural features of the polymer segment. To this end, the abstract quantity, the standard enthalpy of vaporization, is absolutely necessary. Furthermore one requires an experimental estimate of the degree of crystallinity, the heat of fusion, and the glass enthalpy of the amorphous state, all of which are associated with the so-called condensed (c) phase.

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