Heats of Combustion of High-Temperature Polymers

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16. Abstract

The heats of combustion for 47 commercial and developmental polymers of known chemical structure were determined using an oxygen bomb calorimeter according to standard methods. The experimental results were compared to thermochemical calculations of the gross heat of combustion from (1) oxygen consumption and (2) group additivity of the heats of formation of products and reactants. The polymers examined were thermally stable, char-forming thermoplastics and thermoset resins containing a significant degree of aromaticity and heteroatoms including nitrogen, sulfur, phosphorus, silicon, and oxygen in linear and heterocyclic structures. The gross heats of combustion calculated from polymer enthalpies of formation and oxygen consumption thermochemistry were within 4 and 5 percent, respectively, of the experimental values from oxygen bomb calorimetry. The heat released by combustion per gram of diatomic oxygen consumed in the present study was $E = 13.08 \pm 0.87$ kJ/g-O_2 for polymers which combusted completely ($n = 46$). This value is indistinguishable from the universal $E = 13.1$ kJ/g-O_2 used in oxygen consumption calorimetry.

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EXECUTIVE SUMMARY

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INTRODUCTION

Commercial passenger aircraft cabins contain several tons of combustible plastics, thermoset resins, and elastomers in sidewall panels, ceilings, seat parts, foamed cushions, carpets, etc. The potential fire load represented by these interior materials is their heat of combustion. Using full- and bench-scale fire testing, the Federal Aviation Administration (FAA) determined that the fire hazard in an aircraft cabin is a function of the rate at which this heat is released by the burning material in a fire. [1] Consequently, FAA regulations were developed for heat release rate of large-area cabin materials. [2,3] In the FAA test, convected heat released during flaming combustion is calculated from the temperature rise of an air stream flowing past a standard-sized sample of the burning material. Bench-scale fire calorimeters have since been developed which use the oxygen consumption principle [4] to determine the chemical heat release rate of burning materials. [5-7] The oxygen consumption principle is based on the observation that combustion of a wide range of organic compounds [4,8] and common polymers [5,8] produces 13.1 ± 0.7 kJ of heat per gram of diatomic oxygen consumed, independent of the chemical composition of the organic material. The oxygen consumption principle has recently been employed by the FAA for measuring the nonflaming heat release rate of milligram-sized samples of research polymers in a microscale combustion flow calorimeter. [9,10]

In the FAA's Fire-Resistant Materials program, we are developing and evaluating new polymers with extremely low heat release rate in fires. Typically these materials tend to be char-forming, thermally stable polymers containing a high degree of chemical bond unsaturation, aromaticity, and the heteroatoms–nitrogen, sulfur, silicon, phosphorus, and oxygen. The objective of the present work was to measure and document the heats of combustion of some commercial, precommercial, and research polymers for use in calculating their heat release rate in flaming and nonflaming combustion. The accuracy of the universal value of 13.1 kJ of heat per gram of O_2 for combustion of thermally stable, char-forming polymers would be examined. The heats of complete combustion of 47 polymers were measured by the standard experimental procedure for determining gross calorific value using adiabatic oxygen bomb calorimetry and compared to the results of two different thermochemical calculations of the heat of combustion based on (1) oxygen consumption and (2) group additivity of the heats of formation of products and reactants.

COMBUSTION THERMOCHEMISTRY

At constant pressure and when no nonmechanical work is done, the heat (Q) and enthalpy (H) of a process are equal. The flaming combustion of polymers at atmospheric pressure satisfies these conditions. The high pressure adiabatic combustion of a polymer in a bomb calorimeter satisfies these conditions approximately, since the fractional pressure change is small. Consequently, the terms heat and enthalpy are used interchangeably in the following discussions.

OXYGEN CONSUMPTION.

Heats of combustion calculated from oxygen consumption rely on the observation that a wide range of organic compounds, including polymers, have approximately the same heat of complete combustion per gram of diatomic oxygen consumed

$$E = \Delta h_c \left[\frac{n_p M_p}{n_{O_2} M_{O_2}} \right] = \frac{\Delta h_c}{r_o} = 13.1 \pm 0.7 \text{ kJ/g–O}_2 \qquad (1)$$

where Δh_c is the net heat of complete combustion of the sample with all products in their gaseous state, n_p and M_p are the number of moles and molecular weight of the molecule or polymer repeat unit, respectively, n_{O_2} is the number of moles of O_2 consumed in the balanced thermochemical

equation, and $M_{O_2} = 32$ g/mol is the molecular weight of diatomic oxygen. In equation 1 the quantity $r_o = [n_{O_2} M_{O_2}/n_p M_p]$ is the oxygen-to-fuel mass ratio.

To illustrate this thermochemical calculation we determine the net heat of combustion for poly(methylmethacrylate) (PMMA) which has the chemical structure

$$
\begin{array}{c}
CH_3 \\
| \\
-[CH_2-C\,]_n- \\
| \\
C=O \\
| \\
O \\
| \\
CH_3
\end{array}
\tag{2}
$$

The methylmethacrylate repeat unit shown in brackets in equation 2 has the atomic composition $C_5H_8O_2$ so the balanced chemical equation for complete combustion is

$$
C_5H_8O_2 + 6\ O_2 \rightarrow 5\ CO_2 + 4\ H_2O
\tag{3}
$$
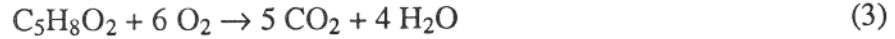
From equation 3 it is seen that 6 moles of O_2 are required to completely convert 1 mole of PMMA repeat unit to carbon dioxide and water. From equation 1 we calculate E for PMMA using the measured net heat of combustion in the present study, $\Delta h_c = -25.0$ kJ/g (see table 1)

$$
E\ =\ (-25.0\ \text{kJ/g–PMMA})\ \frac{(1\ \text{mol PMMA})(100\ \text{g–PMMA/mol})}{(6\ \text{mol } O_2\ \text{consumed})(32\ \text{g/mol–}O_2)}\ =\ -13.02\ \frac{\text{kJ}}{\text{g–}O_2}
$$

This calculation was performed for each polymer to determine E from its known atomic composition and measured heat of combustion. Inverting equation 1

$$
\Delta h_c\ =\ E\left[\frac{n_{O_2} M_{O_2}}{n_p M_p}\right]\ =\ E\,r_o
\tag{4}
$$

shows that the net heat of complete combustion of a polymer is simply calculated if the atomic composition of the polymer is known *a priori* so that the balanced thermochemical reaction equation can be written.

MOLAR GROUP ADDITIVITY OF HEATS OF FORMATION.

Calculation of the heat of the combustion reaction of polymers was carried out using the principle of molar additivity of the heats of formation of the combustion products and reactants. [11] The concept derives from the fact that enthalpy (H) is a state function, and therefore, its change in any process is independent of the path from reactants to products. Thus, the overall enthalpy of a reaction is simply the sum of the enthalpies of the component reactions. In practice, the heat of combustion of the reaction can be calculated by subtracting the heat of formation of the products from the heat of formation of the reactants

$$
\Delta h_c\ =\ \sum_i n_p \Delta h_{f,p}^o\ -\ \sum_j n_r \Delta h_{f,r}^o
\tag{5}
$$

where p and r denote products and reactants, respectively, in the standard state at a temperature of 298 K.

For polymeric reactants, the molar heat of formation can be estimated from the tabulated molar contributions of the chemical groups which constitute the monomer or repeat unit. Using PMMA as an example again with the monomer/repeat unit chemical structure shown in equation 2, the heats of formation of the methylmethacrylate constituent groups at T = 298 K are [11]:

$$
\begin{array}{llll}
1\,(C=O) & = & 1 \times (-132{,}000 + 40T) & = & -120.08 \text{ kJ/mol} \\
1(-O-) & = & 1 \times (-120{,}000 + 70T) & = & -99.14 \text{ kJ/mol} \\
2(CH_3) & = & 2 \times (-46{,}000 + 95T) & = & -35.38 \text{ kJ/mol} \\
1(CH_2) & = & 1 \times (22{,}000 + 102T) & = & 8.40 \text{ kJ/mol} \\
\underline{1(-C-)} & = & \underline{1 \times (20{,}000 + 140T)} & = & \underline{61.72 \text{ kJ/mol}} \\
& & \text{Total} & = & -184.48 \text{ kJ/mol}
\end{array}
$$

Summing these group contributions gives the molar heat of formation of the methylmethacrylate monomer, $\Delta H_f = -184.48$ kJ/mol at standard conditions (T = 298 K). From the stoichiometry of complete combustion:

$$\text{Reactants} \rightarrow \text{Products} = C_5H_8O_2 + 6\,O_2 \rightarrow 5\,CO_2 + 4\,H_2O$$

and the tabulated standard heats of formation of the products

$$\Delta H_f\,(H_2O) = -241.8 \text{ kJ/mol}; \quad \Delta H_f\,(CO_2) = -393.5 \text{ kJ/mol}$$

and reactants

$$\Delta H_f\,(O_2) = 0 \text{ kJ/mol}; \qquad \Delta H_f\,(PMMA) = -184.5 \text{ kJ/mol}$$

J, the molar heat of combustion of PMMA is

$$
\begin{aligned}
\Delta H_c\,(PMMA) &= \Delta H_{prod} - \Delta H_{react} \\
&= [5\,(CO_2) + 4\,(H_2O)] - [(C_5H_8O_2) + 6\,(O_2)] \\
&= [5\,(-393.5 \text{ kJ/mol}) + 4\,(-241.8 \text{ kJ/mol})] - [-184.5 \text{ kJ/mol} + 6\,(0)] \\
&= -2748.7 \text{ kJ/mol}
\end{aligned}
$$

The gross heat of combustion per unit mass is then

$$
\begin{aligned}
Q_c\,(PMMA) &= \Delta H_c\,/\,M_p \\
&= [-2748.7 \text{ kJ/mol}]/[100 \text{ g-MMA/mol}] \\
&= -27.5 \text{ kJ/g}
\end{aligned}
$$

which compares favorably to the oxygen bomb value $Q_c = -26.81$ kJ/g reported in table 1 and literature values $Q_c = -26.20$ kJ/g [12] and -26.64 kJ/g [8] for PMMA.

The hydrogen-deficient polymer polytetrafluorethylene (C_2F_4) requires the addition of water as a reactant in the stoichiometric equation (and the test) to obtain correct estimates of the heat of combustion; i.e., the balanced reaction equation for this polymer is

$$C_2F_4 + O_2 + 2\,H_2O \rightarrow 2\,CO_2 + 4\,HF$$
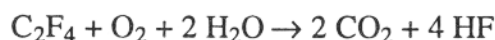
A milliliter of water is added to the bomb calorimeter prior to the combustion test and is available for reaction with the fluorine atoms to yield the mineral acid HF. The hexafluoroethertriphenyl-phosphineoxide (6F-ETPP) polymer contains sufficient hydrogen for the water reaction products so the net balanced stoichiometric equation for this combustion reaction is

$$C_{33}H_{21}O_3PF_6 + 36.5\,O_2 \rightarrow 33\,CO_2 + 6\,H_2O + H_3PO_4 + 6\,HF$$

3
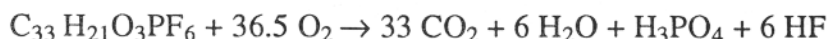
Unfortunately, the molar group contribution of the phosphine oxide group ($\equiv P=O$) to the heat of formation of the polymer is not available so the heat of combustion could not be calculated from heats of formation for his polymer. The calculation method for the heat of combustion from group contributions is seen to be more complex than the oxygen consumption calculation and requires detailed knowledge of the chemical structure of the molecule and its atomic composition.

EXPERIMENTAL

GROSS HEAT OF COMBUSTION.

The gross heat of combustion was measured in an oxygen bomb calorimeter (Model 1341, Plain Jacket Oxygen Bomb Calorimeter, Parr Instrument Co., Moline, Illinois) according to a standard procedure. [13] A weighed sample of approximately 1 gram is placed inside a calibrated adiabatic bomb calorimeter with 1 milliliter of deionized water. Chromel (chromium nickel alloy) wire is connected to the two electrodes in the pressure vessel (bomb) and placed in contact with the sample for ignition. The bomb is sealed and purged twice with 5 atmospheres pressure of pure (99.99%) oxygen and then pressurized with pure oxygen to 20 atmospheres. The bomb is then placed inside a water bath containing 2 liters of water in an insulated jacket. A motorized stirrer is then placed inside the water bath to circulate the water around the bomb. The temperature of the water is measured using a precision thermistor (Omega Model 5831A) and rises slightly due to the mechanical agitation by the stirrer but eventually reaches an equilibrium value which is recorded as the initial temperature, T_o, in the experiment. An electric current is passed through the wire causing ignition and burning of the wire and sample in the high-pressure oxygen. The temperature of the water bath rises a few degrees Celsius above the initial temperature, typically, and reaches a maximum value, T_{max}, which is recorded. The bath temperature then slowly decreases due to convective heat losses to the environment. Three replicates are performed for each sample. The oxygen bomb calorimeter was calibrated by combusting a known mass, m, of standard benzoic acid having a heat of combustion of 26.453 kJ/g. Ten benzoic acid samples of size ranging from 0.3717 to 1.9964 grams were tested. The calibration factor for the bomb calorimeter, C, was calculated from the benzoic acid calibrations as $C = (m \cdot 26.453 \text{ kJ/g})/(T_{max} - T_o) = 10.13 \pm 0.13$ kJ/°K (n= 10).

The gross heat of combustion of the polymer was calculated from the sample mass, m, and the difference between the initial and maximum bath temperature, $\Delta T_{max} = (T_{max} - T_o)$, after correcting for the heat of combustion of the wire. For samples containing atoms besides C, H, and O, combustion products in addition to CO_2 and H_2O are formed and corrections must be made for the heat of formation and/or heat of solution of these compounds.

An ignition correction (e_1) is made for the heat contribution from burning of the nickel chromium alloy fuse wire. The wire is weighed before and after combustion and the weight loss is multiplied by the heat of combustion of the alloy, 5.8576 kJ/g, to calculate the ignition energy, e_1. A correction for the heat of product formation (e_2) and heat of solution of the products (e_3) is required for samples which contain elements other than carbon, hydrogen, and oxygen. A titration is performed to determine the heats of formation and solution (in water) of the additional products, typically mineral acids. In practice, the bomb is rinsed with distilled water and the acidic washings are titrated with 1 M NaOH to the appropriate pH break point for HF, HNO_3, H_3PO_4, or H_2SO_4, depending on the element(s) in the sample. The moles of mineral acid formed in the combustion are calculated from the stoichiometric endpoint titration and multiplied by the energy of formation of the relevant compound to calculate the heat of formation, e_2, and heat of solution, e_3, corrections for the acids formed. [14] The gross heat of combustion, Q_c, is then calculated as

$$Q_c = (C \Delta T_{max} - e_1 - e_2 - e_3)/m \qquad (6)$$

The average standard error of the technique is 0.51 kJ/mol.

4

NET HEAT OF COMBUSTION.

There are no direct methods for measuring the net heat of combustion–which is the gross heat of combustion minus the latent heat of vaporization of the water produced during the reaction. The net or lower heat of combustion is relevant to flaming combustion where water is in the gaseous state at flame temperatures of ≈ 1000 K. As a result, the latent heat of water at 298 K is subtracted from the gross heat of combustion because this amount of heat is required to maintain the combustion product water in the gaseous state. The gross heat of combustion measured by the above procedure is corrected for the heat of vaporization of the water formed during the combustion to give the net heat of combustion, Δh_c, using the relation [8]

$$\Delta h_c = Q_c - 21.96 w_H \tag{7}$$

where w_H is the weight fraction of hydrogen in the sample and Δh_c, Q_c are in kJ/g.

RESULTS

Although the heat or enthalpy of combustion is a negative (exothermic) quantity, positive (absolute) values are listed in the following tables and figures for convenience. Table 1 is a compilation of all of the polymeric materials tested listed by chemical and/or common name, abbreviated name, and Chemical Abstracts Service (CAS) registry numbers where available. Trade names and manufacturer or sample source are listed in table 1 along with atomic composition of the polymer repeat unit. The gross heat of combustion (Q_c), net heat of combustion (Δh_c), and the net heat of combustion divided by the oxygen-to-fuel mass ratio ($\Delta h_c/r_o$) are listed for each polymer. Values for Q_c are averages of triplicate determinations ± 1 standard deviation. When no standard deviation is shown, Q_c is the result of a single test. During the bomb calorimeter testing, it was found that the PBI polymer, which was tested in the form of powder, was difficult to combust because of the tendency to disperse inside the bomb vessel at ignition.

Table 2 lists experimental values for the gross heat of combustion measured in the present study by oxygen bomb calorimetry. The second column in table 2 lists the gross heats of combustion calculated from oxygen consumption thermochemistry using equations 4 and 7

$$Q_c = E \left[\frac{n_{O_2} M_{O_2}}{n_p M_p} \right] + 21.96 \, w_H \tag{8}$$

with the universal value, $E = 13.1$ kJ/g-O_2. Column 3 in table 2 lists the gross heats of combustion calculated from molar group additivity of the heats of formation according to the method described. Data for identical polymers from different sources have been combined in tables 2 and 3.

The quantity $E = \Delta h_c/r_o$ is the heat released by combustion per unit mass of oxygen consumed in a fire where all combustion products are in their gaseous state. An accurate and representative value of E is thus important for calculating the heat released during flaming combustion of polymers from oxygen consumption measurements. Values for E from the present work are listed in the last column of table 1 for comparison to the universal value used in oxygen consumption fire calorimetry, $E = 13.1$ kJ of heat released per gram of diatomic oxygen (O_2) consumed.

TABLE 1. COMBUSTION DATA FOR POLYMERIC MATERIALS

	Material (abbreviated name), [CAS Registry Number]	Trade Name, Manufacturer/ Supplier	Repeat Unit Composition	Q_c (kJ/g)	Δh_c (kJ/g)	$\Delta h_c/r_o$ (kJ/g-O_2)
1	Poly(oxymethylene) (POM) [9002-81-7]	Aldrich Chemical Company, Inc.	CH_2O	17.39 ± 0.13	15.93	14.93
2	Polytetrafluoroethylene (PTFE) [9002-84-0]	Aldrich Chemical Company, Inc.	C_2F_4	6.68	6.68	10.44
3	Polyvinylalcohol (≥99%) (PVOH) [9002-89-5]	Aldrich Chemical Company, Inc.	C_2H_4O	23.31 ± 0.54	21.31	11.72
4	Polyethylene (PE) [9002-88-4]	LDPE, Polysciences, Inc.	C_2H_4	47.74	44.60	13.01
5	Poly(dimethylsiloxane) (PDMS) [9016-00-6]	Dow Corning 346	C_2H_6OSi	19.53 ± 0.74	17.75	13.68
6	Polypropylene (PP) [25085-53-4]	Polysciences, Inc.	C_3H_6	45.80 ± 0.48	42.66	12.44
7	Poly(methylmethacralate) (PMMA) [9011-14-7]	Aldrich Chemical Company, Inc.	$C_5H_8O_2$	26.75 ± 0.14	24.99	13.02
8	Poly(methylmethacrylate) (PMMA) [9011-14-7]	Polycast acrylic (black)	$C_5H_8O_2$	26.86 ± 0.61	25.10	13.07
9	Poly(1,4-phenylenesulfide) (PPS) [9016-75-5]	Aldrich Chemical Company, Inc	C_6H_4S	29.62 ± 0.71	28.81	13.89
10	Poly(phenylenesulfide) (PPS) [9016-75-5]	KETRON PPS, DSM Engineering	C_6H_4S	28.39 ± 0.37	27.58	13.30
11	Poly(2,6-dimethyl-1,4-phenylene-oxide) (PPO) [25134-01-4]	Noryl 0.4 IV virgin General Electric	C_8H_8O	34.21 ± 0.36	32.75	12.93
12	Polystyrene (PS) [9003-53-6]	Polysciences, Inc.	C_8H_8	43.65	41.96	13.64
13	Polyethyleneterephthalate (PET) [25038-59-9]	Polysciences, Inc.	$C_{10}H_8O_4$	24.13 ± 0.39	23.22	13.93
14	Epoxy Novolac, catalytic cure (phenoxy-N) [028064-14-4]	DEN-438, Dow Chemical	$C_{10}H_{11}O$	31.37 ± 0.14	29.73	11.15
15	Poly(1,4-phenyleneethersulfone) (PES) [25667-42-9]	BASF Ultrason E1010/ Natural	$C_{12}H_8O_3S$	25.42 ± 0.55	24.66	14.30
16	Poly(1,4-butanediolterephthalate) (PBT) [26062-94-2]	Polysciences, Inc.	$C_{12}H_{12}O_4$	27.91	26.71	14.13
17	Poly(hexamethyleneadiapamide) (nylon 66) [32131-17-2]	Polysciences, Inc.	$C_{12}H_{22}O_2N_2$	30.90 ± 0.15	28.76	12.31
18	Poly(etherketone) (PEK) [27380-27-4]	P22 (virgin), Victrex USA	$C_{13}H_8O_2$	31.07 ± 0.70	30.17	13.20
19	Poly(benzoyl-1,4-phenylene)	POLYX-1000, MAXDEM, Inc.	$C_{13}H_8O$	38.35	37.37	14.50
20	Poly(p-phenylenebenzobisxazole) (PBO) [852-36-8]	PBO, DOW Chemical Co.	$C_{14}H_6O_2N_2$	29.18 ± 0.21	28.62	14.43
21	Poly(m-phenylene-isophthalamide)	Nomex, Dupont	$C_{14}H_{10}O_2N_2$	26.45 ± 0.09	25.53	12.25
22	Aramid-arylester copolymer	Aramid Z-200, Dupont	$C_{14}H_{10}O_2N_2$	25.27 ± 0.81	24.35	11.68
23	Poly(p-phenylene-terephthalamide)	KEVLAR, Dupont	$C_{14}H_{10}O_2N_2$	26.92 ± 0.54	26.00	12.48
24	Polyamideimide (PAI)	TORLON 4203L, Amoco	$C_{15}H_8O_3N_2$	24.97 ± 0.13	24.31	12.94
25	Poly(acrylonitrile-butadiene-styrene) (ABS) [9003-56-9]	Polysciences, Inc.	$C_{15}H_{17}N$	39.84	38.07	13.04

TABLE 1. COMBUSTION DATA FOR POLYMERIC MATERIALS (Continued)

	Material (abbreviated name), [CAS Registry Number]	Trade Name, Manufacturer/ Supplier	Repeat Unit Composition	Q_c (kJ/g)	Δh_c (kJ/g)	$\Delta h_c/r_o$ (kJ/g-O_2)
26	Bisphenol-E Cyanate Ester [47073-92-7]	AroCy L-10, Ciba Specialty Chemicals	$C_{16}H_{12}O_2N_2$	29.38 ± 0.06	28.38	13.01
27	Polycarbonate of bisphenol-A (PC) [24936-68-3]	Polysciences Inc., 32-36K mol.wt.	$C_{16}H_{14}O_3$	31.53 ± 0.88	30.32	13.37
28	Polycarbonate of bisphenol-A (PC) [24936-68-3]	LEXAN 141, General Electric	$C_{16}H_{14}O_3$	31.06 ± 0.08	29.85	13.16
29	Hexafluorobisphenol-A Cyanate Ester [32728-27-1]	AroCy F-10, Ciba Specialty Chemicals	$C_{17}H_8O_2N_2F_6$	18.71 ± 0.03	18.25	12.23
30	Bisphenol-A Cyanate Ester [1156-51-0]	AroCy B-10, Ciba Specialty Chemicals	$C_{17}H_{14}O_2N_2$	29.92 ± 0.27	28.81	12.84
31	Bisphenol-A Epoxy, catalytic cure (Phenoxy-A) [001675-54-3]	DER-332, Dow Chemical	$C_{21}H_{24}O$	32.50 ± 0.15	30.79	11.40
32	Poly(etheretherketone) (PEEK) [29658-26-2]	450F, Victrex USA	$C_{19}H_{12}O_3$	31.07 ± 0.53	30.16	13.24
33	Poly(etheretherketone) (PEEK) [29658-26-2]	KETRON PEEK 1000, DSM	$C_{19}H_{12}O_3$	31.48 ± 0.44	30.57	13.42
34	Tetramethylbisphenol F Cyanate Ester [101657-77-6]	AroCy M-10, Ciba Specialty Chemical	$C_{19}H_{18}O_2N_2$	31.23 ± 0.05	29.94	12.72
35	Poly(etherketoneketone) (PEKK)	G040 (virgin flake), Dupont	$C_{20}H_{12}O_3$	31.15 ± 0.17	30.27	13.20
36	Polybenzimidazole (PBI) [25928-81-8]	CELAZOLE PBI, Hoechst Celanese	$C_{20}H_{12}N_4$	22.22 ± 0.31	21.36	8.94
37	Polyimide (PI) [26023-21-2]	Aldrich Chemical Company, Inc.	$C_{22}H_{10}O_5N_2$	26.03 ± 0.77	25.45	13.81
38	Novolac Cyanate Ester [P88-1591]	AroCy XU-371, Ciba Spec. Chems.	$C_{24}H_{15}O_3N_3$	28.61 ± 0.53	27.77	12.99
39	Novolac Cyanate Ester [P88-1591]	Primaset PT-30, Allied Signal, Inc.	$C_{24}H_{15}O_3N_3$	30.65 ± 0.05	29.81	13.95
40	Bisphenol-M Cyanate Ester [127667-44-1]	AroCy XU-366, Ciba Spec. Chems.	$C_{26}H_{24}O_2N_2$	34.39 ± 0.15	33.06	13.20
41	Polysulfone of bisphenol-A (PSF) [25135-57-7]	Aldrich Chemical Company, Inc.	$C_{27}H_{22}O_4S$	30.28 ± 0.47	29.19	13.22
42	Polysulfone of bisphenol-A (PSF) [25135-57-7]	UDEL, Amoco	$C_{27}H_{22}O_4S$	30.63 ± 0.35	29.54	13.38
43	Polybenzoxazine of bisphenol-A/aniline (b-a benzoxazine)	Case Western Reserve University	$C_{31}H_{30}O_2N_2$	34.89 ± 0.19	33.46	12.88
44	Arylether of hexafluorobisphenol-A and triphenylphosphine oxide	6F-ETPP, DAYCHEM	$C_{33}H_{21}O_3F_6P$	26.50 ± 0.25	25.74	13.35
45	Polyetherimide (PEI) [61128-46-9]	Polysciences, Inc.	$C_{37}H_{24}O_6N_2$	29.59 ± 0.28	28.70	13.27
46	Polyetherimide (PEI) [61128-46-9]	ULTEM 1000, General Electric	$C_{37}H_{24}O_6N_2$	29.06 ± 0.06	28.17	13.03
47	Polyester of hydroxybenzoic and hydroxynapthoic acids [70679-92-4]	VECTRA C LCP (virgin/ unfilled) Hoechst Celanese	$C_{39}H_{22}C_{10}$	26.54 ± 0.39	25.80	13.27

TABLE 2. MEASURED AND CALCULATED GROSS HEATS OF COMBUSTION FOR POLYMERS

	Polymer	Oxygen Bomb Calorimeter	Oxygen Consumption	Molar Group Contribution
1	Polyoxymethylene	17.39	15.44	18.20
2	Polytetrafluoroethylene	6.68	8.38	7.57
3	Polyvinylalcohol	23.31	25.81	26.20
4	Polyethylene	47.74	48.05	46.00
5	Polydimethylsiloxane	19.53	18.78	N/A
6	Polypropylene	45.80	48.05	46.00
7/8	Polymethylmethacrylate	26.81	26.91	27.50
9/10	Poly(1,4-phenylenesulfide)	29.01	27.98	30.80
11	Poly(2,6-dimethyl-1,4 phenyleneoxide)	34.21	34.65	34.70
12	Polystyrene	43.65	42.00	41.30
13	Polyethyleneterephthalate	24.13	22.75	24.10
14	Epoxy novolac	31.37	36.58	32.06
15	Poly(1,4-phenyleneethersulfone)	25.42	23.34	25.70
16	Poly (1,4-butanediol terephthalate)	27.91	25.97	26.90
17	Poly(hexamethyleneadipamide)	30.90	32.74	32.80
18	Poly(etherketone)	31.07	30.84	31.45
19	Poly(benzoyl-1,4-phenylene)	38.35	34.74	35.90
20	Poly(p-phenylenebenzobisxazole)	29.18	26.54	29.00
21	Poly(m-phenyleneisophthalamide)	26.45	28.22	29.30
22	Aramid-arylester copolymer	25.27	28.22	29.30
23	Poly(p-phenyleneterephthalamide)	26.92	28.22	29.30
24	Poly(amideimide)	24.97	25.28	26.75
25	Poly(acrylonitrile-butadiene-styrene)	39.84	40.01	39.43
26	Bisphenol E Cyanate Ester	29.38	29.58	30.70
27/28	Polycarbonate of bisphenol-A	31.30	30.92	31.20
29	Hexafluorobisphenol A Cyanate Ester	18.71	20.00	18.10
30	Bisphenol A Cyanate Ester	29.92	30.51	31.50
31	Bisphenol-A Epoxy	32.50	31.10	33.50
32/33	Poly(etheretherketone)	31.28	30.75	31.50
34	Tetramethylbisphenol F Cyanate Ester	31.23	32.12	32.60
35	Poly(etherketoneketone)	31.15	30.92	31.50
36	Polybenzimidazole	22.22	32.16	33.40
37	Polyimide	26.03	24.72	26.30
38/39	Phenol Novolac Cyanate Ester	29.63	28.84	29.80
40	Bisphenol M Cyanate Ester	34.39	34.15	34.60
41/42	Polysulfone	30.46	30.02	31.20
43	Poly(bisphenol-A/aniline) benzoxazine	34.89	35.45	35.80
44	Polyhexafluorobisphenol-A-TPPO	26.50	26.01	N/A
45/46	Polyetherimide	29.33	29.21	30.00
47	Polyester of HBA-HNA	26.54	26.22	26.81

Table 3 compares experimental values for the gross heat of combustion of some standard polymers in the present study to literature values for this quantity.

TABLE 3. COMPARISON OF EXPERIMENTAL GROSS HEATS OF
COMBUSTION TO LITERATURE VALUES FOR SEVERAL POLYMERS [8]

Polymers	Q_c (kJ/g) (Present Study)	Q_c (kJ/g) [8]
Polycarbonate of bisphenol-A	31.3	31.0
Polyethylene	47.7	46.2
Polyethyleneterephthalate	24.1	22.2
Polyhexamethyleneadipamide	30.9	29.6
Polymethylmethacrylate	26.8	26.6
Polyphenyleneoxide	34.2	34.6
Polypropylene	45.8	46.4
Polystyrene	43.7	42.5
Polyvinylalcohol	23.3	25.0

Figure 1 is a plot of the heats of combustion calculated from oxygen consumption versus experimental heats of combustion obtained from oxygen bomb calorimetry in table 2. The equivalence line, $y = x$, has a correlation coefficient, $r = 0.93$. The open circle is the data for polybenzimidazole (PBI) which did not combust completely in the bomb calorimeter as evidenced by residual powder after the test.
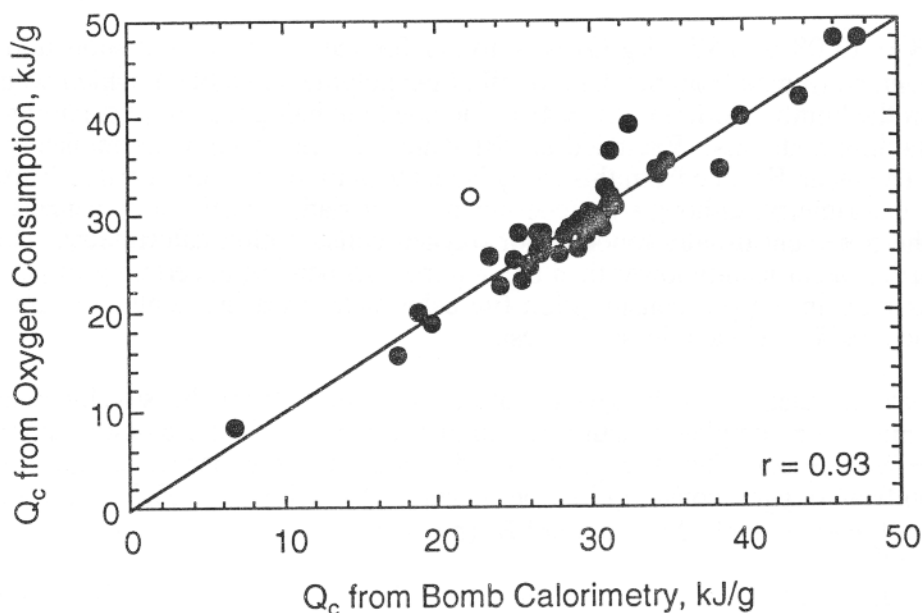

FIGURE 1. CORRELATION PLOT OF CALCULATED VERSUS EXPERIMENTAL HEATS
OF COMBUSTION FOR 46 POLYMERS (LINE IS $y = x$)

Figure 2 is a plot of the heats of combustion calculated from group additivity of the heats of formation *versus* experimental heats of combustion obtained from oxygen bomb calorimetry in table 2. The equivalence line, $y = x$, has a correlation coefficient, $r = 0.95$. The open circle is the data for polybenzimidazole (PBI) which did not combust completely in the bomb calorimeter.
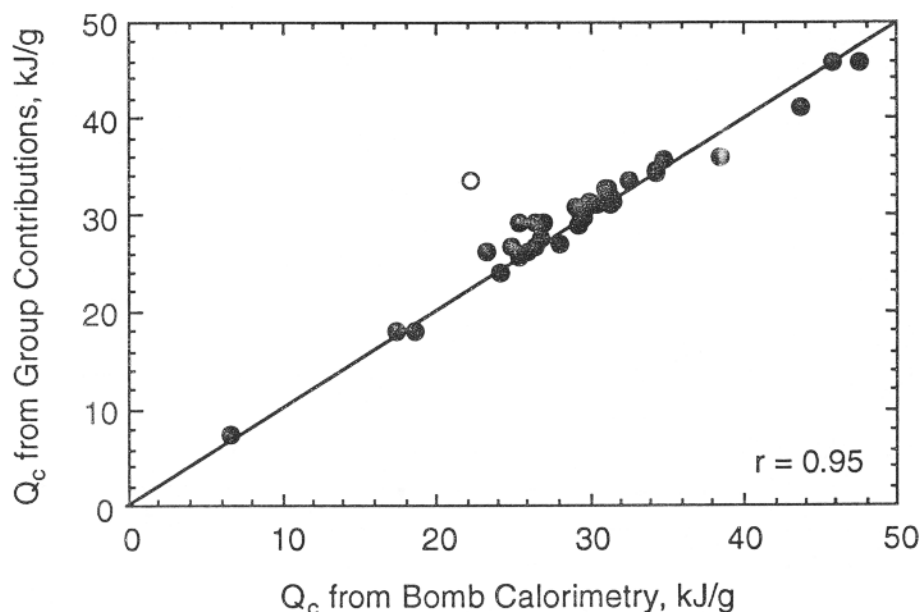
FIGURE 2. CORRELATION PLOT OF CALCULATED VERSUS EXPERIMENTAL HEATS
OF COMBUSTION FOR 44 POLYMERS (LINE IS y = x)

DISCUSSION

A value of E = 13.08 ± 0.87 kJ/g-O_2 was found for the net heat of combustion per gram of diatomic oxygen consumed from the data for all of the polymers in table 1 which went to complete combustion in the bomb calorimeter (n = 46). Included are halogenated, phosphorus-, sulfur-, and nitrogen-containing materials. Excluded is PBI which did not combust completely in the bomb calorimeter. The mean E value from this study is identical to the universal value E used in oxygen consumption calorimetry, although the coefficient of variation C.V. = 7 percent is somewhat higher than the 5 percent usually reported for oxygen consumption calorimetry. Regardless, the uncertainty in E is significantly lower than the reported 15 percent uncertainty in peak heat release and mass loss rates in oxygen consumption fire calorimetry measurements [15] and will not be a factor in the accuracy of a heat release rate test.

Thermochemical calculations of the gross heat of combustion from the stoichiometric amount of oxygen consumed in a complete reaction are simple to perform if the atomic composition of the polymer is known *a priori*. The average relative deviation of the experimental and calculated heats of combustion from oxygen consumption thermochemistry using E = 13.1 kJ/g-O_2 is 4.7 percent for all of the polymers in table 2 excluding PBI (n = 40).

Thermochemical calculations of the gross heat of combustion from heats of formation of products and reactants for the polymers listed in table 2 have an average relative deviation of 3.8 percent from the experimental (bomb) values (n = 38). Excluded from the comparison were PBI which did not combust completely in the test and polydimethylsiloxane and 6F-ETPP for which the group contributions for =Si–O– and ≡P=O, respectively, were unknown or unavailable. Thus, thermochemical calculations of the gross heat of combustion from molar group additivity of the heats of formation of products and reactants achieves better accuracy than calculations based on oxygen consumption for the polymers examined in this study. This is not surprising since the group contributions to the heats of formation used in this study were originally determined from the gross heats of combustion of materials with known composition.

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Nine polymers with known gross heats of combustion [8] were included in the present study to benchmark the experimental method. Table 3 compares literature values for the heat of combustion for these polymers to those obtained experimentally in this study. The average relative deviation between the measured and reported gross heat of combustion of the nine polymers is 3.3%.

CONCLUSIONS

The heats of combustion of 47 polymers of known chemical composition were measured and calculated. The agreement between experimental values for the gross heat of combustion and thermochemical calculations of this quantity from heats of formation and oxygen consumption was 3.8 and 4.7 percent, respectively, for these calculation methods. The value $E = 13.08 \pm 0.87$ kJ/g-O_2 ($n = 46$) for the net heat released by combustion per unit weight of diatomic oxygen consumed was obtained in the present study of high-temperature, heteroatomic polymers. This value of E for thermally stable polymers is statistically indistinguishable from the universal value $E = 13.1$ kJ/g-O_2 used for calculating heat release rates of burning materials from oxygen consumption calorimetry.

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