Correlation between heat of combustion and chemical structure of polymers

S. C. Ng and K. K. Chee*
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia
(Received 24 September 1992)

Two distinct approaches pertaining to the chemical structure are applied to predict the specific heat of combustion (Δh_c) of polymers. It has been found that the experimental and calculated values of Δh_c are in good agreement, particularly for polymers of high hydrogen content and low atomic ratio of halogen/carbon. For copolymers, Δh_c is demonstrated to be a weight-average of its component values derived from the corresponding homopolymers. The practical implications of the present findings are discussed.

(Keywords: specific heat of combustion; chemical structure; correlation)

INTRODUCTION

Combustion of organic compounds including polymers in the presence of oxygen gas may lead to the emission of greenhouse gases, which have a direct impact on global warming. In addition, this particular chemical process usually generates heat, which can be quantified by the molar heat of combustion (ΔH_c). It has been noted that the flame resistance of a material increases as less heat is evolved during combustion[1]. Therefore information on ΔH_c would be useful for fire research. The present work focuses exclusively on this important parameter.

It has been established[1] that the specific heat of combustion, defined by $\Delta h_c = \Delta H_c/M$ at temperature T is given by:

$$\Delta h_c = nk/M \tag{1}$$

where M is the molecular weight of the compound or repeat unit of the polymer, n is the number of moles of oxygen needed for complete combustion of 1 mole of the above structural unit, and k is an empirical constant. An alternative approach for Δh_c is based on the following reaction scheme:

$$\mathrm{P(s)} \xrightarrow[\Delta H_c^0]{+n\mathrm{O_2(g)}} n_1\mathrm{CO_2(g)} + n_2\mathrm{H_2O(1)} + n_3\mathrm{HX(g)} + n_4\mathrm{N_2(g)}$$

$$\uparrow -\Delta H_v^0 \qquad\qquad \uparrow \Delta H_{f2}^0$$

$$\mathrm{P(g)} \xrightarrow[\Delta H_{f1}^0]{-n\mathrm{O_2(g)}} n_1\mathrm{C(s)} + (2n_2+n_3)/2\mathrm{H_2(g)} + n_3/2\mathrm{X_2(g)} + n_4\mathrm{N_2(g)} + (2n_1+n_2)/2\mathrm{O_2(g)}$$

where P represents the repeat unit of the polymer, i.e. $[C_{n_1}H_{(2n_2+n_3)}O_{(2n_1+n_2-2n)}N_{2n_4}X_{n_3}]$ with X = F or Cl, ΔH_{fi}^0 ($i = 1, 2$) are the standard heats of formation, ΔH_v^0 is the heat of vaporization of P, n_j ($j = 1, 2, 3, 4$) are the stoichiometric coefficients, the superscript '0' refers to the standard conditions of $T^0 = 298.15$ K, and s, l and g refer to the solid, liquid and gaseous states, respectively. According to Hess's law:

$$\Delta h_c^0 = (\Delta H_{f2}^0 + \Delta H_v^0 - \Delta H_{f1}^0)/M \tag{2}$$

The value of ΔH_c at T, designated by ΔH_T, can be readily computed by

$$\Delta H_T = \Delta H_c^0 + \int_{T^0}^{T} \Delta_r C_p \, dT \tag{3}$$

where $\Delta_r C_p$ is the total difference between the heat capacities of the products and reactants in the combustion process. However, if T is close to 298.15 K, the second term on the right-hand side of equation (3) can be neglected altogether, as in the present analyses. On this basis, ΔH_c is considered to be independent of T in the present context. In this work, we study critically the validity of the two predictive equations for Δh_c. In addition, a practical means to estimate the compositions of copolymers is developed.

EXPERIMENTAL

Low-density polyethylene, semicrystalline polypropylene, polystyrene, polytetrafluoroethylene, poly(ethylene terephthalate), poly[2,2-propane bis(4-phenyl) carbonate], poly(vinyl alcohol) and poly(vinyl acetate) were purchased from BDH (UK). Poly(methyl methacrylate), poly(isobutyl methacrylate) and poly(vinyl methyl ether) were supplied by TCI (Tokyo), whereas the copolymers of styrene and maleic anhydride (S-*co*-MA), poly(vinylidene fluoride), poly(vinyl isobutyl ether) and polyisobutylene were obtained from Aldrich. The samples of epoxidized natural rubber (ENR) were provided by courtesy of the Rubber Research Institute of Malaysia. All the above polymers were used as received.

The natural rubber sample was prepared from fresh latex and coagulated by formic acid. The resulting product was rinsed thoroughly with distilled water and

* To whom correspondence should be addressed

0032-3861/93/183870-03

dried under vacuum at ambient temperature to constant weight.

2,2′-Azobisisobutyronitrile was used to prepare the copolymers of styrene and methyl methacrylate (S-*co*-MMA) at 60°C. The copolymers were purified by the reprecipitation method using toluene as solvent and methanol as non-solvent. The compositions of the samples of S-*co*-MA and ENR were furnished by the respective suppliers. The latter were in fact confirmed by the glass transition temperature method[2]. Infra-red spectra were obtained with a Jasco Report-100 IR Spectrometer. Each of the S-*co*-MMA samples was solution-cast on to a NaCl cell. The compositions of these copolymers were determined by referring to the absorption peaks at 700 and 1725 cm^{-1}.

A Parr oxygen bomb calorimeter (Model 1341EE) was employed to monitor Δh_c. It was calibrated by using purified benzoic acid and operated at the ambient temperature (27 ± 1°C). The reproducibility of Δh_c data was recorded to be 2%. Least-squares regression analysis was applied to treat the data whenever it was applicable.

RESULTS AND DISCUSSION

A total of 320 values of Δh_c obtained at 20 or 25°C are available in the literature[3,4]. They were screened by equation (1) in order to estimate the constant k. Indeed, the k values do not vary appreciably as shown in *Table 1* for six classes of organic compounds. However, this is not always true, for almost one-third of the above-cited molecules, including those with molecular weight < 50 or in the gaseous state, produce significantly higher or lower k values. As noted, *Table 1* also excludes the compounds containing the following structural features: (1) H/C=O and (O+N)/C ≥ 1, where H, C, O and N refer to the number of respective elements present in the compounds; (2) α-unsaturated acids, alcohols and aldehydes; (3) selective N-compounds containing azo, nitro, nitrosamine, isocyanate, nitrate, nitrile, diamine, tetramine and hydrazine groups; (4) esters of formic, oxalic and maleic acids, and (5) bromine, iodine and sulfur compounds.

Throughout the present study, an optimum $k = -439$ kJ mol^{-1} is chosen for classes 2–6 listed in *Table 1*, since their average k values are fairly close. Indeed, the k values adopted herein are comparable with that proposed by other workers[1].

Table 2 displays the Δh_c values for a number of homopolymers. This information is derived from various sources. The data required for equation (2) are collected from the literature. While the ΔH_f^0 values for the combustion products CO_2(g), H_2O(l), HCl(g) and HF(g) are known accurately[3], the ΔH_{f1}^0 and ΔH_v^0 for the polymer have to be estimated using the group contribution method[5]. Here, ΔH_v^0 is computed from the cohesive energy (E_{coh}) via

$$\Delta H_v^0 = E_{coh} + RT^0 \quad (4)$$

where R is the gas constant. Clearly, the performance of equation (2) depends vitally on the reliability of these group contribution quantities.

The four sets of Δh_c shown in *Table 2* are compared in terms of the standard difference, Δ, defined by:

$$\Delta = \left[\sum_i^m (\Delta h_i' - \Delta h_i'')^2 / m \right]^{1/2} \quad (5)$$

where $\Delta h_i'$ and $\Delta h_i''$ are the Δh_c values registered for the ith polymer by two different approaches, and m is the total number of polymers studied. It is found that the Δh_c values observed by us do compare favourably with those reported previously[1,6] as justified by $\Delta = 0.70$ kJ g^{-1}.

The discrepancies between the experimental and predicted Δh_c data are characterized by the rational Δ values varying from 0.66 to 0.80 kJ g^{-1}, indicating that the predictions of Δh_c are less dependable for flame-resistant polymers such as polytetrafluoroethylene.

Table 1 Average values of k obtained for various classes of organic compounds

No.	Class	$-(k \pm \Delta k)^a$ (kJ mol^{-1})	p[b]
1	Hydrocarbons	436 ± 5	39
2	Alcohols and phenols	438 ± 6	24
3	Alkanals, alkanones and ethers	442 ± 8	32
4	Carboxylic acids, anhydrides, hydroxyl acids, carbonates and esters	438 ± 8	51
5	Nitrogen compounds	439 ± 7	68
6	Halogen compounds	438 ± 10	5

[a] Standard deviation of k
[b] Population size

Table 2 Comparison of experimental and calculated values of specific heat of combustion (Δh_c) for some polymers

No.	Polymer	$-\Delta h_c$ (kJ g^{-1}) Expt.[a]	Expt.[b]	Calc.[c]	Calc.[d]
1	Polyethylene	46.5	46.2	46.6	46.4
2	Polypropylene	46.5	46.7	46.6	46.4
3	Polyisobutylene	–	45.4	46.6	46.4
4	Polybutadiene	45.2	–	44.3	45.2
5	Polyisoprene	44.9	44.3	44.8	45.3
6	Polychloroprene	24.3	–	24.8	24.9
7	Poly(vinyl chloride)	18.0	–	17.6	17.1
8	Poly(vinylidene chloride)	10.5	–	9.1	8.7
9	Poly(vinylidene fluoride)	–	14.3	13.7	14.4
10	Polytetrafluoroethylene	–	5.35	4.39[e]	4.11[e]
11	Poly(methylene oxide)	16.7	–	14.6	17.5
12	Poly(2,6-dimethyl-1,4-phenylene oxide)	–	35.0	34.7	34.4
13	Poly(vinyl methyl ether)	–	30.5	30.2	31.3
14	Poly(vinyl isobutyl ether)	–	35.8	37.3	37.8
15	Polyacrylonitrile	30.6	–	31.0	31.5
16	Poly(vinyl alcohol)	25.1	–	24.9	25.4
17	Cellulose	16.7	–	16.2	17.7
18	Polystyrene	41.5	41.2	41.9	41.4
19	Poly(α-methyl styrene)	–	42.3	42.4	42.0
20	Poly(vinyl acetate)	–	22.8	22.9	23.1
21	Poly(methyl methacrylate)	–	26.3	26.3	26.4
22	Poly(isobutyl methacrylate)	–	32.2	32.4	32.3
23	Poly(ethylene terephthalate)	22.2	23.7	22.8	23.6
24	Poly[2,2-propane bis (4-pheny) carbonate]	31.0	31.1	31.1	31.3
25	Poly(hexamethylene adipamide)	31.4	–	32.0	32.4
26	Poly(*m*-phenylene isophthalamide)	28.7	–	28.6	28.6

[a] Experimental data reported in the literature
[b] Experimental data obtained in this work
[c] Computed using equation (1)
[d] Computed using equation (2)
[e] Based on the combustion products of CO_2(g) and CF_4(g)

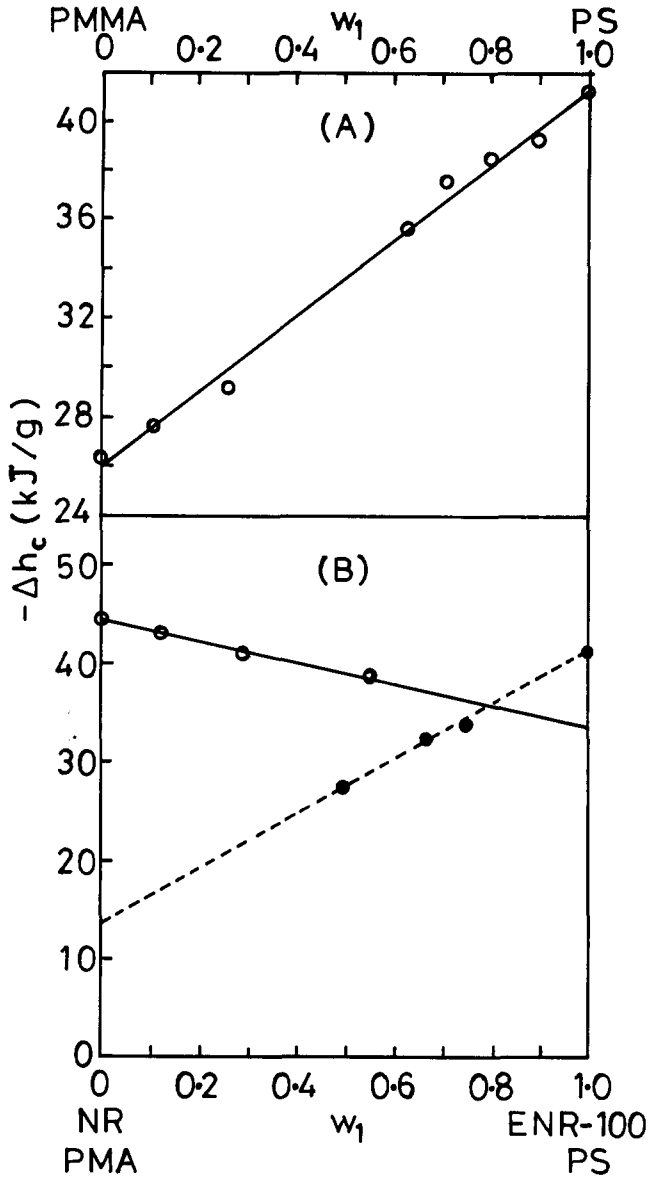

Figure 1 Linear plots of Δh_c against weight fraction of component 1 (w_1) for copolymers of components indicated in the figure: (A) S-*co*-MMA; (B) ENR (○, ——), and S-*co*-MA (●, – – –). Abbreviations: S, styrene, MMA, methyl methacrylate, NR, natural rubber, ENR, epoxidized NR, ENR-100, *cis*-poly(1,2-dimethylene-2-methyloxirane), MA, maleic anhydride, PS, polystyrene, PMMA, poly(methyl methacrylate), and PMA, poly(maleic anhydride)

Apparently, equation (1) outperforms equation (2) in the present analyses. However, the semi-empirical method (equation (2)) is more relevant to poly(methylene oxide), which has a relatively high O/C ratio making the proposed k value grossly unreliable. Hence, we recommend that the two distinct methods of interest should be applied supplementarily for estimating the Δh_c of polymers. Interestingly, the empirical expression (equation (1)) results in a constant $\Delta h_c = -46.6\ \mathrm{kJ\ g^{-1}}$ for polyolefins which have a general repeat unit $-C_lH_{2l}-$, where l is an integer >1.

The additive nature of Δh_c prompts us to propose

$$\Delta h_c = w_1 \Delta h_{c1} + w_2 \Delta h_{c2} \qquad (6)$$

for copolymers containing monomer units M_1 and M_2 with their respective weight fractions equal to w_1 and w_2. Here, Δh_{c1} and Δh_{c2} are the heats of combustion of homopolymers of monomers M_1 and M_2 respectively, and $w_1 + w_2 = 1$. Equation (6) is confirmed by *Figure 1*, which plots Δh_c against w_1 for three series of copolymers. Here, the linear relationships between Δh_c and w_1 are substantiated by the correlation coefficient $R = 0.9966$ for S-*co*-MMA, 0.9982 for S-*co*-MA and -0.9986 for ENR. By extrapolation, *Figure 1B* yields $\Delta h_c = -13.5$ and $-33.6\ \mathrm{kJ\ g^{-1}}$ for poly(maleic anhydride) and *cis*-poly(1,2-dimethylene-2-methyloxirane), respectively. The corresponding values obtained by equation (1) are -13.4 and $-33.9\ \mathrm{kJ\ g^{-1}}$. Thus these results are consistent. However, equation (2) leads to significantly higher values of Δh_c for these two hypothetical polymers, indicating its limitation for cyclic polymers.

It has been shown that Δh_c is intimately related to other important parameters associated with the burning of polymeric materials, such as oxygen index and char residue[1,6,7]. In this connection, the practical implications of equations (1) and (2) are apparent. Moreover, equation (5) may serve as an alternative for characterizing the compositions of copolymers provided that Δh_{c1} and Δh_{c2} are not too close.

ACKNOWLEDGEMENT

The authors thank the MPKSN for financial support under the research fund R&D 04-07-04-124.

REFERENCES

1 van Krevelen, D. W. and Hoftzer, P. J. 'Properties of Polymers: Their Estimation and Correlation with Chemical Structure', Elsevier-Scientific, Amsterdam, 1976, Ch. 26
2 Ng, S. C. and Chee, K. K. *Rubber Chem. Technol.* 1989, **62**, 585
3 Atkins, P. W. 'Physical Chemistry', 4th edn, Oxford University Press, Oxford, 1990
4 Weast, R. C., Astle, M. J. and Beyer, W. H. (Eds) 'CRC Handbook of Chemistry and Physics', 69th edn, The Chemical Rubber Co., Cleveland, OH, 1988–1989
5 van Krevelen, D. W. and Hoftzer, P. J. 'Properties of Polymers: Their Estimation and Correlation with Chemical Structure', Elsevier-Scientific, Amsterdam, 1976, Ch. 7, Ch. 20
6 Johnson, P. R. *J. Appl. Polym. Sci.* 1974, **18**, 491
7 van Krevelan, D. W. *Polymer* 1975, **16**, 615