

# Molar Group Contributions to Polymer Flammability

Richard N. Walters,<sup>1</sup> Richard E. Lyon<sup>2</sup>

<sup>1</sup>Galaxy Scientific Corporation, 3120 Fire Road, Egg Harbor Township, New Jersey 08234

<sup>2</sup>Fire Safety Section AAR-440, Airport and Aircraft Safety Research and Development, William J. Hughes Technical Center, Federal Aviation Administration, Atlantic City International Airport, New Jersey 08405

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**ABSTRACT:** The specific heat-release rate is the molecular-level fire response of a burning polymer. The Federal Aviation Administration obtains the specific heat-release rate of milligram samples by analyzing the oxygen consumed by the complete combustion of the pyrolysis gases during a linear heating program. Dividing the specific heat-release rate (W/g) by the rate of the temperature rise (K/s) of a sample during a test gives a material fire parameter with the units (J/g K) and significance of the heat (release) capacity. The heat-release capacity appears to be a true material property that is rooted in the chemical structure of the

polymer and is calculable from additive molar group contributions. Hundreds of polymers of known chemical compositions have been tested to date, providing over 40 different empirical molar group contributions to the heat-release capacity. Measured and calculated heat-release capacities for over 80 polymers agree to within  $\pm 15\%$ , suggesting a new capability for predicting flammability from the polymer chemical structure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 548–563, 2003

**Key words:** plastics; calculations; thermal properties

## INTRODUCTION

The additivity of molar group contributions to the physical and chemical properties of polymers is the basis of an empirical methodology for relating the chemical structure to the polymer properties.<sup>1–3</sup> The early work in this area<sup>4</sup> focused on calculating the heats of combustion from the individual atoms comprising small molecules. However, performing calculations for large (polymer) molecules based on the interactions of the individual atoms can be very difficult.<sup>2</sup> A simpler approach to correlating the polymer chemical structure to the properties is to group the atomic contributions into characteristic structural elements (e.g.,  $-\text{CH}_3$ ), determine the value of the group contribution to the property of interest parametrically, and add these group contributions according to their molar fractions in the polymer repeat unit. This method has been used to relate the chemical structures of polymers to their thermal, chemical, optical, and mechanical properties with excellent results.<sup>1–3</sup> Of particular interest in this context is the ability to predict the thermal stability parameters of polymers (pyrolysis activation energy, thermal decomposition temperature, and char/fuel fraction) from additive molar group contributions.<sup>1</sup>

A prerequisite for any structure–property correlation is the ability to identify and reproducibly measure the intrinsic property of interest. In the area of poly-

mer flammability, no single material property has been correlated with fire performance, nor does any test measure fire performance unambiguously because the burning rate, ignitability, flammability, and heat-release rate are not intrinsic properties. Rather, they are extrinsic quantities resulting from the reaction of a macroscopic polymer sample to severe thermal exposure. Because the sample size in a flammability or fire test is orders of magnitude larger than the chemical process zone,<sup>5–7</sup> heat and mass transfer dominate the fire response. Therefore, an intrinsic material property for use by scientists in designing fire-resistant polymers is not obtainable from standard fire or flammability tests.

Recently, a material fire parameter with the units and significance of the heat-release capacity<sup>5–7</sup> has been identified that appears to be a good predictor of the fire response and flammability of polymers. A quantitative laboratory pyrolysis–combustion method for directly measuring the heat-release capacity has been reported.<sup>8–10</sup> This article provides empirical molar group contributions to the heat-release capacity that allow its calculation from the polymer chemical structure. The relationship between the measured (or calculated) heat-release capacity of a polymer and its fire behavior or flammability is described.

## THEORY

The solid-state thermochemistry of flaming combustion<sup>5–7</sup> reveals a material fire parameter that has the units of the heat (release) capacity (J/g K):

Correspondence to: R. N. Walters (richard.n.walters@tc.faa.gov).

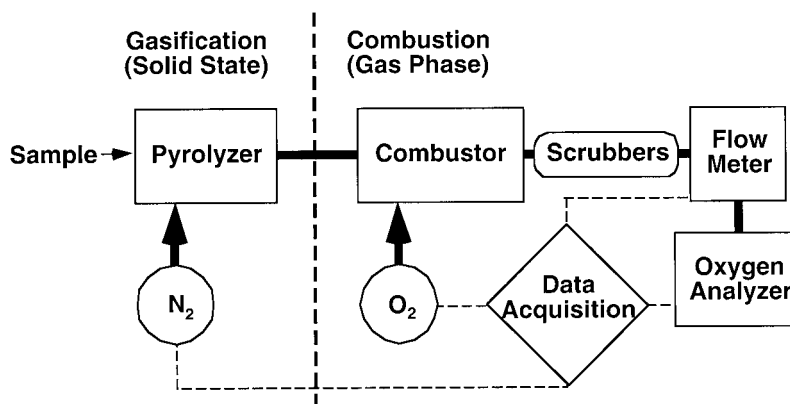


Figure 1 Schematic diagram of the pyrolysis-combustion flow calorimeter.

$$\eta_c = \frac{h_c^0(1 - \mu)E_a}{eRT_p^2} \quad (1)$$

The heat-release capacity ( $\eta_c$ ) is a combination of the thermal stability and combustion properties, each of which is known to be calculable from additive molar group contributions.<sup>1</sup> The component material properties are the heat of complete combustion of the pyrolysis gases [ $h_c^0$  (J/g)], the weight fraction of the solid residue after pyrolysis or burning [ $\mu$  (g/g)], the global activation energy for the single-step mass-loss process or pyrolysis [ $E_a$  (J/mol)], and the temperature at the peak mass-loss rate [ $T_p$  (K)] in a linear heating program at a constant rate [ $\beta$  (K/s)]. The constants in eq. (1) are the natural number ( $e$ ) and the gas constant ( $R$ ). Equation (1) shows the heat-release capacity to be a particular function of the thermal stability and combustion properties, each of which is known to be calculable from additive molar group contributions.<sup>1</sup> Consequently,  $\eta_c$  itself is a material property and should be calculable from the same (or similar) molar groups as the component properties as long as there are no interactions between the chemical structural units. Along with this assumption of group additivity, there is the postulate that for a polymer repeat unit of molar mass  $M$ , there is a molar heat-release capacity [ $\Psi$  (J/mol K)] whose functional form is eq. (1) but which has thermal stability and combustion properties written as the molar quantities  $H$ ,  $V$ ,  $E$ , and  $Y/M$  in place of  $h_c^0$ ,  $(1 - \mu)$ ,  $E_a$ , and  $T_p$ , respectively. If each chemical group  $i$  in the polymer adds to the component molar properties according to its molar fraction  $n_i$  in the repeat unit,

$$\Psi = \frac{HVE}{eR(Y/M)^2} = \frac{\left(\sum_i n_i H_i\right)\left(\sum_i n_i V_i\right)\left(\sum_i n_i E_i\right)}{eR\left(\sum_i n_i Y_i/M_i\right)^2} \quad (2)$$

where  $H_i$ ,  $V_i$ ,  $E_i$ ,  $Y_i$ , and  $M_i$  are the molar heat of combustion, molar fraction of fuel, molar activation energy, molar thermal decomposition function,<sup>1</sup> and molar mass of component  $i$ , respectively. Expanding the summations in eq. (2) and retaining only the non-interacting terms for which  $i = j = k \dots$  (i.e., neglecting terms containing products and quotients with mixed indices), we have the following:

$$\Psi = \sum_i n_i \frac{H_i V_i E_i}{eR(Y_i/M_i)^2} = \sum_i n_i \Psi_i \quad (3)$$

Equation (3) shows that there is a molar group contribution to the heat-release capacity  $\Psi_i$  that adds according to its molar fraction in the repeat unit of the polymer. If  $N_i$  and  $M_i$  are the number of moles and the molar mass, respectively, of group  $i$  in the polymer with the repeat unit molar mass  $M$

$$n_i = \frac{N_i}{\sum_i N_i} \quad \text{and} \quad M = \sum_i n_i M_i = \sum_i \frac{N_i}{\sum_i N_i} M_i$$

then the heat-release capacity on a mass basis is

$$\eta_c = \frac{\Psi}{M} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i} \quad (4)$$

Equations (2)–(4) provide the physical basis for an additive heat-release capacity function, but the values of the molar contributions of chemical groups must be derived empirically (i.e., experimentally). To this end, the heat-release capacities of more than 200 polymers with known chemical structures have been measured with the measurement technique described later, and these experimental values have been used to generate over 40 group contributions.<sup>11,12</sup>

## EXPERIMENTAL

### Materials

Polymer samples were unfilled, natural, or virgin-grade resins obtained from Aldrich (Milwaukee, WI) and Polysciences, Inc. (Warrington, PA), and research universities or directly from the manufacturers. The oxygen and nitrogen gases used for calibration and testing, obtained from Matheson Gas Products (Bridgeport, NJ), were dry and greater than 99.99% pure.

### Methods

A pyrolysis-combustion flow calorimeter<sup>8-10</sup> was used for all experiments (see Fig. 1). In this device, a pyrolysis probe (Pyroprobe 2000, CDS Analytical, Oxford, PA) is used to thermally decompose milligram-size samples in flowing nitrogen at a controlled heating rate. The samples are heated at a constant rate (typically 4.3 K/s) from a starting temperature that is several degrees below the onset degradation temperature of the polymer to a maximum temperature of 1200 K (930°C). The 930°C final temperature ensures the complete thermal degradation of organic polymers so that the total capacity for heat release is measured during the test and eq. (1) applies. Flowing nitrogen sweeps the volatile decomposition products from the constant-temperature (heated) pyrolysis chamber, and oxygen is added to obtain a nominal composition of 4:1 N<sub>2</sub>/O<sub>2</sub> before a 900°C furnace is entered for 60 s to effect complete nonflaming combustion. The combustion products (carbon dioxide, water, and possibly acid gases) are then removed from the gas stream with

Ascarite and Drierite scrubbers. The mass flow rate and oxygen consumption of the scrubbed combustion stream are measured with a mass flowmeter and zirconia oxygen analyzer (Panametrics model 350, Waltham, MA), respectively.

The specific heat-release rate ( $\dot{Q}_c$ ) in the pyrolysis-combustion flow calorimeter is determined from oxygen consumption measurements with the assumption that 13.1 kJ of heat is released per gram of diatomic oxygen consumed by combustion.<sup>13-16</sup> Because  $\dot{Q}_c$  is equal to the fractional mass-loss rate multiplied by the heat of complete combustion of the pyrolysis products,

$$\dot{Q}_c(t) = \frac{E}{m_0} \Delta \dot{O}_2(t) = -\frac{h_{c,v}^0(t)}{m_0} \frac{dm(t)}{dt} \quad (5)$$

where  $E = 13.1 \pm 0.6$  kJ/g of O<sub>2</sub>,  $\Delta \dot{O}_2$  is the instantaneous mass consumption rate of oxygen,  $m_0$  is the initial sample mass,  $h_{c,v}^0$  is the instantaneous heat of complete combustion of the volatile pyrolysis products, and  $dm/dt$  is the instantaneous mass-loss (fuel-generation) rate of the sample during the test. The advantage of synchronized oxygen consumption calorimetry for determining the specific heat-release rate is the ease and speed of the method in comparison with the simultaneous measurement of the mass-loss rate of the solid and the heat of combustion of the pyrolysis gases.<sup>17</sup> At  $T_p$ , the specific heat-release rate has an analytical form:<sup>5-7,18</sup>

$$\dot{Q}_c^{max} = \frac{E}{m_0} \Delta \dot{O}_2^{max} = \frac{-h_{c,v}^0(t)}{m_0} \left[ \frac{dm(t)}{dt} \right]_{max} = h_c^0 \frac{\beta(1-\mu)E_a}{eRT_p^2} \quad (6)$$

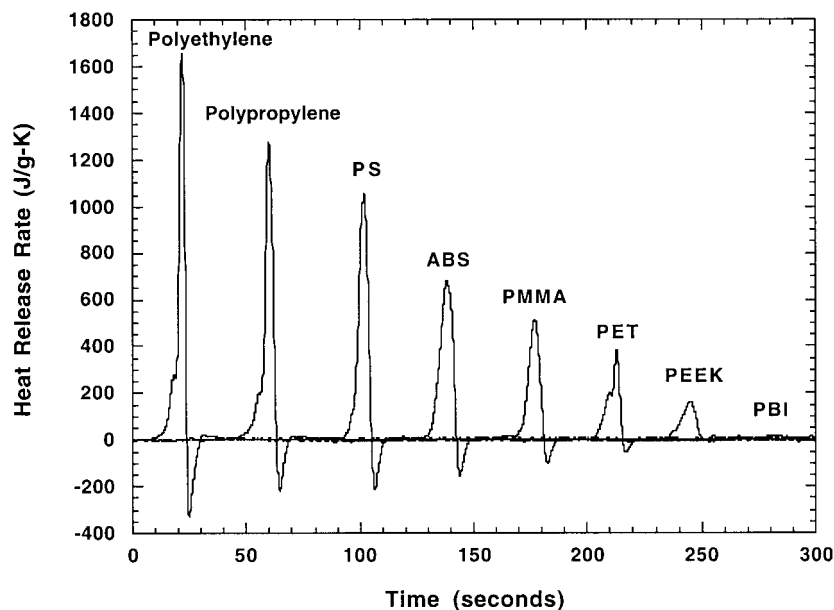


Figure 2 Specific heat-release rates for several polymers measured with the microscale calorimeter.

TABLE I  
Polymer Structure and Values Derived from Pyrolysis-Combustion Flow Calorimetry

Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Polyethylene (PE)	LDPE Polysciences, Inc.	[9002-88-4]	C <sub>2</sub> H <sub>4</sub>	$\text{---CH}_2\text{-CH}_2\text{---}$	1676	41.6	0	28.06
Polyoxymethylene (POM)	Polysciences	[9002-81-7]	CH <sub>2</sub> O	$\text{---CH}_2\text{-O---}$	169	14	0	30.03
Polypropylene (PP)	Polysciences	[25085-53-4]	C <sub>3</sub> H <sub>6</sub>	$\text{---CH}_2\text{-CH---}$   CH <sub>3</sub>	1571	41.4	0	42.08
Poly(vinyl alcohol) ( $\geq 99\%$ ; PVOH)	Aldrich Chemical Co., Inc.	[9002-89-5]	C <sub>2</sub> H <sub>4</sub> O	$\text{---CH}_2\text{-CH---}$   OH	533	21.6	3.3	44.03
Poly(ethylene oxide)	Polysciences	[25322-68-3]	C <sub>2</sub> H <sub>4</sub> O	$\text{---CH}_2\text{-CH}_2\text{-O---}$	652	21.6	1.7	44.05
Polyisobutylene	Aldrich	[9003-27-1]	C <sub>4</sub> H <sub>8</sub>	$\text{---CH}_2\text{-C---}$   CH <sub>3</sub>   CH <sub>3</sub>	1002	44.4	0	56.11
Poly(vinyl chloride)	PVC	[9002-86-2]	C <sub>2</sub> H <sub>3</sub> Cl	$\text{---CH}_2\text{-CH---}$   Cl	138	11.3	15.3	62.48
Poly(vinylidene fluoride)	PVDF (MW = 120,000), Polysciences	[24937-79-9]	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	$\text{---CH}_2\text{-C---}$   F   F	311	9.7	7	64.02
Polyacrylamide	Polysciences	[9003-05-8]	C <sub>3</sub> H <sub>5</sub> NO	$\text{O=C---}$   NH <sub>2</sub>   $\text{---CH}_2\text{-CH---}$	104	13.3	8.3	71.08
Poly(acrylic acid)	Polysciences	[9003-01-4]	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	$\text{---CH}_2\text{-CH---}$   C=O   OH	165	12.5	6.1	72.06
Poly(vinyl acetate) (PVAc)	Polysciences	[9003-20-7]	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	$\text{---CH}_2\text{-CH---}$   C=O   O   C   O   CH <sub>3</sub>	313	19.2	1.2	86.09
Poly(methacrylic acid)	Polysciences (MW = 100,000)	[25087-26-7]	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	$\text{---CH}_2\text{-C---}$   CH <sub>3</sub>   C=O   OH	464	18.4	0.5	86.09
Polychloroprene	Neoprene, Polysciences	[9010-98-4]	C <sub>4</sub> H <sub>5</sub> Cl	$\text{---CH}_2\text{-C=C---}$   Cl   H	188	16.1	12.9	88.54

TABLE I Continued

Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Poly(tetrafluoroethylene) (PTFE)	Aldrich	[9002-84-0]	C <sub>2</sub> F <sub>4</sub>		35	3.7	0	100.02
Poly(methyl methacrylate) (PMMA)	Aldrich	[9011-14-7]	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		514	24.3	0	100.12
Poly(methyl methacrylate) (PMMA)	Polysciences (MW = 75,000)	[9011-14-7]	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		461	23.2	0	100.12
Poly(ethyl acrylate)	Polysciences (MW = 70,000)	[9003-32-1]	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		323	22.6	0.3	100.12
Polymethacrylamide	Polysciences	[25014-12-4]	C <sub>4</sub> H <sub>7</sub> NO <sub>2</sub>		103	18.7	4.5	101.1
Polystyrene (PS)	Polysciences	[9003-53-6]	C <sub>8</sub> H <sub>8</sub>		927	38.8	0	104.15
Isotactic polystyrene	Questra	[25086-18-4]	C <sub>8</sub> H <sub>8</sub>		880	39.9	0	104.15
Poly(2-vinyl pyridine)	Polysciences (MW = 200,000-400,000)	[25014-15-7]	C <sub>7</sub> H <sub>7</sub> N		612	34.7	0	105.14
Poly(4-vinyl pyridine)	Polysciences (MW = 300,000)	[25232-41-1]	C <sub>7</sub> H <sub>7</sub> N		568	31.7	0	105.14

TABLE I Continued

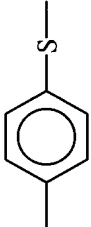
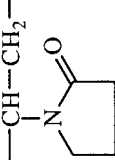
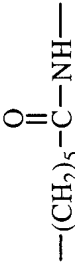
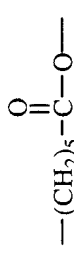
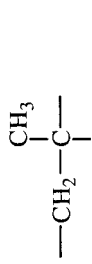
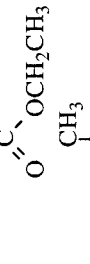
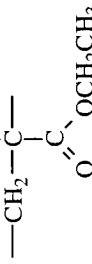
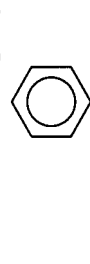
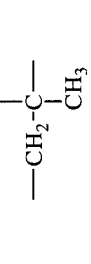
Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Poly(1,4-phenylene sulfide) (PPS)	Aldrich	[9016-75-5]	C <sub>6</sub> H <sub>4</sub> S		165	17.1	41.6	108.16
Poly( <i>n</i> -vinyl pyrrolidone)	Polysciences	[9003-39-8]	C <sub>6</sub> H <sub>9</sub> NO		332	25.1	0	111.14
Polycaprolactam	Nylon 6	[25038-54-4]	C <sub>6</sub> H <sub>11</sub> NO		487	28.7	0	113.16
Polycaprolactone	Polysciences	[24980-41-4]	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>		526	24.4	0	114.14
Poly(ethyl methacrylate)	Polysciences (MW = 250,000)	[9003-42-3]	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>		470	26.4	0	114.14
Poly(ethyl methacrylate)	Aldrich (MW = 850,000)	[9003-42-3]	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>		380	26.8	0	114.14
Poly(α-methyl styrene)	Aldrich	[52014-31-7]	C <sub>9</sub> H <sub>10</sub>		730	35.5	0	118.18
Poly(2,6-dimethyl 1,4-phenyleneoxide) (PPO)	Noryl 0.4 IV virgin, General Electric	[25134-01-4]	C <sub>8</sub> H <sub>8</sub> O		409	20	25.5	120.15
Poly(4-vinyl phenol)	Polysciences (MW = 22,000)	[24979-70-2]	C <sub>8</sub> H <sub>8</sub> O		261	27.6	2.8	120.15

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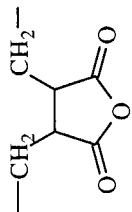
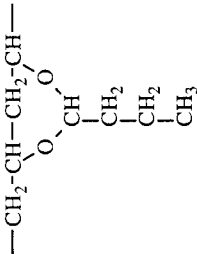
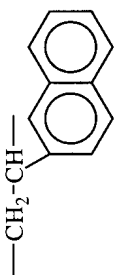
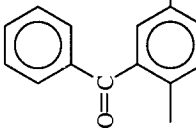
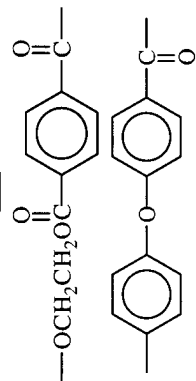
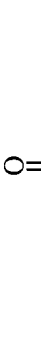

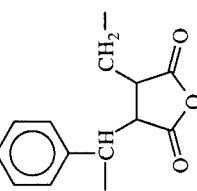
Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Poly(ethylene maleic anhydride)	Polysciences	[9002-26-2]	$C_6H_6O_3$		138	12.1	2.8	126.11
Poly(vinyl butyral)	Polysciences (MW = 100,000-150,000)	[63148-65-2]	$C_8H_{14}O_2$		806	26.9	0.1	142.1
Poly(2-vinyl naphthalene)	Aldrich (MW = 175,000)	[28406-56-6]	$C_{12}H_{10}$		834	39	0	154.21
Poly(benzoyl 1,4-phenylene)	POLYX-1000, MAXDEM, Inc.	[NA]	$C_{13}H_8O$		41	10.9	65.2	180.21
Poly(ethylene terephthalate) (PET)	Polysciences	[25038-59-9]	$C_{10}H_8O_4$		332	15.3	5.1	192.17
Poly(ether ketone) (PEK)	P22 (virgin), Victrex USA	[27380-27-4]	$C_{13}H_8O_2$		124	10.8	52.9	196.2
Poly(lauro lactam)	Nylon 12, Polysciences	[25030-74-8]	$C_{12}H_{23}O$		743	33.2	0	197.32
Poly(styrene maleic anhydride)	Polysciences	[9011-13-6]	$C_{12}H_{10}O_3$		279	23.3	2.2	202.21

TABLE I Continued

Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Poly(acrylonitrile butadiene styrene) (ABS)	ABS, Polysciences	[9003-56-9]	C <sub>15</sub> H <sub>17</sub> N		669	36.6	0	211.31
Poly(1,4-butanediol terephthalate) (PBT)	Polysciences	[26062-94-2]	C <sub>12</sub> H <sub>12</sub> O <sub>4</sub>		474	20.3	1.5	220.22
Poly(hexamethylene adipamide)	Nylon 6/6, Polysciences	[32131-17-2]	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub> N <sub>2</sub>		615	27.4	0	226.32
Polyazomethine	UMASS	[NA]	C <sub>15</sub> H <sub>9</sub> N <sub>3</sub>		36	8.7	77.8	231.26
Poly(1,4-phenylene ether sulfone) (PES)	BASF Ultrason E1010/ Natural BASF	[25667-42-9]	C <sub>12</sub> H <sub>8</sub> O <sub>3</sub> S		115	11.2	29.3	232.26
Poly(p-phenylene benzobisoxazole) (PBO)	PBO, Dow Chemical Co.	[852-36-8]	C <sub>14</sub> H <sub>6</sub> O <sub>2</sub> N <sub>2</sub>		42	5.4	69.5	234.21
Poly(p-phenylene terephthalamide)	Kevlar, Dupont	[308069-56-9]	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub>		302	14.8	36.1	238.25
Poly(m-phenylene isophthalamide)	Nomex, Dupont	[24938-60-1]	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub>		52	11.7	48.4	238.25
Poly(ethylene naphthylate) (PEN)	Eastman Chemical Co.	[24968-11-4]	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>		309	16.8	18.2	242.23
Dicyclopentadienyl bisphenol cyanate ester	XU-71787, Dow Chemical	[1355-71-0]	C <sub>17</sub> H <sub>17</sub> NO		493	20.1	27.1	251.32
Polycarbonate of bisphenol A (PC)	Polysciences (MW = 32,000-36,000)	[24936-68-3]	C <sub>16</sub> H <sub>14</sub> O <sub>3</sub>		359	16.3	21.7	254.28



TABLE I Continued

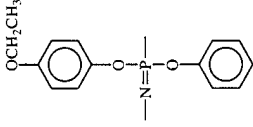
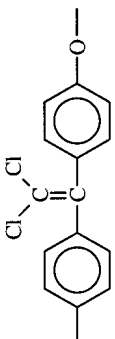
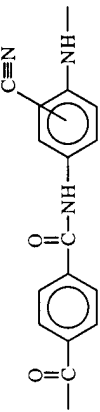
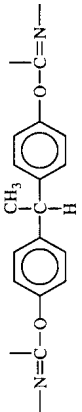
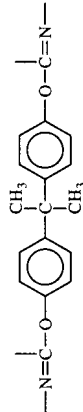
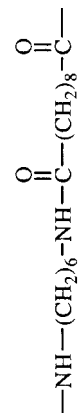
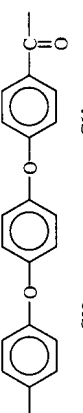
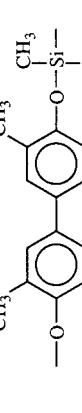
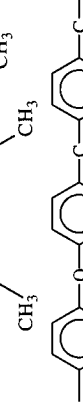
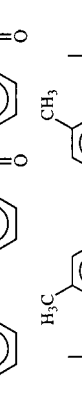
Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Polyphosphazene	Eypel-A, Penn State	[NA]	$C_{14}H_{14}PNO_3$		204	21.9	20	259.24
Poly(dichloroethyl diphenyl ether)	Rice University (MW = 9350)	[NA]	$C_{14}H_8OCl_2$		16	5.2	57.1	263.12
Cyano-substituted Kevlar	UMASS	[NA]	$C_{15}H_9N_3O_2$		54	9.1	58.3	263.26
Bisphenol E polycyanurate	AroCy L-10, Ciba Specialty Chemicals	[47073-92-7]	$C_{16}H_{12}O_2N_2$		316	14.7	41.9	264.28
Bisphenol A polycyanurate	AroCy B-10, Ciba Specialty Chemicals	[1156-51-0]	$C_{17}H_{14}O_2N_2$		283	17.6	36.3	278.31
Poly(hexamethylene sebacamide)	Nylon 6/10, Polysciences	[9008-66-6]	$C_{16}H_{30}O_2N_2$		878	35.7	0	282.43
Poly(ether ether ketone) (PEEK)	450F, Victrex USA	[29658-26-2]	$C_{19}H_{12}O_3$		155	12.4	46.5	288.3
Poly(siloxytetraalkyl biphenylene oxide) (PSA)	General Electric	[NA]	$C_{18}H_{18}SiO_2$		119	15.7	60.1	294.42
Poly(ether ketone ketone) (PEKK)	G040 (virgin flake), Dupont	[74970-25-5]	$C_{30}H_{12}O_3$		96	8.7	60.7	300.31
Tetramethyl bisphenol F polycyanurate	AroCy M-10, Ciba Specialty Chemical	[101657-77-6]	$C_{19}H_{18}O_2N_2$		280	17.4	35.4	306.36

TABLE I Continued

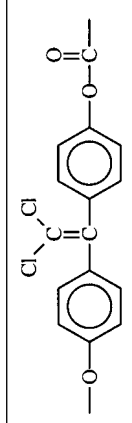
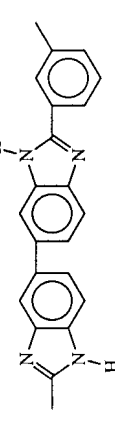
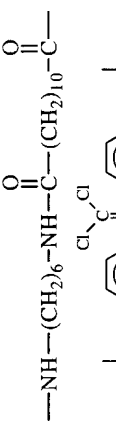
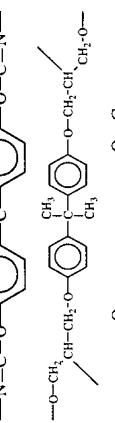
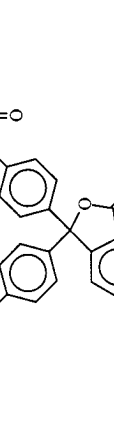
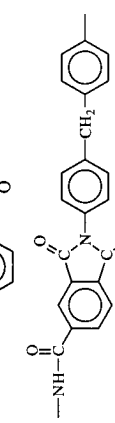
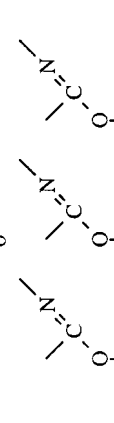
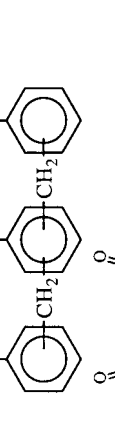
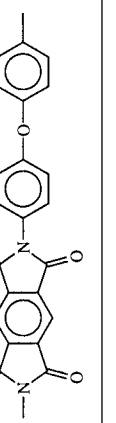
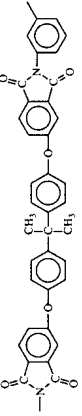
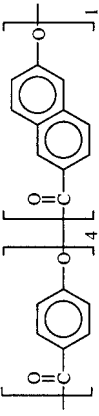
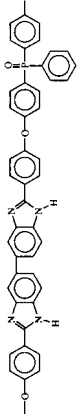
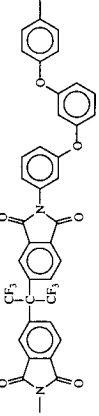
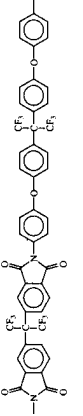
Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Bisphenol C polycarbonate	BPCPC, General Electric	[NA]	$C_{15}H_{18}O_3Cl_2$		29	3.0	50.1	307.13
Polybenzimidazole (PBI)	CELAZOLE PBI, Hoechst Celanese	[25928-81-8]	$C_{20}H_{12}N_4$		36	8.6	67.5	308.34
Poly(hexamethylene dodecane diamide)	Nylon 6/12, Polysciences	[26098-55-5]	$C_{18}H_{34}N_2O_2$		707	30.8	0	310.48
Bisphenol C, polycyanurate	BPCCE, Ciba Specialty Chemicals	[NA]	$C_{16}H_8O_2Cl_2$		24	4.2	53.3	331.16
Bisphenol A epoxy, catalytic cure phenoxy A	DER-332, Dow Chemical	[001675-54-3]	$C_{21}H_{24}O_4$		657	26.0	3.9	340.42
Phenolphthalein polycarbonate	Dow Chemical	[NA]	$C_{21}H_{12}O_5$		28	8	49.8	344.32
Poly(amide imide) (PAI)	TORLON 4203L, Amoco	[42955-03-3]	$C_{15}H_{18}O_3N_2$		33	7.1	53.6	354.36
Novolac polycyanurate	Primaset PT-30, Allied Signal XU-371, Ciba	[173452-35-2] [30944-92-4]	$C_{23}H_{15}O_3N_3$		122	9.9	51.9	381.39
Polyimide (PI)	Aldrich	[26023-21-2]	$C_{22}H_{10}O_5N_2$		25	6.6	51.9	382.33

TABLE I Continued

Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Hexafluorobisphenol A polycyanurate	AroCy F-10, Ciba Specialty Chemicals	[32728-27-1]	$C_{17}H_8O_2N_2F_6$		32	2.3	55.2	386.25
Bisphenol C epoxy	BPCE	[NA]	$C_{20}H_{18}O_4Cl_2$		506	10	36	393.26
Bisphenol M polycyanurate	AroCy XU-366, Ciba Specialty Chemicals	[127667-44-1]	$C_{26}H_{23}O_2N_2$		239	22.5	26.4	396.49
Poly(phenyl sulfone)	Radel R5200, Amoco	[25839-81-0]	$C_{24}H_{16}SO_4$		153	11.3	38.4	400.45
Bisphenol C polyarylate	BPCPA, UMASS	[NA]	$C_{22}H_{12}O_4Cl_2$		21	7.6	42.7	411.02
Biphenol phthalonitrile	Navy	[NA]	$C_{28}H_{14}N_4O_2$		15	3.5	78.8	438.44
Polysulfone of bisphenol A PSF	Udel, Amoco	[25135-57-7]	$C_{27}H_{22}O_4S$		345	19.4	28.1	442.53
LaRC-1A	NASA Langley	[105030-42-0]	$C_{28}H_{14}N_2O_6$		38	6.7	57	474.43
Epoxy Novolac, catalytic cure phenoxy N	DEN-438, Dow Chemical	[028064-14-4]	$C_{10}H_{11}O$		246	18.9	15.9	474.55
Bisphenol A phthalonitrile	U.S. Navy	[NA]	$C_{31}H_{20}N_4O_2$		40	5.9	73.6	480.52
Technora	Teijin	[NA]	$C_{34}H_{24}N_4O_5$		131	15.3	41.8	568.59
Bisphenol A6F phthalonitrile	U.S. Navy	[NA]	$C_{31}H_{14}N_4O_2F_6$		9	2.8	63.8	588.46

TABLE I Continued

Material (abbreviated name)	Trade name, manufacturer/supplier	CAS number	Repeat unit composition	Repeat unit structure	Heat release capacity (J/g K)	Total heat release (kJ/g)	Char (%)	MW (g/mol)
Poly(ether imide) (PEI)	Uitem 1000, General Electric	[61128-46-9]	C <sub>37</sub> H <sub>23</sub> O <sub>6</sub> N <sub>2</sub>		121	11.8	49.2	592.61
Polyester of hydroxybenzoic and hydroxynaphthoic acids	Vectra C LCP (virgin/unfilled), Hoechst Celanese	[70679-92-4]	C <sub>39</sub> H <sub>20</sub> O <sub>10</sub>		164	11.1	40.6	650.6
LaRC-TOR	NASA Langley	[191985-77-0]	C <sub>44</sub> H <sub>29</sub> N <sub>4</sub> O <sub>3</sub> P		135	11.7	63	692.71
LaRC-CP2	NASA Langley	[79062-55-8]	C <sub>37</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub>		14	3.4	57	700.55
LaRC-CP1	NASA Langley	[87186-94-5]	C <sub>46</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> F <sub>12</sub>		13	2.9	52	926.66

NA = not applicable; MW = molecular weight.

The rate-independent heat-release capacity is obtained from eq. (6) by the division of the maximum specific heat-release rate by the constant sample heating rate [ $\beta$  (K/s)]:

$$\eta_c \equiv \frac{\dot{Q}_c^{max}}{\beta} = \frac{E}{\beta m_0} \Delta \dot{Q}_2^{max} = \frac{h_c^0(1 - \mu)E_a}{eRT_p^2} \quad (7)$$

The quantities measured in the test are the initial sample mass and  $\dot{Q}_c$  (W/g). The time integration of the specific heat-release rate gives the total heat released by the complete combustion of the pyrolysis gases per unit of the initial sample mass [ $h_c^0$  (J/g)].  $\eta_c$  (J/g K) is calculated from the peak specific heat-release rate and the linear heating rate of the sample according to eq. (7). Weighing the sample after the test allows for the calculation of  $\mu$  (g/g) and the average heat of complete combustion per unit mass of volatiles.

## RESULTS

Pyrolysis-combustion flow calorimeter data for the specific heat-release rates of polyethylene (PE), polypropylene (PP), polystyrene (PS), an acrylonitrile-butadiene-styrene terpolymer (ABS), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), poly(ether ether ketone) (PEEK), and polybenzimidazole (PBI) are shown in Figure 2, having been horizontally shifted for clarity. Dividing the maximum specific heat-release rate (W/g) measured during the test (peak height in Fig. 2) by the constant sample heating rate ( $\beta = 4.3$  K/s in these tests) gives the heat-release capacity of the polymer (J/g K) for materials that thermally decompose in a single step. Materials exhibiting multiple heat-release peaks are beyond the scope of this report and will be addressed in the future.

The measured heat-release capacities for more than 100 polymers with known chemical structures are shown in Table I. These data have been used to generate the group contributions shown in Table II. The molar group contributions were obtained by  $\Psi_i$  being treated as adjustable parameters in the linear system of equations for polymers with known chemical structures and measured  $\eta_c$  values. The optimization calculation continued until the sum of the squares of the relative error between the measured  $\eta_c$  value and the value calculated from group contributions was a minimum. The calculation converged rapidly to the unique  $\Psi_i$  values listed in Table II, which were independent of initial estimates.

Figure 3 is a plot of the calculated and measured heat-release capacities for over 80 polymers for which optimized  $\Psi_i$  values were determined. The correlation coefficient between the measured and predicted heat-release capacities is  $r = 0.96$ , and the average relative error is  $\pm 15\%$ .

TABLE II  
Structural Groups and Their Molar Contribution to the Heat Release Capacity

Structural group	Contribution (kJ/mol K)	Structural group	Contribution (kJ/mol K)	Structural group	Contribution (kJ/mol K)
	118 <sup>a</sup>	—H	8.1	—OH	—19.8
	77.0		7.6	—Br	—22.0
	69.5	—CH <sub>2</sub> —O—	4.18		—22.0
	30.6		1.8		—23.2 <sup>a</sup>
	29.5		0.1		—25.5
	28.8		—8.8	—Cl	—34.7
	28.3	—S—	—10.9 <sup>a</sup>		—36.4 <sup>a</sup>
	26.6	—O—	—11.6		Pendant: —39.5 Backbone: —13.7
—CH <sub>3</sub>	22.5		—13.8		—43.0 <sup>a</sup>
	19.0	—NH <sub>2</sub>	—13.9 <sup>a</sup>		—49.0
	18.7	—CF <sub>3</sub>	—14.8		—53.5 <sup>a</sup>
	16.7	—C≡N	—17.6		—66.7
	15.1		—18.9 <sup>a</sup>		—74.5
	9.7		—19.2		—76.7

<sup>a</sup> Molar group contribution derived from a single polymer.

### Calculation of the Heat-Release Capacity

The following example illustrates the calculation of the heat-release capacity from molar group contribu-

tions for a diglycidyl ether of bisphenol A (BPA epoxy) cured by anionic ring-opening polymerization. This polymer has the following repeat unit chemical structure:

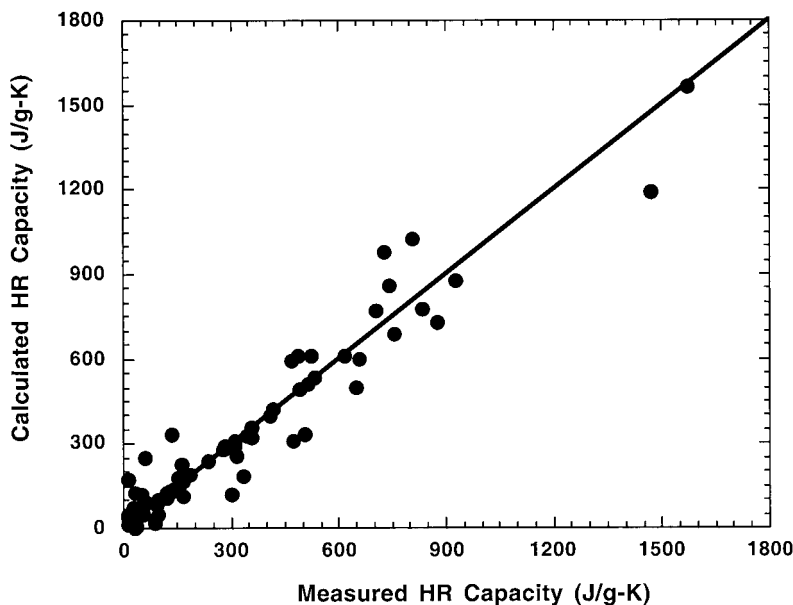
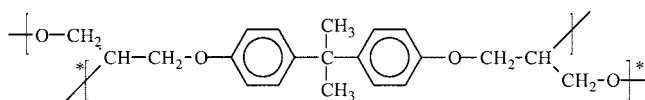


Figure 3 Calculated and measured heat-release capacities for 80 pure polymers.



The polymer repeat unit consists of six basic chemical groups, and the heat-release capacity is calculated from the associated  $N_i$ ,  $M_i$ , and  $\Psi_i$  values for these groups, which are listed in Table III.

The molar heat-release capacity is obtained by the summing of the group contributions according to their molar fraction in the repeat unit and division by the molar mass of the repeat unit to give the heat-release capacity on a mass basis (J/g K).

$$\eta_c = \frac{\Psi}{M} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i} = \frac{204.5 \text{ kJ/mol K}}{340 \text{ g/mol}} = 601 \text{ J/g K}$$

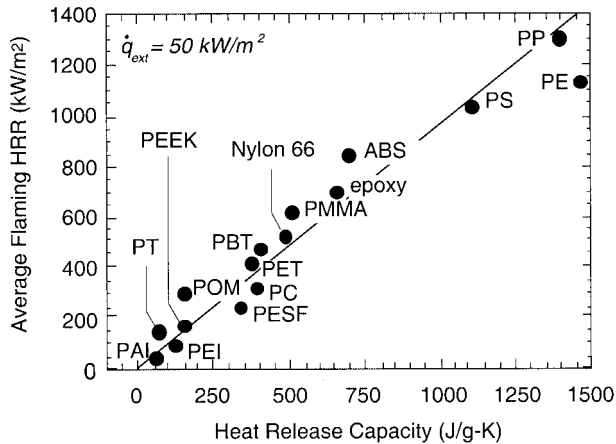
The predicted value of 601 J/g K compares reasonably well with the measured value of 657 J/g K for this polymer.

### Heat-Release Capacity and Fire Hazard

The primary indicator of the fire hazard of a material is the heat-release rate in forced flaming combustion.<sup>19</sup> Figure 4 is a plot of the average flaming heat-release rate of samples (10 cm × 10 cm × 0.64 cm, ≈80 g) of pure polymer measured in a fire calorimeter at an external heat flux  $\dot{q}_{\text{ext}} = 50 \text{ kW/m}^2$  according to standard methods<sup>20–22</sup> versus the measured heat-release capacity. Proportionality is observed between the average flaming heat-release rate of kilogram-size samples and the heat-release capacity of milligram-size samples of the same polymer with a slope of 1.0 (kg/s)/m<sup>2</sup>/K, which is in general agreement with predictions for steady burning at this external heat flux.<sup>5–7</sup>

TABLE III  
Group Contributions Used in the Calculation of the Heat Release Capacity of Bisphenol A Epoxy

Chemical group ( <i>i</i> )	<i>N</i>	<i>M<sub>i</sub></i> (g/mol)	$\Psi$ (kJ/mol K)	<i>N<sub>i</sub>M<sub>i</sub></i> (g/mol)	<i>N<sub>i</sub>Ψ</i> (kJ/mol K)
	1	12	28.3	12	28.3
	2	13	26.6	26	53.2
	4	14	16.7	56	66.8
	2	15	22.5	30	45.0
	2	76	28.8	152	57.6
	4	16	-11.6	64	-46.4
Total				340	204.5



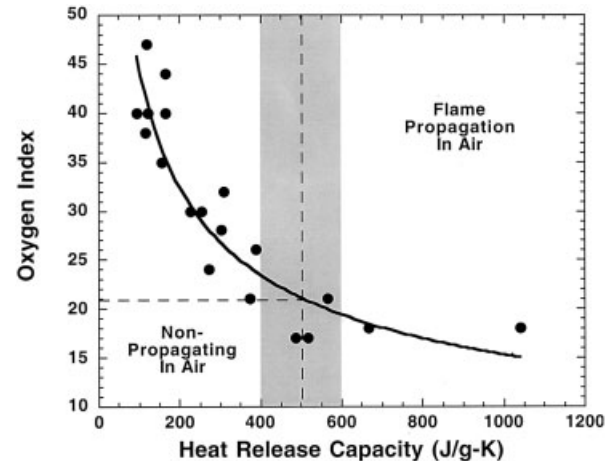
**Figure 4** Average flaming heat-release rate (HRR) versus the heat-release capacity for several polymers.

Consequently,  $\eta_c$  is a reasonable predictor of the fire hazard with an empirical correlation (e.g., Fig. 4) or physically based calculations.<sup>5-7</sup>

### Heat-Release Capacity and Flammability

*Flammability* is taken here to mean the tendency of a thin sample of a material ignited by a small flame to continue burning in the absence of external radiant heat after the removal of the ignition source. Self-extinguishing behavior in these tests implies a certain resistance to ignition and/or flame propagation, and standard methods have been developed to measure this characteristic. These flame tests are widely used to rank the burning propensity of combustible solids, but they do not yield any material property information. Two common flammability test methods are the Underwriters Laboratories UL 94 test for upward vertical (V) and horizontal burning (HB)<sup>23</sup> and the critical oxygen concentration for flame extinguishment or limiting oxygen index (LOI) in downward burning.<sup>24</sup>

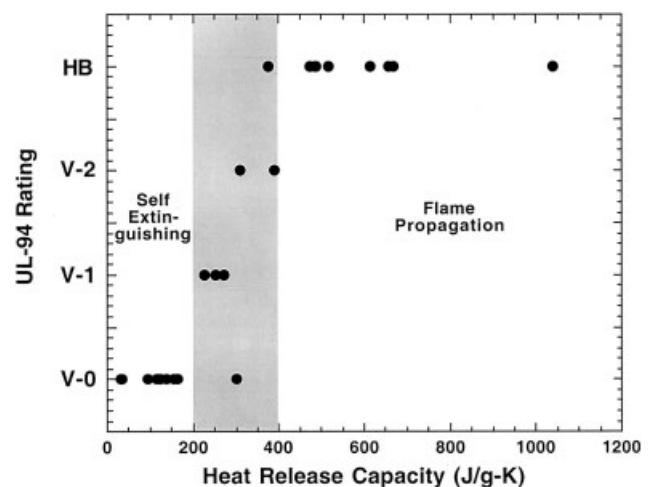
In flammability tests, the flame heat flux at the sample tip must provide all of the heat energy to continue the burning process after the removal of the Bunsen burner (UL 94) or methane diffusion flame (LOI) used to cause ignition. If the heat flux from the sample surface flame is constant (UL 94 test) or increases in a known way with oxygen concentration (LOI), the criterion for self-extinguishing behavior in these tests can be formulated in terms of a critical heat-release capacity if it is assumed that a minimum heat-release rate of about  $100 \text{ kW/m}^2$ <sup>25</sup> is needed to sustain flaming combustion. Such an analysis for the UL 94 test<sup>6</sup> indicates that polymers with  $\eta_c$  values lower than about  $300 \text{ J/g K}$  should self-extinguish because they do not release heat at a high enough rate to overcome heat losses and so the flame cannot propagate. Therefore, for pure polymers with  $\eta_c \leq 300 \text{ J/g K}$ , self-extinguishing behavior in the UL 94 vertical



**Figure 6** LOI versus the measured heat-release capacity.

test (a V rating) is expected. Figure 5 contains UL 94 data<sup>26</sup> and measured heat-release capacities for several pure polymers. A transition from a self-propagating (HB) flame behavior to a self-extinguishing (V-0) flame behavior occurs in the vicinity of  $\eta_c = 300 \text{ J/g K}$ , as predicted from the critical heat-release-rate criterion.

The criterion for self-extinguishing behavior in the LOI test must take into account the fact that an increase in the oxygen concentration of the flowing gas stream in the test chamber increases the temperature (radiant heat flux) of the sample diffusion flame and, therefore, the amount of thermal energy deposited in the polymer. Because the heat-release rate of the sample increases with the flame heat flux, which in turn increases with oxygen concentration, an inverse relationship between  $\eta_c$  and the limiting oxygen concentration is expected and observed, as shown in the LOI data<sup>1,27,28</sup> plotted versus  $\eta_c$  in Figure 6.



**Figure 5** UL-94 ratings versus the measured heat-release capacities of pure polymers.

Comparing Figures 5 and 6 shows that self-extinguishing behavior in the UL 94 vertical test occurs at a lower heat-release capacity ( $\eta_c = 300 \pm 100$  J/g K) than in the LOI test ( $\eta_c = 550 \pm 100$  J/g K) under ambient conditions (298 K, LOI = 21% O<sub>2</sub>). The reason for this is that the upward burning UL 94 test is more severe than the downward burning LOI test because of convective and radiative preheating of the sample by its flame and so requires more material fire resistance (lower heat-release capacity) for self-extinguishing behavior under ambient conditions.

### CONCLUSIONS

The heat-release capacity is a physically based material property that is a good predictor of the fire behavior and flammability of pure polymers. The heat-release capacity is simply calculated for pure polymers from their chemical structures with additive molar group contributions that have been determined empirically with a high level of confidence ( $\pm 15\%$ ). The proposed methodology for predicting the fire behavior and flammability of polymers from their chemical structures allows for the molecular-level design of ultra-fire-resistant polymers without the expense of synthesizing and testing new materials.

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