Determination of the Heats of Gasification of Polymers Using Differential Scanning Calorimetry

November 2007

DOT/FAA/AR-TN07/62

U.S. Department of Transportation

Federal Aviation Administration

NOTICE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
DOT/FAA/AR-TN07/62		

4. Title and Subtitle	5. Report Date
DETERMINATION OF THE HEATS OF GASIFICATION OF POLYMERS USING DIFFERENTIAL SCANNING CALORIMETRY	November 2007
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
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	11. Contract or Grant No.

12. Sponsoring Agency Name and Address	13. Type of Report and Period Covered
U.S. Department of Transportation Federal Aviation Administration Air Traffic Organization Operations Planning Office of Aviation Research and Development Washington, DC 20591	Technical Note
	14. Sponsoring Agency Code ANM-115

15. Supplementary Notes

16. Abstract

The amount of heat that is required to gasify unit mass of material is one of the key properties that define its ignition resistance and fire response. Knowledge of this property is necessary to assess a material's fire hazard in a particular fire scenario. Nevertheless, even for the most common polymers, the values of this property are not well established. Here, a methodology is presented for determining the heat of gasification using differential scanning calorimetry and applied to a set of ten common plastics and engineering polymers.

17. Key Words	18. Distribution Statement
Gasification, Pyrolysis, Polymer, Calorimetry	This document is available to the U.S. public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	20	

Form DOT F 1700.7 (8-72)   Reproduction of completed page authorized

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS AND ACRONYMS

H_g	Heat of gasification
C_{mat}	Heat capacity of material
C_{prod}	Heat capacity of decomposition products
H_{melt}	Heat of melting
T_{melt}	Temperature of melting
H_{dec}	Heat of decomposition
T_{dec}	Temperature of decomposition
HF_{DSC}	Heat flow measured in DSC apparatus
HF_{samp}	Contribution to HF_{DSC} associated with a sample of material
J/g	Joules per gram
μ	Char yield
T_{char}	Temperature at which μ is measured
L_g	Char-weight-adjusted integral heat of gasification
T_{init}	Initial temperature
T_{final}	Final temperature
T_{trans}	Slope change point
DSC	Differential scanning calorimetry

EXECUTIVE SUMMARY

The amount of heat that is required to gasify unit mass of material is one of the key properties that define its ignition resistance and fire response. Knowledge of this property is necessary to assess a material's fire hazard in a particular fire scenario. Nevertheless, even for the most common polymers the values of this property are not well established. Here, a methodology is presented for determining the heat of gasification using differential scanning calorimetry and applied to a set of ten common plastics and engineering polymers.

INTRODUCTION

The heat of gasification (H_g) is a thermodynamic quantity that is equal to the amount of energy required to gasify unit mass of material at a constant pressure. Hereafter, it is assumed that the only pressure of interest is atmospheric pressure (101,325 Pascals). H_g depends on the initial temperature of material (T_{init}) and final temperature of its gasification products (T_{final}). H_g also depends on the composition of the products, which may potentially depend on the temperature history. Unfortunately, even for the most common polymers, the exact composition of the gasification products is usually unknown and very difficult to measure. Therefore, as a first order approximation, it is assumed that the composition is not affected by the rate at which material is heated.

The heat of gasification can be presented as a sum of contributions of heat capacity and heats of processes that occur when material is gasified:

$$H_g = \int_{T_{init}}^{T_{dec}} C_{mat}dT + H_{melt} + H_{dec} + \int_{T_{dec}}^{T_{final}} C_{prod}dT \qquad (1)$$

C_{mat} and C_{prod} are temperature-dependent heat capacities of the material and products of its thermal decomposition. H_{melt} is the heat of melting. H_{dec} is the heat of decomposition, which also includes the heat of vaporization of volatiles formed during the decomposition. The decomposition and vaporization occur at T_{dec}.

Equation 1 can be simplified by assuming that $C_{prod} \approx C_{mat}$:

$$H_g = \int_{T_{init}}^{T_{final}} C_{mat}dT + H_{melt} + H_{dec} \qquad (2)$$

Taking into account that an initial material and its decomposition products have identical elemental composition and similar chemical structures, this is a reasonable assumption. Furthermore, for most polymers, thermal decomposition occurs within a range of temperatures that is only 100°-200°C wide, which means that T_{dec} and T_{final} are close. This makes C_{prod} contribution to H_g relatively small. It should be noted, however, that in the case of materials that decompose to produce a high yield of solid residue (char), the heat capacity of the residue may still play an important role in the pyrolysis or combustion.

The assumption of $C_{prod} \approx C_{mat}$ has one more significant implication. The heat of decomposition becomes a temperature-independent quantity (because of the conservation of energy). Thus, within this framework, the heat of gasification is a function defined by two material-specific constants, H_{melt} and H_{dec}, and temperature-dependent heat capacity. In this study, differential scanning calorimetry (DSC) was used to measure parameters of this function for polymethylmethacrylate, polyoxymethylene, polyethylene, polypropylene, polystyrene,

polyamide 6,6, polyethylene terephthalate, bisphenol A polycarbonate, polyvinylidene fluoride, and polyvinyl chloride. While values of some of these parameters are available in the literature [1-3], to the authors' knowledge, this is the first work where a complete characterization of the heats of gasification was obtained from DSC measurements.

METHODOLOGY

The heat flow measured in a power-compensation DSC apparatus (HF_{DSC}) consists of contributions from several sources:

$$HF_{DSC} = HF_{samp} + (C_{samp.cell} - C_{ref.cell})\frac{dT}{dt} + HL_{samp.cell} - HL_{ref.cell} \qquad (3)$$

The contribution of interest is that of a sample of material, HF_{samp}. In addition, HF_{DSC} includes a heat flow associated with the difference between heat capacities of the sample and reference enclosures, $C_{samp.cell}$ and $C_{ref.cell}$, and difference between heat loss rates, $HL_{samp.cell}$ and $HL_{ref.cell}$, from these enclosures to the environment.

The part of the DSC heat flow that is not associated with a sample, baseline heat flow, can be evaluated by performing an empty sample pan experiment at the same heating rate (dT/dt). However, the baseline changed significantly from experiment to experiment (even after many hours of equilibration). This instability was attributed to heat loss terms. Fortunately, the heat loss contribution can be evaluated during a DSC run by stopping the temperature ramp and measuring the heat flow at constant temperature ($dT/dt = 0$).

In this study, this approach was used to measure heat loss contributions to HF_{DSC} in both sample and empty sample pan (or baseline) experiments. The heating program consisted of 5°C/min temperature increases separated by 5-minute-long isothermal regions. The temperatures of the regions, which were 100°-350°C apart, were selected carefully to make sure that the sample did not undergo any phase transition or decomposition during the isotherms (i.e., HF_{samp} during the isotherms was 0). The heat loss contributions were assumed to have a linear dependence on temperature between measurement points and were subtracted from DSC heat flow curves. Subsequently, heat loss-corrected baseline was subtracted from the corresponding heat-loss-corrected sample curve to obtain HF_{samp} dependence on temperature. The sample heat flow was divided by the heating rate and initial sample mass to cast it to the units of heat capacity. An example of unprocessed sample and baseline heat flow curves and resulting HF_{samp} are shown in figure 1.
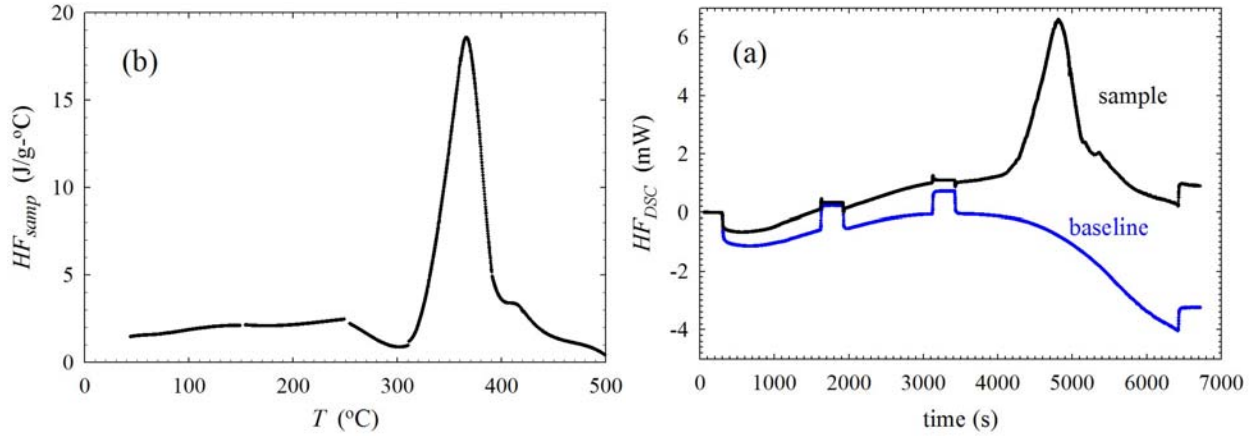
Figure 1. The DSC Heat Flow Curves Obtained for a Sample of Polymethylmethacrylate (Endothermic is positive) (a) Unprocessed Sample and Baseline Curves and (b) Sample Heat Flow Derived From the Data Shown in (a) and Cast to the Units of Heat Capacity

The heat capacity of material was obtained from HF_{samp} curves by fitting them with two linear functions of temperature:

$$C_{mat} = \begin{cases} C_{L0} + C_{L1}T, \ T < T_{trans} \\ C_{R0} + C_{R1}T, \ T \geq T_{trans} \end{cases} \tag{4}$$

The slope change point (T_{trans}) was assumed to correspond to the maximum of a melting peak or inflection point of an apparent glass transition. Melting and decomposition peaks, which were excluded from the data used in the determination of heat capacity, were integrated to determine the heats of these processes (H_{melt} and H_{dec}). In the case of melting, the heat capacity expression was used as a baseline for the integration. In the case of decomposition, the baseline was assumed to be a straight line connecting the points on HF_{samp} curve corresponding to the beginning and end of sample mass loss. The mass loss information was obtained from a separate thermogravimetric analysis experiment, which was conducted using the same heating program as that used in the DSC.

EXPERIMENTAL SETUP AND MATERIALS

The heat flow measurements were performed using a Perkin-Elmer DSC 7 with a flow-through cover. The sample and reference enclosures were ventilated with ultra-high-purity nitrogen at the rate of 35 cm^3/min. The measurements were performed within 40°-600°C temperature range.

Several sample sizes, heating rates, and sample container configurations were tested. Two- to four-mg samples heated at 5°C/min yielded the most reproducible results. The samples were cut into thin flat squares, placed into an aluminum pan, and covered by a bent aluminum lid, as shown in figure 2. Small gaps between the lid and pan walls ensured that volatile decomposition products can escape readily. An empty aluminum pan with a bent lid was used as a reference. In the case of the samples containing halogens (i.e., samples of polyvinylidene fluoride and

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polyvinyl chloride), several experiments were performed using graphite pans with bent gold-covered copper lids. This was done to ensure that potential chemical interactions of the decomposition products with container surfaces did not factor in the measured heat flows. Thermogravimetric analyses were performed using a Perkin-Elmer TGA 7.
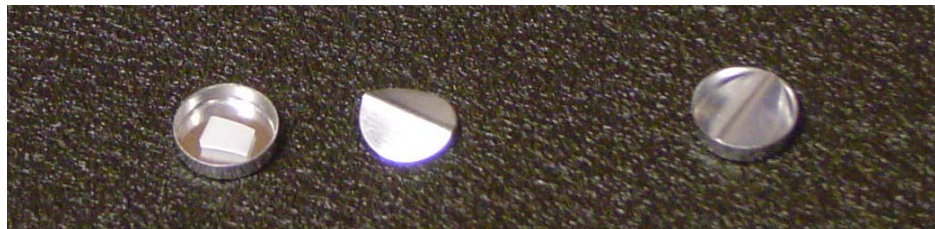

Figure 2. Sample Container Configuration Used in the DSC Measurements

The polymers used in this study were provided in the form of large (approximately 2 by 1 m) sheets, which were about 6-mm thick. The need for large quantities was dictated by the requirements of bench-scale flammability tests that the authors intend to conduct in the future. The information on the polymers is summarized in table 1.

Table 1. Polymers Used in This Study

Polymer	Manufacturer	Trade Name	Distributor
Polymethylmethacrylate	Atofina	Plexiglas G	Modern Plastics
Polyoxymethylene (copolymer)	K-Mac Plastics	Kepital Acetal	Curbell
Polyethylene (high density)	Poly Hi Solidur	HD Natural SR.	Modern Plastics
Polypropylene	HPG International	Versadur 500	Modern Plastics
Polystyrene (high impact)	Westlake Plastics	HIPS	Modern Plastics
Polyamide 6,6	Quadrant EPP	Nylon 101	Modern Plastics
Polyethylene terephthalate	Ensinger	Ensitep	Modern Plastics
Bisphenol A polycarbonate	GE Plastics	Lexan 9034	Modern Plastics
Polyvinylidene fluoride	Elf Atochem	Kynar 740	Curbell
Polyvinyl chloride	HPG International	Versadur 150	Modern Plastics

RESULTS AND DISCUSSION

Between four and eight DSC experiments, each consisting of a baseline and sample run, were performed for every polymer. Temperature dependencies of heat capacities were obtained by simultaneous least-square fitting of all sample heat flow curves (obtained for the same material) with equation 4. The resulting parameters are given in table 2. A comparison of the heat capacities with those reported in the literature [1] is presented in figure 3. Taking into account that the structures of the materials used in these studies are not identical, the agreement is reasonable.

Table 2. Parameters (of equation 4) Describing Dependence of Measured Heat Capacities on Temperature

Polymer	C_{L0} (J/g-°C)	C_{L1} (J/g-°C^2)	T_{trans} (°C)	C_{R0} (J/g-°C)	C_{R1} (J/g-°C^2)
Polymethylmethacrylate	1.01	0.00858	130	1.78	0.00240
Polyoxymethylene	1.11	0.00811	165	1.34	0.00275
Polyethylene	1.41	0.00896	134	1.76	0.00508
Polypropylene	1.38	0.01013	158	2.15	0.00247
Polystyrene	1.10	0.00644	148	1.91	0.00072
Polyamide 6,6	1.66	0.00573	262	2.41	0.00056
Polyethylene terephthalate	0.97	0.00453	253	1.72	0.00086
Bisphenol A polycarbonate	1.05	0.00377	147	1.68	0.00134
Polyvinylidene fluoride	0.98	0.00558	167	0.76	0.00467
Polyvinyl chloride	0.42	0.01080	78	1.40	0.00091

J/g = Joules per gram

Figure 3. Comparison of the Heat Capacities Measured in This Study With Literature Data (The results of current measurements are depicted by black solid lines. The data from reference 1 are blue-dashed lines.)

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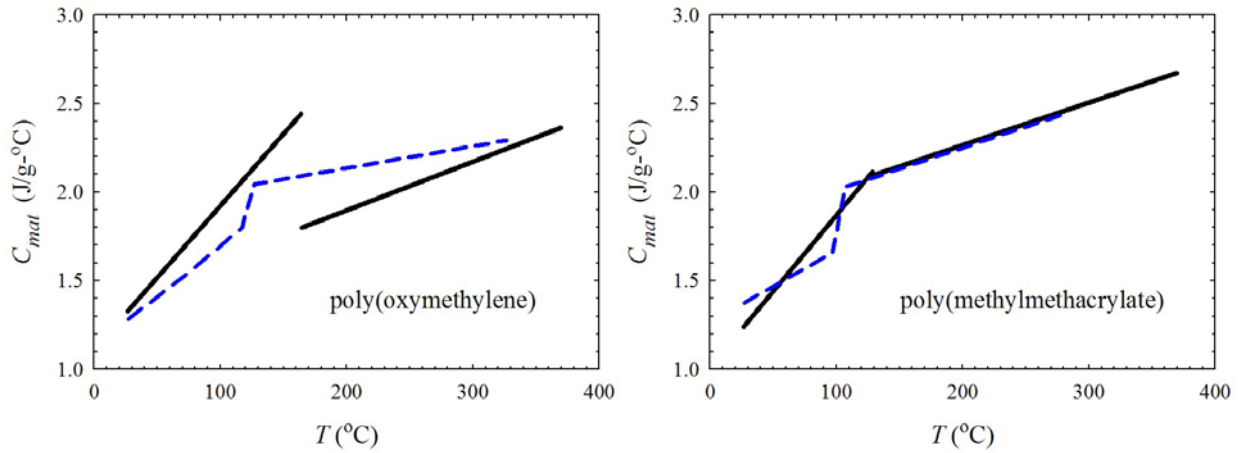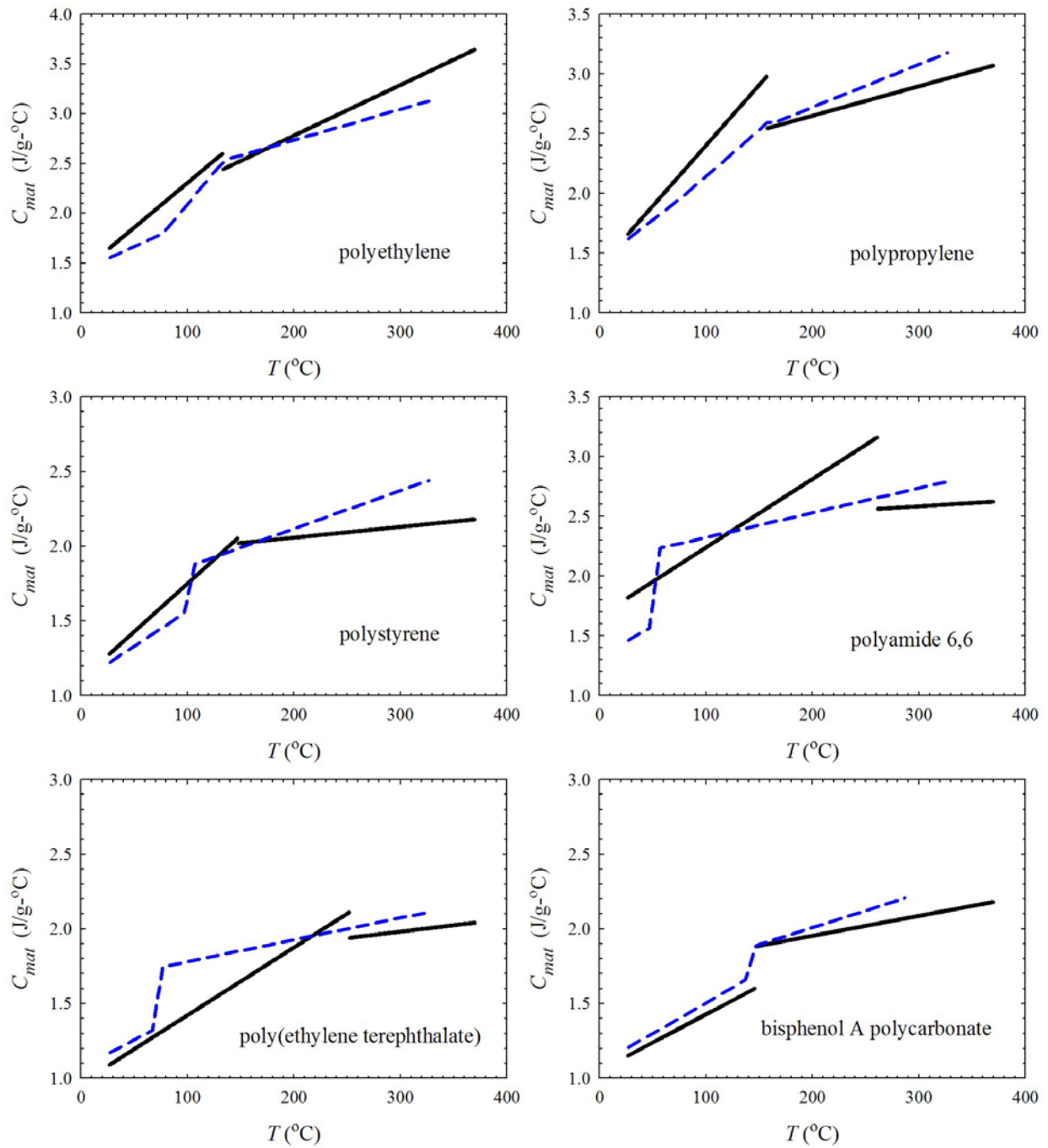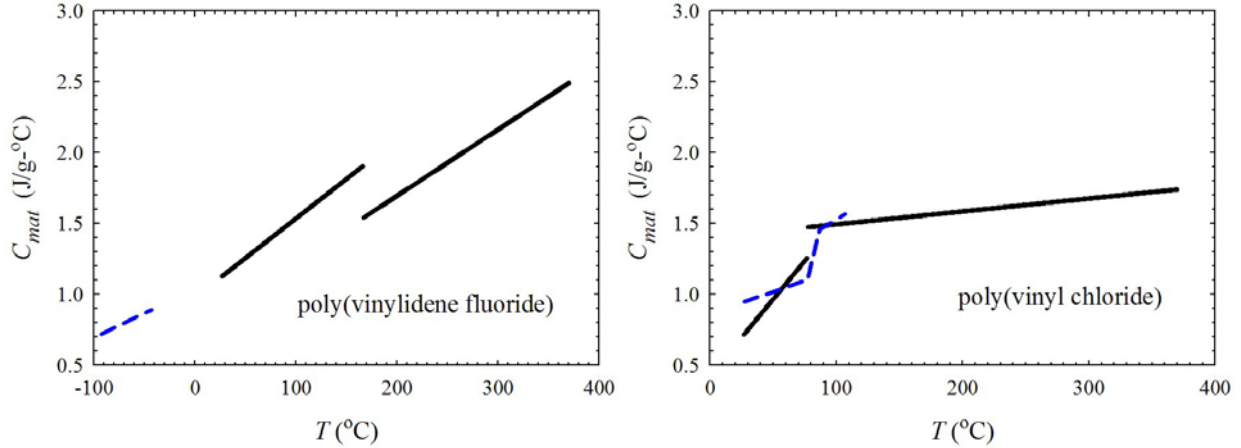1 are blue-dashed lines.) (Continued)

Figure 3. Comparison of the Heat Capacities Measured in This Study With Literature Data
(The results of current measurements are depicted by black solid lines. The data from reference
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Table 3 contains temperatures and heats of melting obtained by averaging the data from individual sample heat flow curves. The uncertainties in H_{melt} are ±1 standard deviation of the data. The temperatures of melting (T_{melt}), which were assumed to correspond to the maximums of the melting peaks, are in good agreement with the melting points listed in reference 1. The degrees of crystallinity, which were evaluated as the ratio of the measured heat of melting and the heat of melting of a fully crystalline polymer (see table 3), were also found to be within the expected ranges [1 and 4].

Table 3. Temperatures and Heats of Melting

Polymer	T_{melt} (°C)	H_{melt} (J/g)	$H_{melt.crystal}$* (J/g)	Crystallinity (%)
Polymethylmethacrylate	No melting peak observed			
Polyoxymethylene	165	141 ±4	325	43
Polyethylene	134	218 ±18	292	75
Polypropylene	158	80 ±4	207	39
Polystyrene	No melting peak observed			
Polyamide 6,6	262	55 ±5	190	29
Polyethylene terephthalate	253	37 ±3	140	26
Bisphenol A polycarbonate	No melting peak observed			
Polyvinylidene fluoride	167	47 ±2	98	48
Polyvinyl chloride	No melting peak observed			

J/g = Joules per gram
* The heat of melting of a fully crystalline polymer from reference 1.

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The data on decomposition are summarized in table 4. While each material decomposed over a range of temperatures, a single characteristic temperature (T_{dec}) corresponding to the maximum of the decomposition peak was recorded. Polyvinyl chloride was the only material that, according to a thermogravimetric analysis, had two distinct mass loss steps. Table 4 shows results for each of these steps. As is the case with the data on melting, both T_{dec} and H_{dec} are averages of the values determined from individual sample heat flow curves. The uncertainties in H_{dec} are ±1 standard deviation.

Table 4. Temperatures and Heats of Decomposition

Polymer	T_{dec} (°C)	H_{dec} (J/g)	$H_{dec.lit}$* (J/g)
Polymethylmethacrylate	366	870±200	800
Polyoxymethylene	369	2540±300	--
Polyethylene	478	920±120	670
Polypropylene	447	1310±70	630
Polystyrene	427	1000±90	820
Polyamide 6,6	438	1390±90	560
Polyethylene terephthalate	433	1800±80	--
Bisphenol A polycarbonate	499	830±140	--
Polyvinylidene fluoride	475	2120±250	--
Polyvinyl chloride	276	170±170	--
	475	540±390	--

* The heat of decomposition from reference 2.

In general, there are no well-established values for the heats of decomposition of polymers. One exception is polymethylmethacrylate for which H_{dec} can be calculated from the heat of polymerization and heat of vaporization of the monomer [2]. The calculated value, 920 Joules per gram (J/g), compares favorably with the result of the present study, 870 J/g. Table 4 also contains the heats of decomposition measured by Frederick and Mentzer [2] using the du Pont-type DSC (a somewhat less direct technique that requires a calibration curve to convert measured temperatures to heat flow). Their heats of decomposition of polymethylmethacrylate and polystyrene are close to those obtained in this work. However, in the case of polypropylene and polyamide 6,6, their values are much lower.

The parametric description of C_{mat} (equation 4), together with H_{melt} and H_{dec}, can be used within the framework of a pyrolysis or combustion model to describe the thermal behavior of a material. These parameters can also be substituted into equation 2 to obtain an integral value for the heat of gasification for specific initial and final temperatures. The values of H_g for $T_{init} = 25$°C and $T_{final} = T_{dec}$ are given in table 5 ($T_{final} = 475$°C was used for polyvinyl chloride). This

table also lists all contributions to the H_g including the values of heat capacity integral (sensible heat), which were determined by integrating equation 4:

$$\int_{T_{init}}^{T_{final}} C_{mat}dT = C_{L0}(T_{trans} - T_{init}) + \frac{C_{L1}}{2}(T_{trans}^2 - T_{init}^2) + C_{R0}(T_{final} - T_{trans}) +$$

$$+ \frac{C_{R1}}{2}(T_{final}^2 - T_{trans}^2) \qquad (5)$$

Note that, the integration from $T_{init} = 25°C$ to $T_{final} = T_{dec}$ involves extrapolation of the heat capacity dependencies beyond the temperature ranges of the fitted experimental data. This, together with the way in which parameters of these dependencies were obtained, made evaluation of the uncertainties in the sensible heat difficult. For simplicity, it was assumed that, for all polymers, these uncertainties are equal to the average relative uncertainty of H_{melt} and H_{dec}, which was found to be ±16%. Absolute values of these uncertainties are given in table 5. Table 5 also contains uncertainties in the integral value of H_g, which were calculated by propagating errors [5] from the sensible heat, H_{melt}, and H_{dec}.

Table 5. Integral Heats of Gasification and Their Components

Polymer	$\int_{25°C}^{T_{dec}} C_{mat}dT$ (J/g)	H_{melt} (J/g)	H_{dec} (J/g)	$H_g^{25°C-Tdec}$ (J/g)
Polymethylmethacrylate	740±120	0	870±200	1610±230
Polyoxymethylene	690±110	141±4	2540±300	3370±320
Polyethylene	1370±220	218±18	920±120	2510±250
Polypropylene	1150±180	80±4	1310±70	2540±190
Polystyrene	800±130	0	1000±90	1800±160
Polyamide 6,6	1050±170	55±5	1390±90	2500±190
Polyethylene terephthalate	730±120	37±3	1800±80	2570±140
Bisphenol A polycarbonate	910±150	0	830±140	1740±210
Polyvinylidene fluoride	910±150	47±2	2120±250	3080±290
Polyvinyl chloride	710±110	0	710±430*	1420±440

* The sum of the heats of decomposition obtained for two decomposition steps.

Some polymers used in this study did not vaporize completely and left a considerable amount of postdecomposition residue (char). The char yields (μ) and temperatures at which they were measured (T_{char}) are given in table 6. This information was obtained from thermogravimetric analyses performed using the same heating programs that were used in the corresponding DSC

experiments. The last column in table 6, L_g, is the integral heat of gasification (specified in table 5) that was renormalized per unit mass of volatilized material; i.e., $L_g = H_g/(1- \mu)$. This quantity is frequently used in fire protection engineering calculations to assess the material's response to external heat flux [3].

Table 6. Char Yields and Char-Weight-Adjusted Integral Heats of Gasification

Polymer	μ (wt. fraction)	T_{char} (°C)	L_g (J/g)
Polymethylmethacrylate	0	--	1610±230
Polyoxymethylene	0	--	3370±320
Polyethylene	0	--	2510±250
Polypropylene	0	--	2540±190
Polystyrene	0.03	550	1860±160
Polyamide 6,6	0.03	500	2580±200
Polyethylene terephthalate	0.15	530	3020±160
Bisphenol A polycarbonate	0.24	575	2290±280
Polyvinylidene fluoride	0.38	600	4970±470
Polyvinyl chloride	0.20	600	1780±550

CONCLUSIONS

In this work, the heat of gasification was defined as a function of the initial and final temperatures of the gasification process. A methodology for determining parameters of this function using power-compensation differential scanning calorimetry was developed and applied to a set of ten noncharring and charring polymers. The results of the measurements were verified against literature data. These parameters were used to obtain integral values of the heats of gasification for heating materials from room temperature through their decomposition. For most of the studied polymers, the contributions to the integral heats from heat capacity and melting were found to be approximately equal to the contributions from decomposition and vaporization.

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