

## Determination of Heats of Volatilization for Polymers by Differential Scanning Calorimetry

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### Synopsis

In the design of thermal degradation processes for polymers, the energy to degrade or volatilize the materials often must be known. The heats of volatilization for six polymers were measured by differential scanning calorimetry (DSC), where the area under the degradation endotherm peak was shown to be directly proportional to the heat of volatilization. Values measured for poly(methyl methacrylate), which yields monomer quantitatively in the temperature range investigated, agree well with theoretically predicted values. Reproducibility of the method is shown by an average standard deviation of  $\pm 10\%$  for the six polymers investigated. Caution must be used when applying data obtained by this method to thermal conditions widely differing from those employed in the DSC.

### INTRODUCTION

The decreasing availability and increasing cost of crude oil necessitates a more efficient use of this raw material. For example, polymeric materials could be considered an intermediate in the flow of crude oil to fuel. This possibility has been discussed by Cross and Park.<sup>1</sup> The polymeric materials may be re-used and recycled until their useful life has ended. Ultimately, the polymeric scrap would be consumed as a fuel. This would be ecologically beneficial in that landfill requirements are reduced and that the caloric value of the polymeric material is utilized.

Methods of recovering the energy value from polymeric scrap depend upon the source and volume of the scrap. For example, when combined in sufficiently small percentages with municipal trash or with coal, polymeric scrap could be burned directly in conventional boiler systems. However, for high concentrations of polymeric scrap, conventional incineration systems are unsatisfactory. An alternative approach is conversion of the polymeric material to a low molecular weight liquid or gaseous fuel by thermal degradation. To design a process for gasification of polymeric scrap, the energy required to volatilize scrap polymer must be known. These energy requirements are not available in the literature; furthermore, no standard methods exist for predicting them.

Volatilization of a polymeric material consists of two steps: thermal degradation and vaporization of the low molecular weight degradation products. Theo-

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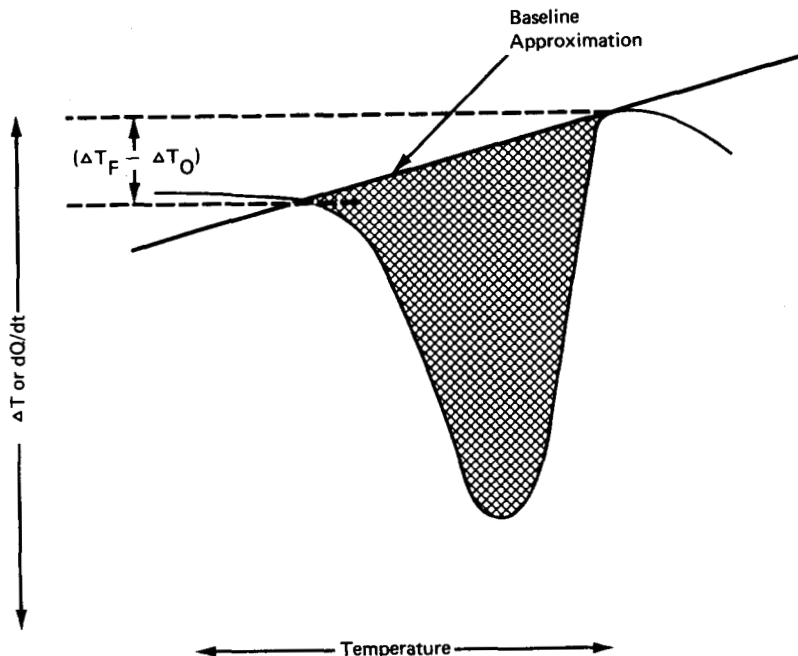


Fig. 1. Graphic integration of DSC curve for heat of volatilization.

To reduce eq. (4) to a more manageable form, the heat capacity difference between sample and reference pans (term II) is eliminated by using a linear baseline to approximate the area under the endotherm (Fig. 1). Also, since it can be expected that  $R_c \gg R_s$ ,<sup>3</sup> term III becomes  $\int C_s [d(\Delta T)/dt] dt$ . If the polymeric sample weight is a small fraction of the pan weight, then  $C_s$  is approximately the same as  $C_{s0}$ , the initial weight of sample and pan. Term III can then be estimated as

$$\int_{t_0}^{t_f} C_s \frac{d(\Delta T)}{dt} dt \leq C_{s0} \int_{t_0}^{t_f} \frac{d(\Delta T)}{dt} dt = C_s (\Delta T_f - \Delta T_0) \quad (5)$$

where  $(\Delta T_f - \Delta T_0)$  is the difference in baseline between the beginning and end of the endotherm (Fig. 1). According to eq. (5),  $C_{s0}(\Delta T_f - \Delta T_0)$  is an upper limit for term III. Since calculated values for  $C_{s0}(\Delta T_f - \Delta T_0)$  in no case exceeded 0.5% of the value of term I, term III can be neglected. Thus, the volatilization energy may be expressed as

$$\Delta H_{\text{vol}} = \frac{1}{m} \int_{t_0}^{t_f} \frac{\Delta T(t)}{R_c} dt. \quad (6)$$

### EXPERIMENTAL

du Pont aluminum DSC sample pans were pressed with a pan shaper to ensure flatness of the pan bottoms for good heat transfer. Also, preshaping the pans allowed a sufficiently loose fit between pan and lid so that volatile products could escape readily. The pan and lid were weighed together to 0.001 mg. Approximately 0.5 mg polymer was added to each pan, and the lids were placed

on in an inverted position. The filled pans were weighed and the polymer weight determined by difference. The samples were stored under vacuum until used.

DSC analyses were performed using a du Pont 990 thermal analysis system in the DSC mode. After the sample and reference pans were positioned, the sample chamber was evacuated and purged three times with nitrogen. The analyses were performed under a nitrogen atmosphere, at 10°C/min heating rate. Heating was continued to 550°C, the upper temperature limit for the DSC cell. In all cases, this was sufficient to complete the volatilization endotherm. At least three samples of each material were analyzed.

The specific heat of volatilization was determined according to eq. (6). A linear baseline was drawn as shown in Figure 1. The area bounded by the endotherm peak and baseline was integrated graphically by planimetry. The term  $R_c$  in eq. (6) can be obtained by calibrating the DSC cell with a reference standard, such as  $\text{Al}_2\text{O}_3$ . However, the DSC system employed was calibrated to plot heat generation rate ( $dQ/dt$ ) rather than  $\Delta T$  versus temperature (or time). Therefore, integration of the endotherm peak area yielded ( $\Delta m \cdot \Delta H_{\text{vol}}$ ) directly.

## RESULTS AND DISCUSSION

Specific heats of volatilization for the six polymers analyzed are shown in Table I. The heats of volatilization vary from 1.4% to 3.0% of the respective heats of combustion.<sup>4</sup> Thus, pyrolysis prior to combustion requires a small percentage of the heat of combustion.

PMMA pyrolyzes to yield 95% monomer, and its heat of volatilization can be calculated readily from eq. (1). Thus, it serves as an internal standard for this method. The heat of polymerization for methyl methacrylate is -135 cal/g,<sup>5</sup> and its heat of vaporization is 86 cal/g.<sup>6</sup> According to eq. (1), assuming only monomer is formed upon decomposition,  $\Delta H_{\text{vol}}$  equals 221 cal/g. This compares favorably with the experimentally measured value of  $192 \pm 8$  cal/g.

For comparison, the same calculations were made for polyethylene, polypropylene, and polystyrene, assuming that the thermal degradation products in each case were monomers. The results, shown in Table II, clearly show that, for the polymers which pyrolyze to fragments larger than monomer units,  $\Delta H_{\text{vol}}$  predicted by eq. (1) is considerably higher than that actually measured. Even for polystyrene, which depolymerizes thermally to yield 40-60% monomer,<sup>2</sup>  $\Delta H_{\text{vol}}$  is predicted to be 36% greater than the experimental value. Thus, by comparing the results for PMMA and polystyrene, the sensitivity of the DSC

TABLE I  
Heats of Volatilization for Typical Automotive Thermoplastics

Material	$\Delta H_{\text{vol}}$ , cal/g	$\Delta H_{\text{comb}}$ , cal/g	$\frac{\Delta H_{\text{vol}}}{\Delta H_{\text{comb}}} \times 100$ , %
Polyethylene	159 $\pm$ 13	11,200	1.4
Polypropylene	151 $\pm$ 10	10,900	1.4
Poly(methyl methacrylate)	192 $\pm$ 8	6,400	3.0
Polystyrene	196 $\pm$ 8	9,950	2.0
Nylon 6	188 $\pm$ 8	7,610	2.5
Nylon 66	135 $\pm$ 11	7,500	1.8

TABLE II  
 Predicted Versus Experimental Heats of Volatilization for Typical Automotive Thermoplastics

Material	$-\Delta H_p^a$ cal/g	$\Delta H_v^b$ cal/g	$\Delta H_{vol}$ , cal/g	
			Equation (1)	Experimental
Polyethylene	811	114	925	159
Polypropylene	488	105	593	151
Polystyrene	161	103	264	192
Poly(methyl methacrylate)	135	86	221	196

<sup>a</sup> Reference 5.

<sup>b</sup> Reference 6.

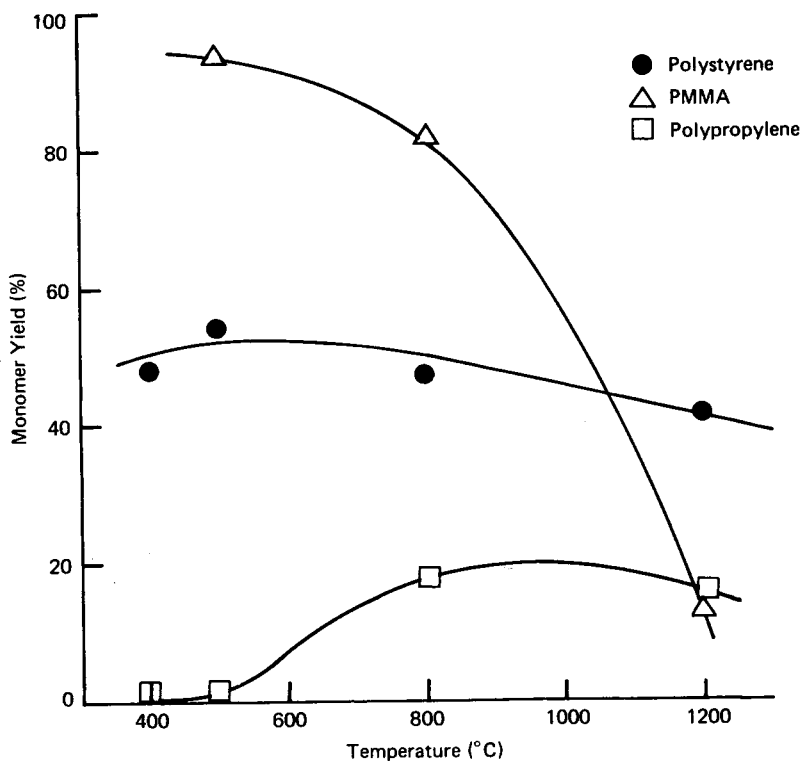


Fig. 2. Monomer yield vs. temperature for isothermal pyrolysis of polymers in vacuo (reference 2).

technique to pyrolysis product distribution is established. This sensitivity, and the agreement between predicted and measured  $\Delta H_{vol}$  for PMMA, support the validity of this method for measuring heats of volatilization.

It should be noted that the heats of volatilization are dependent on the distribution of pyrolysis products which vary with both heating rate and pyrolysis temperature. For example, Madorsky<sup>2</sup> has reported that the monomer yield from PMMA below 500°C is constant at 95%. At higher temperatures, monomer yield varies for different polymers, as shown in Figure 2. In the range of 500–1200°C, methyl methacrylate yield drops to 13%, styrene yield is relatively

constant, near 50%, and propylene yield increases from 0% to 18%. Yields of other pyrolysis products from these three polymers also varied over that temperature range, with smaller fragments formed as temperature increases.

As smaller fragments are produced, the volatilization energy required increases. This can be seen from Table II. If polyethylene or polypropylene volatilized completely to monomer instead of larger hydrocarbons, their heats of volatilization would be 925 cal/g and 593 cal/g, respectively. Thus, as pyrolysis temperature increases,  $\Delta H_{v,01}$  for a given polymer also increases. Because of limitations of the DSC system,  $\Delta H_{v,01}$  could not be measured at higher temperatures. Nevertheless, the effect of temperature on  $\Delta H_{v,01}$  at higher temperatures should not be ignored when designing gasification systems to operate at temperatures above the DSC range.

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### References

1. J. A. Cross and W. R. Park, *The Role of Plastics in Resource Recovery*, Midwest Research Institute, Kansas City, Missouri, May 23, 1973.
2. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley, New York, 1964.
3. J. K. Gillham and C. C. Mentzer, *J. Appl. Polym. Sci.*, **17**, 1143 (1973).
4. J. I. Throne and R. G. Griskey, *Mod. Plast.*, **49**, 96 (1972).
5. F. Rodriguez, *Principles of Polymer Systems*, McGraw-Hill, New York, 1970, p. 96.
6. G. E. Ham, *Vinyl Polymerization*, Vol. 1, Marcel Dekker, New York, 1967, p. 450.

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