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Thermochimica Acta 367–368 (2001) 401–405

thermochimica acta

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Flammability kinetics from TGA/DSC/GCMS, microcalorimetry and computational quantum chemistry[☆]

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Received 20 October 1999; accepted 28 April 2000

Abstract

Flammability hazards and mechanisms have been analyzed for mg-scale samples of polymers by integrating the use of a new TGA/DSC/GCMS technique, the PCFC microcalorimeter developed by Lyon, and computational quantum chemistry. The first apparatus is based on a Rheometrics STA 1500. Head space immediately above the polymer is sampled through a microprobe and heated transport line into a multiport valve of a Hewlett-Packard 5890 Series II GC with 5972 Mass Selective Detector. The PCFC microcalorimeter is based on continuous analysis of the oxygen required to consume pyrolysis gases. The two apparatus yield complementary data on the rate and composition of gases evolved in pyrolysis, and they are shown here to be in good agreement. Kinetics of decomposition are established from the data and from computed rate constants.

Keywords: Flammability hazards; Pyrolysis gases; Fire-safe polymers

1. Introduction

Developing new, more fire-safe polymers is one way to prevent injuries and deaths due to fires in an aircraft. Air travel is unquestionably safe; no fatalities were recorded for US carriers in 1998. Still, crashes occur. Over time, 50% of the deaths in airplane crashes have been assessed as "impact-survivable", and of those, 40% have been due to fires. The Federal Aviation Administration (USA) has set a goal of eliminating deaths due to burning materials inside aircraft, and it is driving research to find highly fire-resistant thermosets, thermoplastics, fibers and elastomers [1].

Development has a two-fold challenge: finding polymers and finding how fire-resistant they are. Good empirical tests are available for commercially available polymers, requiring quantities from tons for a whole-aircraft test to a little as 100 g for the standard OSU fire calorimeter [2] or cone calorimetry [3]. However, lab syntheses of new polymers have yields only in the milligram to gram range.

Lyon and co-workers [4] have developed a milligram-scale "pyrolysis-combustion flow calorimetry"

[☆] Extended abstract for 27th Annual Conference on Thermal Analysis and Applications, North American Thermal Analysis Society, September 20–22, 1999, Savannah Marriott Riverfront, Savannah GA, USA.

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PII: S0040-6031(00)00661-4

(PCFC) apparatus to test polymer flammability. It is based on obtaining the "heat release rate", the rate at which heat would be released above the polymer if its gas-phase pyrolysis products burned completely. As a sample is flash-heated at 5°C/s to 1200°C, inert N_2 sweeps the pyrolysis gases into a mixing volume with O_2 such that the N_2/O_2 mixture would have approximately the composition of atmospheric air. The mixture is oxidized to completion in a hot flow-tube reactor, H_2O and CO_2 products are removed and the O_2 depletion is measured continuously as a function of time. This measurement is converted to heat release rate by a correlation equation [5]. The same principle of oxygen depletion is exploited in the OSU calorimeter, but smaller system volume and well-controlled residence time and heating allow use of small samples. Results correlate well to larger-scale flammability tests.

In the present work, a commercial simultaneous-thermal-analysis apparatus was adapted to give direct measurements of gas evolution rate and composition. The multiplicative product of the instantaneous gas evolution rate (polymer mass loss) and the mixture's heat of combustion gives the heat release rate explicitly. Thus, a distinctly different direct measurement can be compared to results of the FAA microcalorimeter. In addition, qualitative and quantitative determinations of the evolved volatile products provide kinetic information about the specific reaction mechanisms. Computational quantum chemistry is used to develop unknown bond energies, rate constants and viable mechanisms.

2. Apparatus and procedure

A Rheometrics STA-1500 was adapted for the experimental task. It is capable of providing direct weight measurements by time-programmed thermogravimetric analysis (TGA) as well as heat consumption/release by differential scanning calorimetry (DSC) to detect thermal events that do not involve mass change. For analyzing off-gases, a Hewlett Packard 5890 Series II Gas Chromatograph with 5972 Series Mass Selective Detector was used. The two instruments were connected by a heated transfer line. A 1 m-long, uncoated silica capillary tube was enclosed in a stainless-steel tube wrapped with a resistive heater, insulated and maintained at a chosen temperature by a temperature controller. This capillary tube was attached to the GC sampling valve, which was normally under vacuum. The vacuum system was made of a coiled 2 m-long, 1/4 in.-diameter copper tube that was pulled under vacuum (100 kPa) constantly. A needle valve was attached at the exit of the GC sampling valve to control the evacuation flow at a constant rate.

Manufacturer's software was used to control each component instrument (Rheometrics STA V.6.3.0, Hewlett-Packard "GC-MS" version A.03.00). The software interprets GC/MS data using the 1992 NIST mass spectra database.

The STA was operated with a 60 sccm flow of helium and a heating rate of 10°C/min. The GC-MS unit was set to start at an initial decomposition temperature and then to sample once every 3 or 4 min, depending on the products of the standard polymers. For fire-retardant polymers where intermediate cyclization or mass loss was apparent, the GC-MS analyses were less frequent in order to permit longer analysis times.

For computing structures and thermochemistry of molecules and transition states, Gaussian 94 [6] was used on SGI Indigo^2 and O2 workstations.

3. Results and discussion

3.1. PMMA example

For developing this technique, a number of standard polymers were tested. Polymethylmethacrylate provides a good example because of literature understanding that it depolymerizes rather cleanly to the monomer.

The decomposition proceeded in three general stages, as shown by the TGA/DSC output (Fig. 1). The first stage began at about 120°C, based on DSC data, although the small detectable mass loss (2%) and its corresponding thermal effect occurred only from 150 to 200°C in this stage. The second stage destroyed about 40% of the sample, most rapidly at 270°C with an apparent change of mechanism at about 290°C. Finally, the sample completely decomposed by 410°C, reaching a maximum in rate of mass loss and heat uptake at 370°C. GC/MS analyses

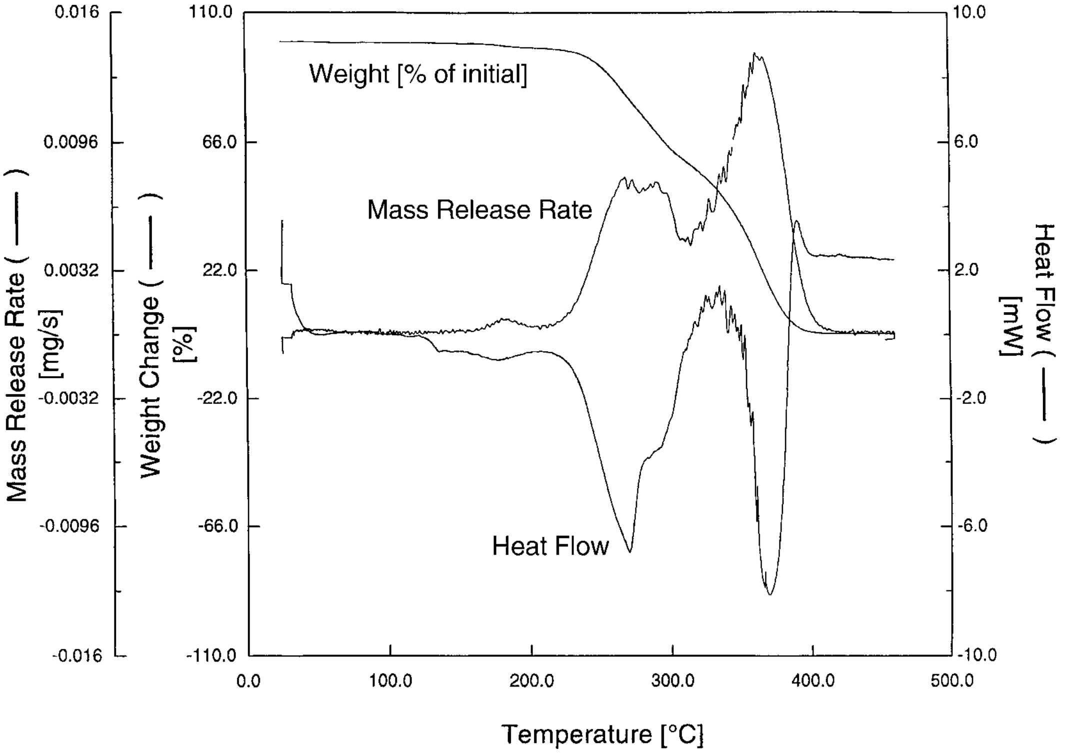

Fig. 1. Typical TGA/DSC data: polymethylmethacrylate (PMMA).

from both stages of pyrolysis showed predominantly the monomer, plus a small amount of butyl methacrylate (Fig. 2).

TGA data were differentiated to yield decomposition rates over the time-temperature history of the sample. Analyzing the rates as first-order kinetics, we obtained similar activation energies E_{act} but different Arrhenius pre-exponential factors in different regions. At the lower temperatures, a fairly clean rate constant of $1.6 \times 10^8 \exp(-130/RT)$ or $E_{\mathrm{act}} = 31$ kcal/mol was obtained over 179–253°C. The highest-temperature region, where the greatest decomposition occurs, had an empirical A-factor of $1.4 \times 10^{11}\ \mathrm{s}^{-1}$ and $E_{\mathrm{act}} = 145$ kJ/mol (35 kcal/mol, 315–394°C).

Decomposition of anionically polymerized PMMA is usually attributed to random chain scission [7]. However, it is clear that decomposition is not due to homolytic bond fission in the canonical polymer structure. A different first-order analysis assuming quasi-isothermal conditions yields an activation-energy expression of

$$E_{\mathrm{act}} = -RT \ln\left[-\frac{1}{At}\ln\left(\frac{P}{P_{\mathrm{o}}}\right)\right]$$

Detectable onset of decomposition was defined as that at 1% decomposition in a time on the order of a minute. For an approximate A-factor of $10^{15}\ \mathrm{s}^{-1}$, the final-stage onset of 315°C (588 K) corresponds to $E_{\mathrm{act}} = 180$ kJ/mol (43 kcal/mol) with only weak sensitivity to the terms within the logarithms. Both this semi-quantitative number and the measured activation energies are much lower than the weakest homolytic bond dissociation energy in the nominal molecular structure (about 75 kcal/mol).

Note that these rate constants are for mass loss, so reactions not causing mass loss are not detected unless they are rate-determining steps. However, for initiation by homolytic bond fission followed by beta scission (activation energies 25–45 kcal/mol), the former should be rate-determining.

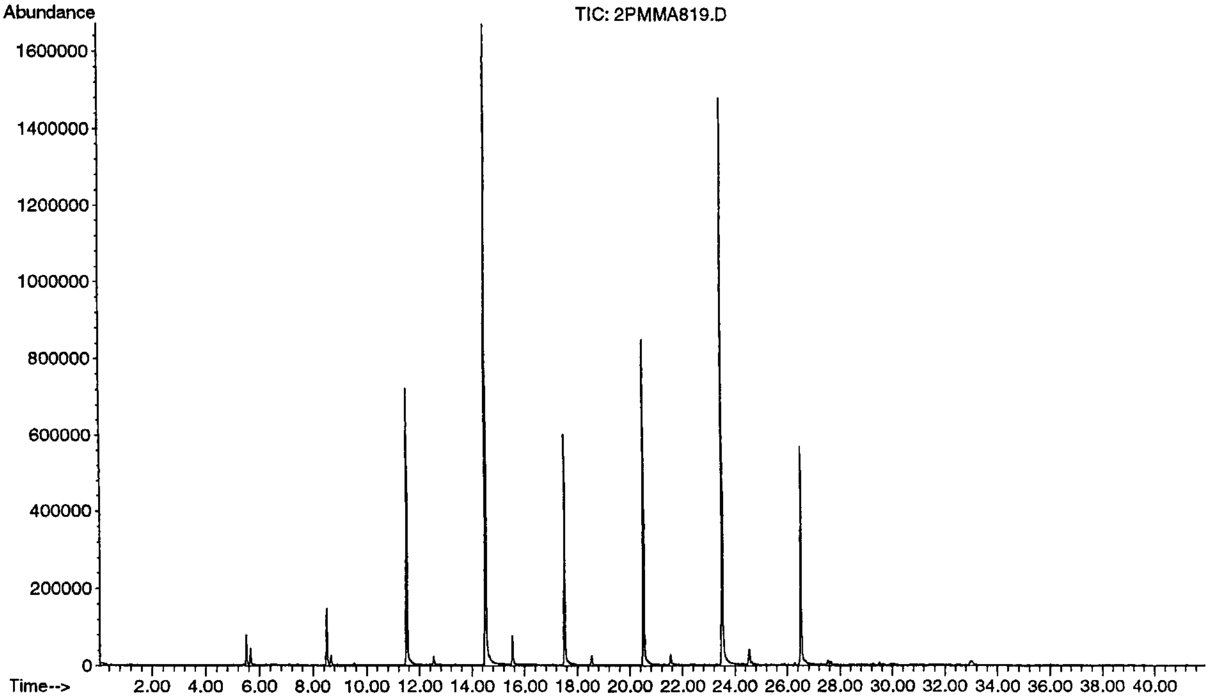

Fig. 2. Total-ionization mass spectrum corresponding to the pyrolysis gases from PMMA.

The likely explanation is initiation by the rupture of weakly bound end groups or other defect sites in the polymer. Termination of polymerization steps, such as by radical combination, can form relatively weak bonds. Verification will require more characterization of the polymer and polymerization process used.

However, measurement of the mass loss rate and of the species being evolved allowed direct calculation of the heat release rate as the instantaneous product of gas evolution rate times its heat of combustion. Inguilizian [8] showed that the peak heat release rate agreed with a factor of two with the FAA microcalorimeter, and Lyon has subsequently explained the difference as resulting from a small mixing effect in the microcalorimeter (unpublished results). Both results correlate well with large-scale tests, mutually validating the two methods as milligram-scale measurements of polymer flammability.

3.2. PHA fire-resistant polymer

Polyhydroxyamides were developed as early as 1964 [9,10] as precursors for extremely fire-resistant polybenzoxazoles. The simplest PHAs contain a hydroxyl ortho to a –NH–(CO)– linkage between aromatic rings. In Fig. 3, an overall reaction is shown for the initial decomposition of this PHA. The initial mass loss of 10% begins at about 250°C, but little further mass loss occurs until about 600°C. The rate of mass loss is a bit noisy but well defined and the heat flow is well characterized until about 900°C, where radiative heat losses cause the baseline to drift away.

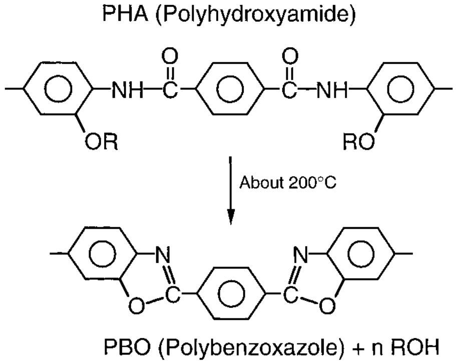

Fig. 3. Reaction for initial polyhydroxyamide decomposition.

A sequence of elementary reactions resulting in the overall reaction of Fig. 3 was developed using *ab initio* calculations of transition states and intermediates. The sequence must involve a modestly reactive intermediate, as suggested by the small mass consumption between 250 and 600°C. In fact, the proposed sequence [11] proceeds through an open-chain structure when H_2O is eliminated concertedly, although this structure closes into a five-membered ring with a barrier of only a few kcal/mol. The weakness of the hypothesized sequence is that it has a keto/enol-like H shift from the NH group to the carbonyl O, which has a high barrier in the homogeneous gas-phase model compound. However, in the real polymer, adventitious H_2O could facilitate this step. If it is not rate-limiting, then the observed activation energy of about 35 kcal/mol is in excellent agreement with the next highest-barrier step.

4. Conclusion

The validated technique can be and is being used to develop mechanisms of polymer decomposition, complementary to the FAA's PCFC unit.

Acknowledgements

We gratefully acknowledge financial support of this work by BP/Amoco Polymers, Boeing Commercial Airplane Group, Dupont Advanced Fiber Systems, the Federal Aviation Administration, General Electric Plastics, Schneller Inc., Solutia Inc. and the US Army.

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