

MASS SPECTROMETRIC THERMAL ANALYSIS OF POLY(METHYL METHACRYLATE) OF HIGH MOLECULAR WEIGHT

R. SAKAMOTO, T. OZAWA, AND M. KANAZASHI

Electrotechnical Laboratory, Tanashi, Tokyo (Japan)

(Received July 19th, 1971)

ABSTRACT

Mass spectrometric thermal analysis (MTA) of poly(methyl methacrylate) of high molecular weight is made, and MTA curves observed are analyzed to obtain kinetic parameters by two methods proposed by one of the authors. Satisfactory results are obtained by both methods.

INTRODUCTION

Mass spectrometric thermal analysis (MTA) has been applied to various fields¹. In MTA, volatile products formed from a sample heated at a constant rate are analyzed with a mass spectrometer. Since one can obtain information about composition of the volatilized products and their rates simultaneously by MTA, it has an advantage over the other methods of thermal analysis. However, little kinetic analysis of MTA curves has been done. In the previous paper², one of the present authors proposed methods of kinetic analysis of thermoanalytical curves of the derivative type. These methods are applied to thermal depolymerization of poly(methyl methacrylate) (PMMA) of high molecular weight, the mechanism of which has been extensively investigated by many workers^{3,4}, and the kinetic analysis is satisfactorily made. In this paper, we report the results of our kinetic analysis of MTA curves and their comparison with other reports.

EXPERIMENTAL

PMMA was supplied by Dr. Mita of the Institute of Space and Aeronautical Science of Tokyo University. It was polymerized in vacuum by using benzaldehyde anion as an initiator at -78°C , and was purified by reprecipitation. The molecular weight is estimated to be 3,900,000 by measurement of the solution viscosity.

The sample powder (2–5 mg) is put in a groove of 3 mm depth, 0.8 mm width and 15 mm length cut in a sample container, which is a stainless steel disk of 20 mm diameter and 6 mm thickness. The sample container is located beneath the ionization chamber of a time-of-flight mass spectrometer of the Bendix type. The temperature of the sample container is measured and controlled with a thermocouple, inserted through a hole drilled on the side of the container, so that the junction of the thermo-

couple is located beside the center of the groove. The heating rate is 1, 2, 5 or 10°C/min. The volatilized products pass directly to the ionization chamber through two slits above the container, parallel to the groove; the groove and the slits are parallel to the grid to draw out the ions. By this arrangement, the products are analyzed immediately. The ionization energy is set at 20 eV to avoid severe fragmentation, which makes identification of various decomposition products complicated. The pressure around the sample is $<10^{-5}$ torr.

RESULTS AND DISCUSSION

A typical mass spectrum observed is shown in Fig. 1. Ions of mass number 100, 69 and 41 are observed; the ion of mass number 100 is a parent ion of the mono-

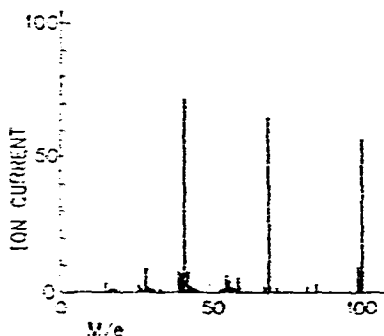
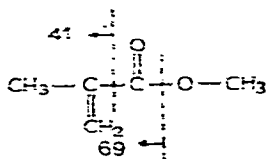


Fig. 1. A typical mass spectrum observed at 296°C. The ionization energy is 20 eV and the heating rate is 2°C/min.

mer and the other ions are all formed by the fragmentation of the monomer, as follows:



The decomposition product of this polymer in high vacuum is mainly its monomer, and this observation is in agreement with the previous observations^{4,5}.

The MTA curves for the mass number of 100, which are the plots of ion current against temperature, are shown in Fig. 2. If the experimental conditions (*e.g.* pumping speed) are kept constant, the ion current is proportional to the rate of volatilization. The curve shifts to the higher temperature as the heating rate increases, and this fact is in accordance with the theoretical relationship. In order to obtain the activation energy², the logarithm of the heating rate is plotted against the reciprocal absolute

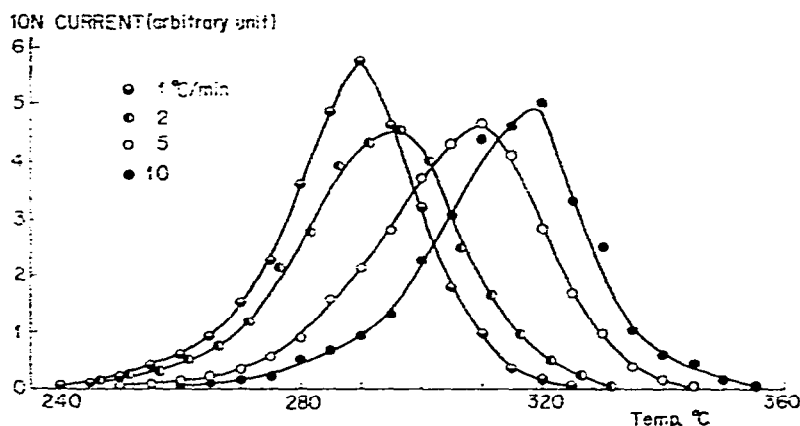


Fig. 2. The MTA curves for the ion, m/e 100. The heating rates are indicated.

peak temperature (Fig. 3). As seen in Fig. 3, a straight line is obtained, and from the slope and the intercept, the activation energy and the logarithm of the pre-exponential factor are estimated to be 49.2 kcal/mole and 16.11 (sec^{-1}), respectively. By using the activation energy obtained, we can draw the experimental master curve² (Fig. 4), which is the plot of the logarithm of the reduced rate, $dC/d\theta$ versus the logarithm of the reduced time, θ . The plots obtained at various heating rates are superposed on a single experimental master curve by a longitudinal shift; this is necessary since we measure not the rate of conversion, but the ion current proportional to the rate of conversion. This fact means that the decomposition reaction is a simple one governed over the entire reaction range by the single activation energy estimated above.

The master curve is compared with the theoretical relationships between $dC/dA\theta$ and $A\theta$ for various mechanisms, and the curve which fits best is that of the first order reaction (shown in Fig. 4 as a solid line). In the comparison of the master curve with the theoretical one, a lateral shift is made, and this shift corresponds to the logarithm of the pre-exponential factor of 16.2 (sec^{-1}). In the beginning of the

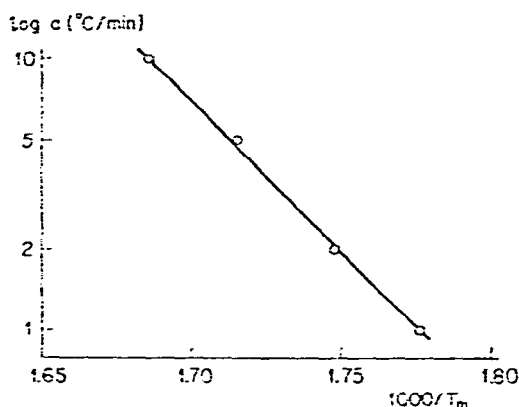


Fig. 3. Plots of the logarithm of the heating rates vs. reciprocal absolute peak temperature.

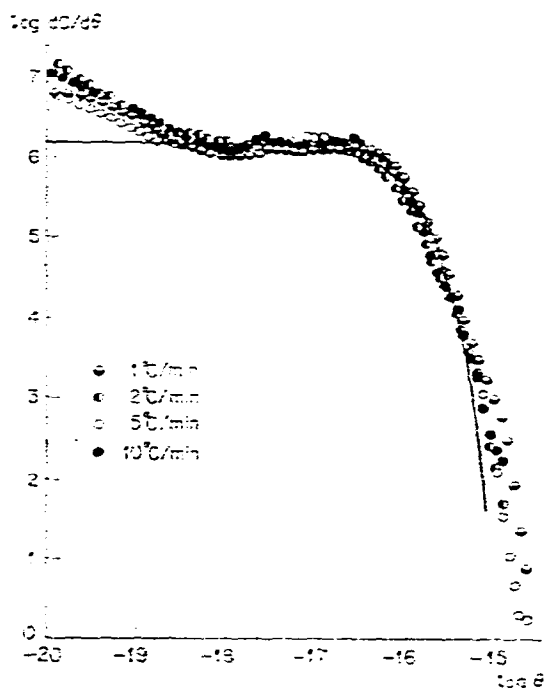


Fig. 4. The experimental master curve and the theoretical curve best fitted to the first order reaction. The heating rates are indicated.

reaction (up to the conversion of about 0.5%), some deviation from the theoretical curve is observed, but the agreement is satisfactory in most of the region of conversion. From this fact, we can deduce that the depolymerization of PMMA proceeds by the mechanism of a first order reaction. The deviation in the beginning might be caused by some minor reactions of diffusion of the product.

The other method proposed by one of the authors² is applied to the MTA curves, since the product is only the monomer and the integration of the MTA curve is proportional to the conversion. First, the MTA curves are integrated by the method of Simpson, and the conversion is estimated as a function of the temperature. Assuming a first order reaction, and using the conversion, we can obtain the reduced rate, $dC/dA\theta$ as a function of the temperature for each curve. The difference between the logarithm of the reduced rate obtained, and the logarithm of the reduced rate calculated, gives the rate constant of the reaction². In Fig. 5 the Arrhenius plot is made for the rate constants estimated in this way. The rate constants estimated for the different heating rates lie on a straight line. From this fact, a mechanism of the first order is deduced and the activation energy and the pre-exponential factor are estimated to be 50.4 kcal/mole and 16.6 (sec^{-1}), respectively. These values are both in good agreement with those estimated by the previous method.

Wilson and Hamaker⁶ observed by MTA that PMMA polymerized with azo-bis-isobutyronitrile initiator, depolymerizes through a two stage reaction. On the

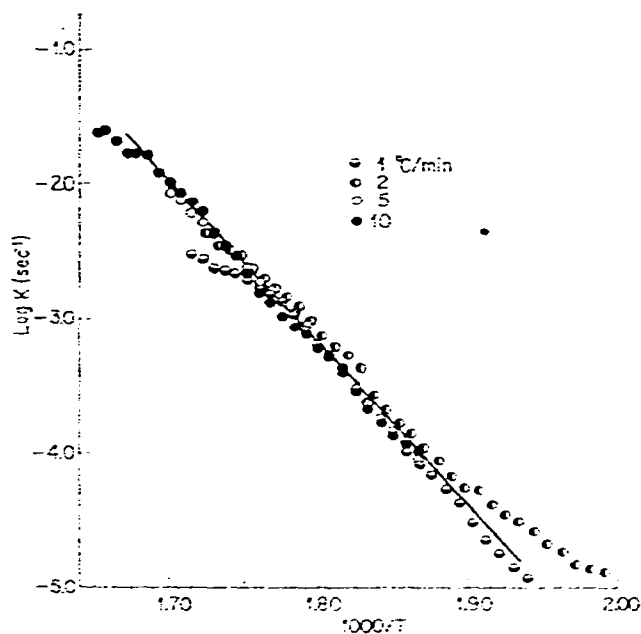


Fig. 5. Arrhenius plots assuming a first order reaction. The heating rates are indicated.

other hand, Madorsky and Strauss⁵ observed a small percentage of volatilization at 150°C, then PMMA partially depolymerized at about 230°C, and the residue, stable at 230°C, depolymerized further at about 300°C. Wall⁷ pointed out a difference in the activation energy of depolymerization reported by several workers; the activation energies reported ranged from 27 to 52 kcal/mole. This difference seems to be caused by the fact that PMMA depolymerizes through a few stages with different mechanisms: *i.e.* depolymerization initiated at the chain end, that initiated randomly in the main chain, and so on. Thus, we must discriminate the stages of depolymerization and also the reaction temperature, when comparing these reports.

Since PMMA studied in this report has a high molecular weight and depolymerizes in a single stage in the high temperature range, the depolymerization initiated at the chain end can be neglected, and the results of our kinetic analysis must be compared with the results obtained for the last stage in the high temperature range. Madorsky and Strauss⁵ reported the first order depolymerization with an activation energy of 52 kcal/mole, for the last stage of depolymerization in the temperature range 296–311°C; while Wilson and Hamaker⁶ obtained results which showed that the reaction in the last stage is of the 1st order, with an activation energy of 44.9 kcal/mole, estimated in the same manner as the second method in this report. Our results are in sufficiently good agreement with these reports, and the methods applied in this paper are proved to be satisfactory. Because these methods are based on general kinetic relationships, they are more widely applicable, especially to high polymers and solid reactions.

In our laboratory, research aimed at elucidating the difference in activation

energy mentioned above is now in progress using various types of PMMA, and we shall report the results in the near future.

ACKNOWLEDGEMENT

The authors would like to express their appreciation to Dr. I. Mita of the Institute of Space and Aeronautical Science of Tokyo University for supplying the sample. They also wish to express their thanks to Mr. K. Yada of the computation center of our laboratory for his assistance in machine computation.

REFERENCES

- 1 H. L. FRIEDMAN, *Thermochim. Acta*, 1 (1970) 199.
- 2 T. OZAWA, *J. Therm. Anal.*, 2 (1970) 301.
- 3 H. H. G. JELLINECK, *Degradation of Vinyl Polymers*, Academic Press, New York, 1955, p. 65.
- 4 S. L. MADORSKY, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964, p. 176.
- 5 S. STRAUS AND S. L. MADORSKY, *J. Res. Nat. Bur. Stand.*, 50 (1953) 165; S. L. MADORSKY, *J. Polym. Sci.*, 11 (1953) 491; S. STRAUS AND S. L. MADORSKY, *J. Res. Nat. Bur. Stand.*, 66A (1962) 401.
- 6 D. E. WILSON AND F. M. HAMAKER, in R. F. SCHWENKER, JR. AND P. D. GARN, (Eds.), *Thermal Analysis*, Vol. 1, Academic Press, New York, 1969, p. 517.