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THERMOGRAVIMETRIC STUDIES OF METAL POLY(METHYL METHACRYLATES)

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ABSTRACT

The thermal stabilities of metal poly(methyl methacrylate)s (PMMA) have been studied by thermogravimetry (TG) between 25 and 550 °C under nitrogen flow. The kinetic data thus obtained show that the thermostabilities decrease in the order, Au-PMMA > Bi-PMMA > In-PMMA > Cu-PMMA > Ge-PMMA > Sb-PMMA > Pd-PMMA > Sn-PMMA > Ga-PMMA, suggesting that thermal stability is dependent upon the metal incorporated in the backbone. The order of reaction for the thermal decomposition of these metal polymers was found to be zero. The pre-exponential factor, the reaction order and the activation energy of the decomposition for metal poly(methyl methacrylates) have been determined and the reactions found to be zero order.

INTRODUCTION

The thermal stability of polymers is particularly interesting due to their potential applications as substituents of pure metals [1] and for their semiconductor properties [2].

By considering the thermal behaviour of polymers as a function of the weight loss and the temperature of the system, it is possible to obtain some information about their stability. Nowadays, industry is trying to find new thermostable polymers to be used in aircraft, electronics and car parts.

Thermogravimetry (TG) has been used as a method of investigation of the thermal stability and characteristics of thermal decomposition of polymers. Kinetic parameters such as activation energy, pre-exponential factor and reaction order, give a quantitative measure of thermal stability [3]. Since there have been no reports concerning polymers with incorporated metals such as metal poly(methyl methacrylates) prepared by chemical liquid

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deposition [4] we have developed thermal degradation studies. We report here upon several poly(methyl methacrylates) containing metals such as Pd, Au, Cu, Ga, In, Ge, Sn, Sb and Bi.

EXPERIMENTAL

Colloid synthesis

Colloid synthesis using a metal atom reactor has been previously reported [5–7].

Polymerization

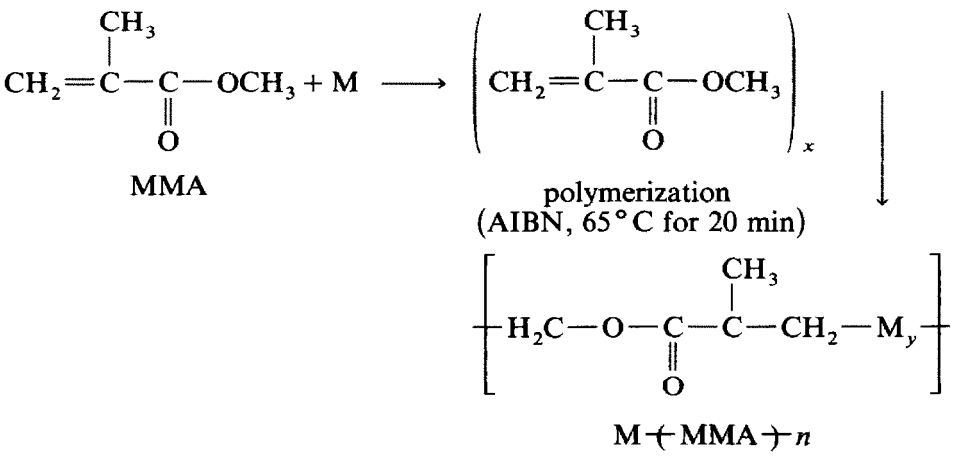
As a typical example, Au colloid (10 ml) was placed in a schlenk ware flask with 0.1 mol% of azodiisobutyronitrile (AIBN) under N_2 flow. The schlenk was closed and placed in an isothermal bath at 65 °C for 3 h. The contents of the schlenk were poured into a beaker containing methanol. The purple polymer was filtered off and dried under vacuum (10^{-2} Torr) for 24 h at 20 °C. The yield of the polymer was then determined.

Thermogravimetry

Thermogravimetric data was obtained using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (2–6 mg) were placed in Al pans and heated under flowing nitrogen (50 ml min^{-1}) at a rate of 10 °C min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of polymers with metal incorporated from sols or metal dispersed in monomers is rather new [8]. The polymers obtained have a wide range of molecular weight and color, depending upon the metal.



The polymers show a low metal incorporation (2%); this is due to the sol concentration which is around 10^{-3} M. The viscosimetric molecular weights range between 2.7 and 5×10^5 [8].

In Fig. 1 we can observe the change in sample weight as a function of time and temperature when the nine metal poly(methyl methacrylates) are heated from 298 to 823 K. Table 1 shows the thermal decomposition temperatures (T_D) for each polymer. These values were taken from the first large change in the slope of the TG curve.

The polymers degrade in one stage and present a T_D around 500 K. The data suggest that the thermal stability of these polymers is influenced by the metal attached to the chain. It is interesting to note that Au-PMMA and Bi-PMMA present the highest T_D values (573 and 598 K), and also the highest E_a values. Ga-PMMA is the most unstable polymer with a T_D of 473 K and the lowest E_a.

The decomposition reaction is irreversible so that the rate dependent parameters such as activation energy and order of reaction may be calcu-

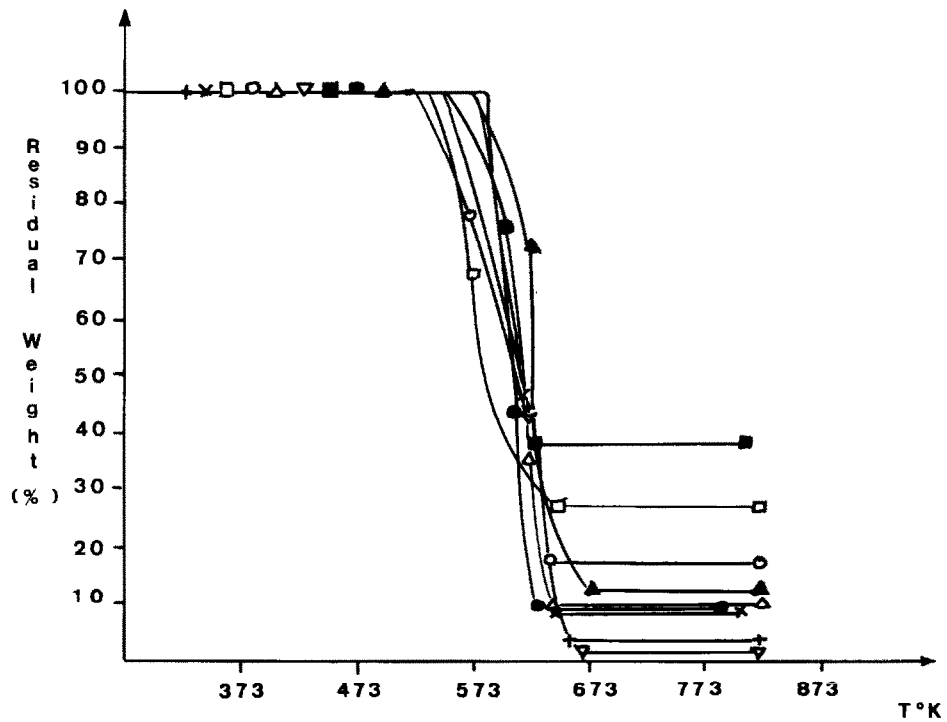


Fig. 1. Thermogravimetric curves of metal poly(methyl methacrylates) at a heating rate of 10 °C min^{-1}: ▲, Bi-PMMA; ■, Sn-PMMA; +, Au-PMMA; ×, Pd-PMMA; □, Cu-PMMA; ○, Ge-PMMA; △, Ga-PMMA; ▽, In-PMMA; ●, Sb-PMMA.

TABLE 1

Kinetic parameters for metal poly(methyl methacrylates)

Polymer	Z (s^{-1})	E_a (kJ mol^{-1})	n	T_D (K)
Au-PMMA	2.6×10^4	99.33	0	573
Bi-PMMA	2.3×10^2	78.91	0	598
In-PMMA	1.4×10^2	74.27	0	548
Cu-PMMA	2.4×10^2	70.67	0	513
Ge-PMMA	4.8×10^1	64.10	0	498
Sb-PMMA	2.5×10^1	63.97	0	548
Pd-PMMA	1.5×10^1	61.50	0	523
Sn-PMMA	1.4×10^1	61.09	0	523
Ga-PMMA	4.3	51.58	0	473

lated from a single experimental curve [9]. The specific rate constant (k) can be expressed in the Arrhenius form

$$k = Z\exp(-E/RT) \tag{1}$$

where Z is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

According to Freeman and Carroll [9] if we consider a reaction in the liquid or solid state, in which one of the products is volatile and all the others are in the condensed state

$$a\mathrm{A} \rightarrow b\mathrm{B(g)} + c\mathrm{C} \tag{2}$$

the rate expression for the disappearance of reactant A from the mixture is

$$-\mathrm{d}X/\mathrm{d}t = kX^n \tag{3}$$

where X is the amount of reactant A, k is the specific rate constant and n is the order of the reaction with respect to A.

The thermal decomposition kinetics of the thermogravimetric weight loss were attributed to the kinetic equation

$$\frac{-\mathrm{d}\alpha}{\mathrm{d}t} = K(1-\alpha)^n \tag{4}$$

where α is a fraction of the sample weight reacted at time t, n is the reaction order and K is the specific rate constant. The reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$ was calculated using a differential technique and incorporating the heating rate ($10\,^\circ\mathrm{C\ min^{-1}}$), using the data from temperature versus sample weight fraction [10]. Equations (1), (3) and (4) are combined incorporating v and using the logarithmic form

$$\beta = \ln\left|-\frac{\mathrm{d}\alpha/\mathrm{d}T}{v(1-\alpha)^n}\right| = \ln A - \frac{E}{RT} \tag{5}$$

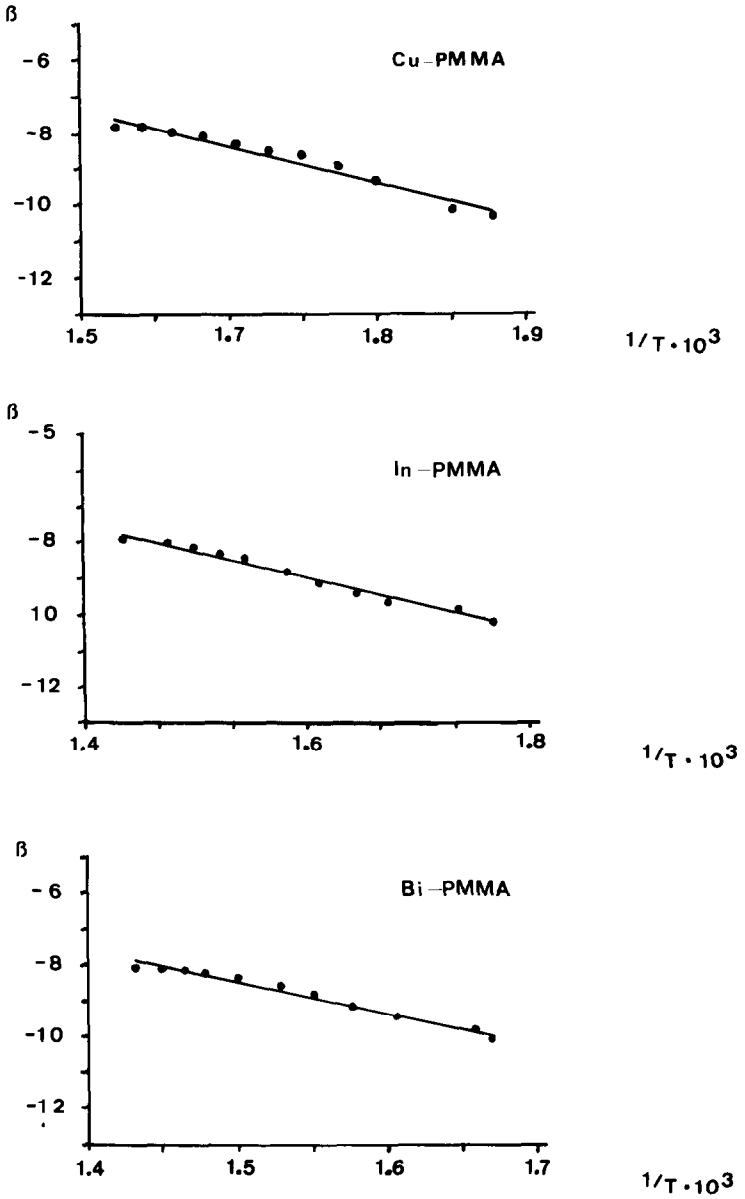


Fig. 2. Arrhenius plot for the thermal degradation of metal poly(methyl methacrylates) according to eqn. (5).

To calculate the kinetic parameters E and Z and assuming a first-order reaction model, a multiple regression program was used. Plotting β versus $1/T$ should give a straight line (see Fig. 2). From the slope and intercept E and Z can be determined.

For all the metal polymers the linear relationship obtained indicated that the order of the reaction is zero. The coefficients of linear correlation vary

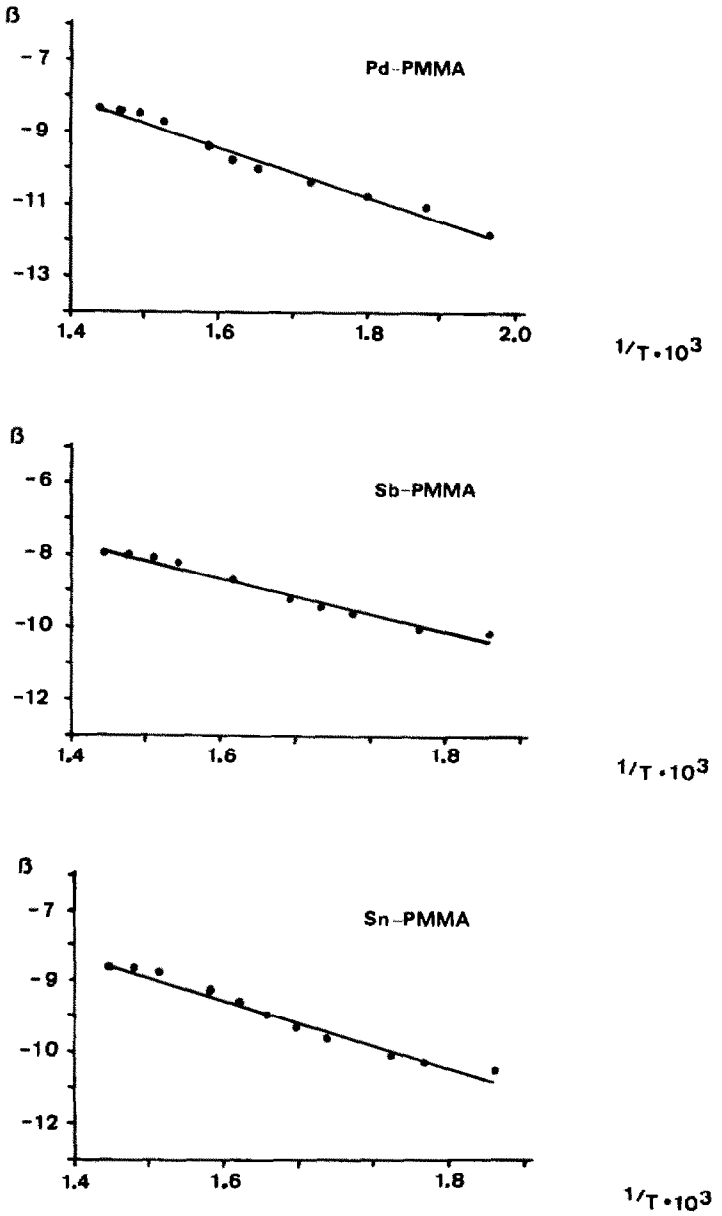
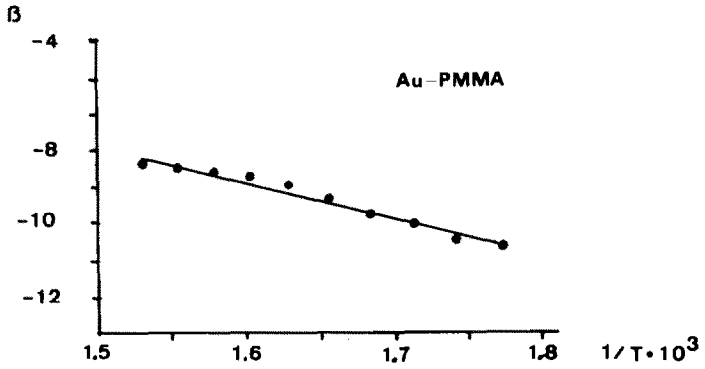
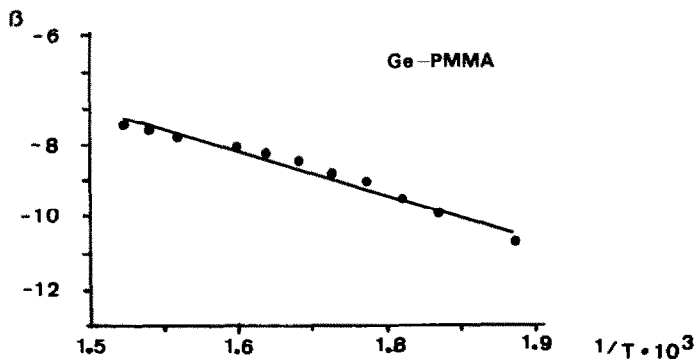


Fig. 2 (continued).

from 0.986 to 0.996. The kinetic parameters E and Z calculated from these plots are summarized in Table 1.

In general, all the polymers showed low activation energies, but larger than some poly(dialkylphenyl methacrylates) [11]. They range from 51.58 to 99.33 for Ga and Au, respectively.





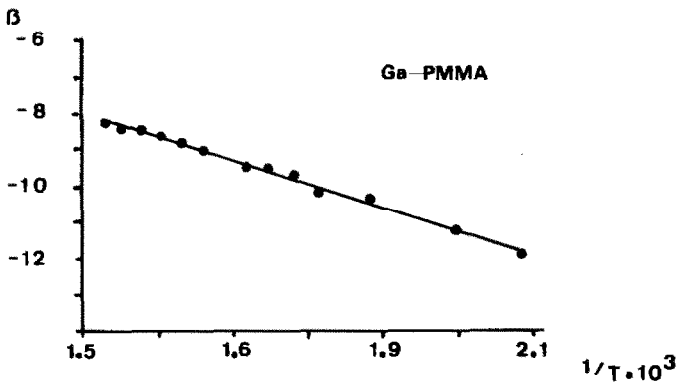


Fig. 2 (continued).

The kinetic parameters obtained for the thermal decomposition of these polymers show a relationship between the metal and activation energy. Au-PMMA is a very stable dispersion and also gold is a very stable metal; Ga, for instance, is easily oxidized and Ga-PMMA shows a lower E_a and

also the lowest T_D. Furthermore, we can suggest that for similar metals like Ge and Sn their activation energy values are in the same range, which might indicate the influence of the metal. Finally, we can conclude that the order of reaction for the decomposition of metal poly(methyl methacrylates) is zero, although no previous literature references have been found concerning the kinetics of the decomposition of this recently reported family of polymers [8,12].

ACKNOWLEDGEMENTS

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