Thermochimica Acta, 200 (1992) 361–369
Elsevier Science Publishers B.V., Amsterdam

Thermogravimetric studies of metal (styrene–methyl methacrylate) copolymers.
Part 5

Galo Cárdenas T. [a] and Luis H. Tagle D. [b]

[a] *Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción (Chile)*
[b] *Departamento de Química Orgánica, Facultad de Química,*
Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)

(Received 16 August 1991)

Abstract

Metal (styrene–methyl methacrylate) copolymers were obtained by radical polymerization with azodiisobutyronitrile.

The thermal stabilities of the metal copolymers (PS–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: Pd–(PS–PMMA) > Au–(PS–PMMA) > Ge–(PS–PMMA) > Bi–(PS–PMMA) > Sn–(PS–PMMA) > Cu–(PS–PMMA) > In–(PS–PMMA) > Ga–(PS–PMMA), suggesting that thermal stability is dependent upon the metal incorporated in the backbone. The order of reaction from the thermal decomposition of these metal copolymers was found to be zero. The pre-exponential factor, the reaction order and the activation energy of the decomposition for metal (styrene–methyl methacrylate) copolymers have been determined and the reactions found to be zero order in most of them.

INTRODUCTION

The thermal stability of polymers is very important owing to the demand for polymers which could be used in high-temperature applications. Several studies have investigated the relationships between thermal stability and chemical structure [1].

The interest in producing non-metallic materials with high temperature stability is growing again and it is important that the difficulties and limitations of TG be appreciated by those who apply the technique. TG and DTA can be combined to measure in more detail some of the chemical changes that take place when a polymer is heated beyond its point of decomposition [2,3].

Correspondence to: G. Cárdenas T., Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción, Chile.

0040-6031/92/$05.00

Degradation reactions are initiated or strongly influenced by impurities in the sample, especially if these are incorporated into the polymer chain.

Thermogravimetry (TG) has been used to determine the activation energy, pre-exponential factor and reaction order, assuming a simple mechanism and a rate expression.

This is the first report of styrene–methyl methacrylate copolymers with metals in the backbone, prepared by chemical liquid deposition [4]. Several copolymers containing the metals palladium, gold, copper, gallium, indium, germanium, tin, antimony and bismuth are described.

EXPERIMENTAL

Colloid synthesis

Colloid synthesis using codeposition with metal atoms has recently been reported by our group [5–8].

Polymerization

As a typical example, copper colloid (10 ml) was placed in a polymerization flask with 0.1 mol.% of azodiisobutyronitrile (AIBN) under nitrogen flow. The flask was closed and placed in an isothermal bath at 65°C for 1 h. The contents of the flask were quenched in 100 ml of methanol. The black copolymer was filtered off and dried under vacuum (10^{-2} Torr) for 24 h at 25°C. The yield of the polymer was then determined.

Thermogravimetry

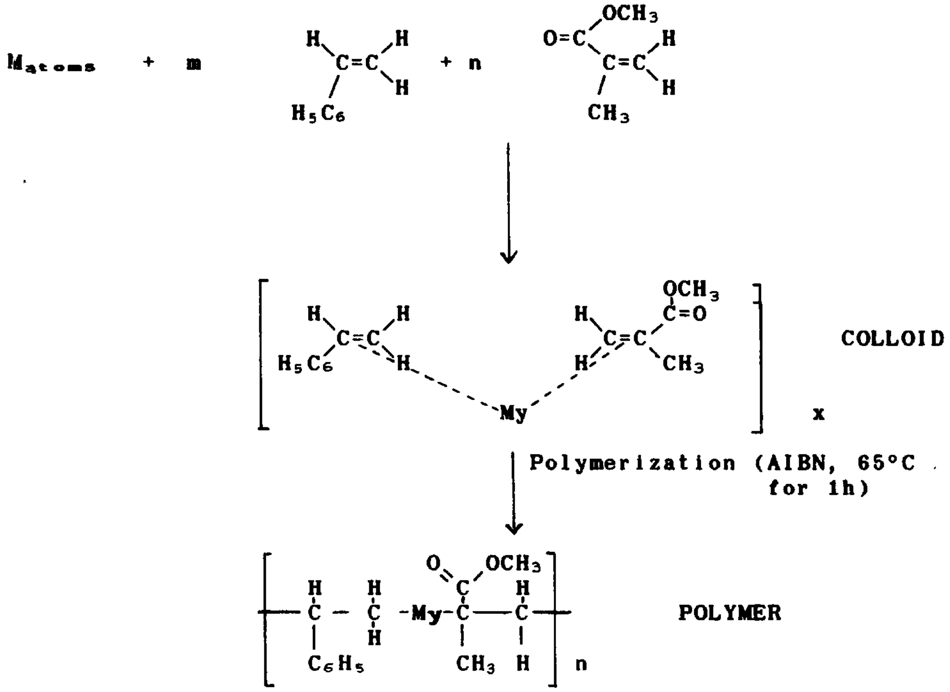
Thermogravimetric data were obtained using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature-program control. Samples (2–5 mg) were placed in aluminium pans and heated under flowing nitrogen (50 ml $\min^{-1}$) at a rate of 10°C $\min^{-1}$ between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of polymers with metal incorporated from sols or with metal dispersed in the monomers, was recently reported by our group [7–9].

The polymers obtained have a wide range of molecular weight, colour and stability, depending upon the metal.

The copolymers show metal incorporation ranging between 0.9% and 11%, with the exception of Au–PSMMA (22%). The average molecular



M = Pd, Cu, Au, Ga
In, Ge, Sn, Sb, Bi.

weights ($\overline{Mv}$) range between 85.6 × 10^3 and 187 × 10^3 [10]. These copolymers exhibit lower $\overline{Mv}$ values than the methyl methacrylates already reported [11].

Figure 1 shows the change in sample weight as a function of time and temperature when the eight metal (styrene–methyl methacrylate) copolymers are heated from 298 to 823 K. Table 1 shows the thermal decomposition temperatures (T_D) for each copolymer. These values can be considered to be very close to those reported for PMMA [11]. In these copolymers, Pd and Au copolymers are the most stable and Ga–PMMA is the least stable (470 K).

The copolymers degrade in one step with T_D values between 500 and 600 K. At temperatures in the region of 503 K, the macromolecules break down at the chain-ends and the monomer is evolved by reverse polymerization until all the chains have been destroyed [12]. The thermal stability of these copolymers is directly related to the metal incorporated: Bi–PSMMA and Au–PSMMA have the highest E_a values (66.33 and 54.60 kJ mol^{-1}) and high T_D values; Ga–PSMMA is also the most unstable copolymer, with a T_D of 470 K and the lowest E_a value (15.35 kJ mol^{-1}). This value is even lower than that obtained for poly(methyl methacrylate) [9].

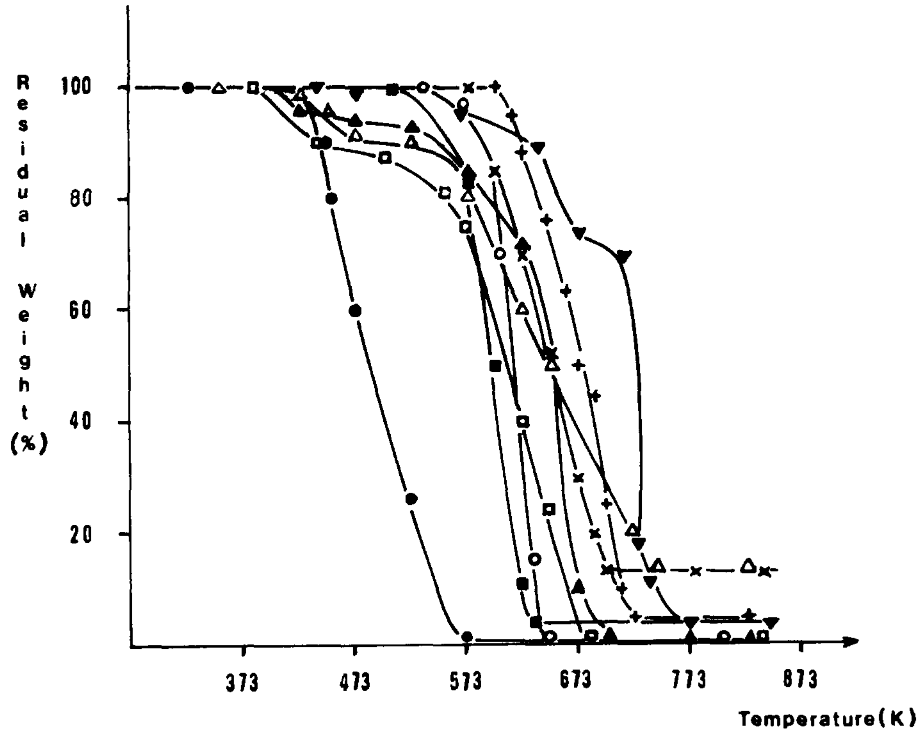


Fig. 1. Thermograms of metal (styrene–methyl methacrylate) copolymers obtained heating the polymers from 298 to 823 K at 10°C min^{-1}: +, Pd–(PS–PMMA); ×, Au–(PMMA); ▲, Ge–(PS–PMMA); ○, Bi–(PS–PMMA); ■, Sn–(PS–PMMA); □, Cu–(PMMA); ●, In–(PS–PMMA); △, Ga–(PS–PMMA).

We propose that metals are important in the thermal behaviour of th copolymers. The T_D values were taken from the first substantial change the slope of the TG curve.

The rate equation for a mechanism involving a sequence of consecut reactions, such as a free radical chain-reaction, can be expressed i reasonably simple form. The decomposition reaction is irreversible so t the rate-dependent parameters such as activation energy and order reaction may be calculated from a single experimental curve [9]. T specific rate constant k can be written according the Arrhenius equati

$$k = Z\,e^{-E_a/RT}$$

in which Z is the pre-exponential factor, E the activation energy, R the constant and T the absolute temperature.

According to Freeman and Carroll [13], if we consider a reaction in liquid or solid state, in which one of the products is volatile and all others are in the condensed state

$$aA \rightarrow bB(g) + cC$$

TABLE 1

Kinetic parameters for metal (styrene–methyl methacrylate) copolymers

Polymer	Z (s^{-1})	E_a (kJ mol^{-1})	n	T_D (K)
In–PSPMMA [a]	8.4×10^1	26.15	−0.5	473
Bi–PSPMMA	1.6×10^7	66.33	0	573
Cu–PSPMMA	1.1×10^{-1}	17.27	0	480
Sn–PSPMMA	1.2×10^5	51.58	0	523
Ga–PSPMMA	3.7×10^{-2}	15.35	0	470
Ge–PSPMMA [a]	1.0×10^0	22.2	0	583
Pd–PSPMMA	3.5×10^1	35.70	0	598
Au–PSPMMA [a]	1.2×10^5	54.60	−0.5	588
PSPMMA	1.2×10^3	45.12	0	505

[a] Secondary reactions probably take place during the decomposition. In addition, the In polymers decompose at low temperatures.

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

$$-\mathrm{d}X/\mathrm{d}t = kX^n \qquad (3)$$

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

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

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 v (10°C min^{-1}) using temperature versus sample weight fraction data [13]. Equations (1), (3) and (4) were combined, incorporating v and using the logarithmic form

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

To calculate the kinetic parameters E and Z and to assess 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 [14].

For most of the copolymers, the linear relationship obtained indicated that the order of the reaction is zero. Au and In copolymers exhibit the best correlation for $n = -0.5$, which is probably owing to a more complex decomposition mechanism. The only exception is the Ge copolymer in

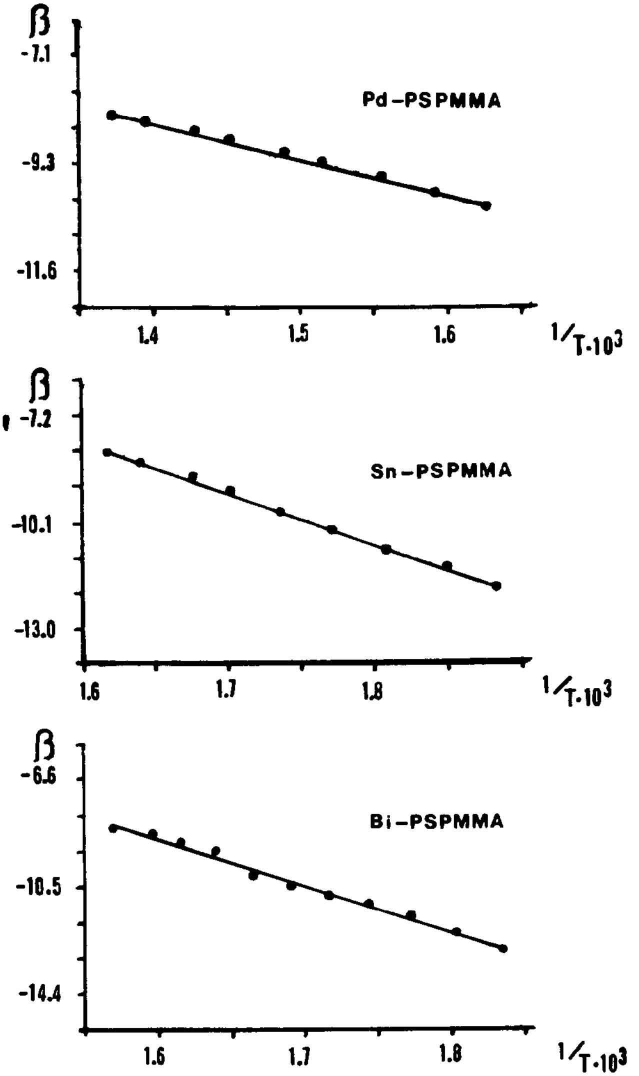


Fig. 2. Arrhenius plot for metal (styrene–methyl methacrylate) copolymers according to eqn. (5).

which secondary reactions can take place during the decomposition; although this copolymer has a low E_a value, it is not comparable with the others because of its unusual TG behaviour. In general metal polystyrenes are more stable [15].

In fact, Au, Sn and Bi copolymers showed high activation energies that are, however, smaller than the corresponding poly(methyl methacrylates) [11]. The coefficients of linear correlation vary from 0.984 to 0.997. The kinetic parameters E and Z calculated from these plots are summarized in Table 1.

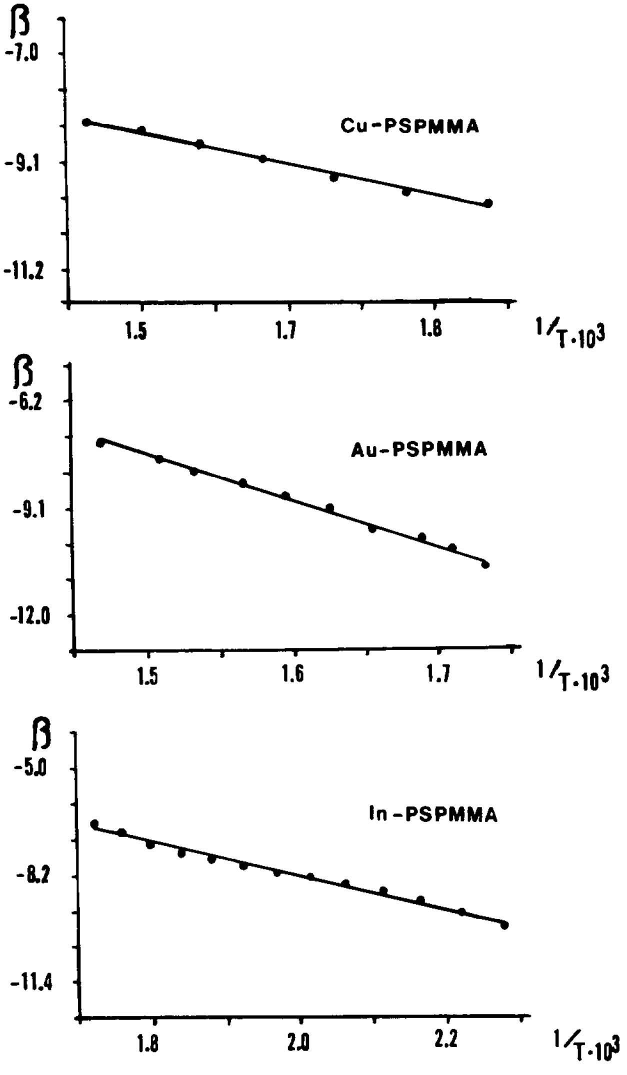


Fig. 2 (continued).

These copolymers have much lower activation energies than the corresponding metal polystyrenes recently reported [16]: they range from 15.35 to 66.33 for Ga–PSPMMA and Bi–PSPMMA, respectively.

The kinetic parameters obtained for the thermal decomposition of these polymers show a relationship between the metal and the activation energy. Au–, Sn– and Bi–PSPMMA are stable dispersions, and, moreover, Au–PSPMMA is not easy to oxidise. However, Ga–PSPMMA is oxidised more easily, having a lower E_a and also the lowest T_D. This behaviour is identical to that of Ga–PMMA already reported [11,15]. In addition, we can propose that for similar metals, such as Bi and Sn, their activation energies are in

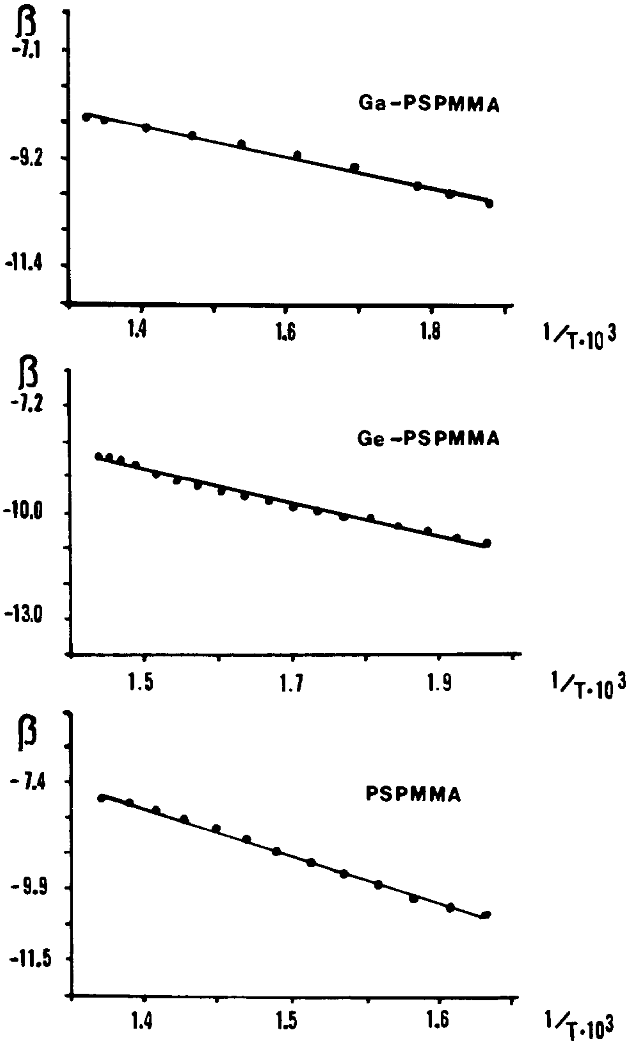


Fig. 2 (continued).

the same range, which might indicate the influence of the metal. Finally, we conclude that the order of reaction for the decomposition of metal (styrene–methyl methacrylate) copolymers is zero for most of the metals studied.

ACKNOWLEDGMENTS

The support of Fondecyt (Grant 89/0702) and Dirección de Investigación from Universidad de Concepción (Grant 91.1386-1) is gratefully acknowledged.

REFERENCES

1 R.H. Still, in N. Grassie (Ed.), Development in Polymer Degradation, Vol. 1, Applied Science, London, 1977, p. 1.
2 J.R. MacCallum, in G. Allen (Ed.), Comprehensive Polymer Science, Vol. 1, Pergamon, London, 1989, p. 903.
3 I.C. McNeiel, in G. Allen (Ed.), Comprehensive Polymer Science, Vol. 1, Pergamon, London, 1989, p. 456.
4 G. Cárdenas-Triviño and K.J. Klabunde, Bol. Soc. Chil. Quim., 33 (1988) 163.
5 G. Cárdenas-Triviño, K.J. Klabunde and E.B. Dale, Langmuir, 3 (1987) 986.
6 G. Cárdenas-Triviño, K.J. Klabunde and E.B. Dale, Proc. Opt. Eng. SPEI, 821 (1987) 206.
7 K.J. Klabunde, J. Habdas and G. Cárdenas-Triviño, Chem. Mater., 1 (1989) 481.
8 G. Cárdenas-Triviño, C. Retamal C. and K.J. Klabunde, Bol. Soc. Chil. Quim., 35 (1990) 223.
9 G. Cárdenas-Triviño, C. Retamal C. and K.J. Klabunde, Polymer Bull., 25 (1991) 315.
10 G. Cárdenas T. and C. Retamal C., XIX Jornadas Chilenas de Química, Nov. 1991, Catillo (Chile), p. 200.
11 G. Cárdenas T., C. Retamal C. and K.J. Klabunde, Thermochim. Acta, 176 (1991) 233.
12 J.R. MacCallum, Br. Polym. J., 11 (1979) 121.
13 E.S. Freeman and B. Carroll, J. Phys. Chem., 621 (1958) 394.
14 W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.
15 G. Cárdenas-Triviño, C. Retamal C. and K.J. Klabunde, J. Appl. Polym. Sci. Appl. Polym. Symp., 49 (1991) 15.
16 G. Cárdenas T., C. Retamal C. and L.H. Tagle D. Thermochim. Acta, in press.