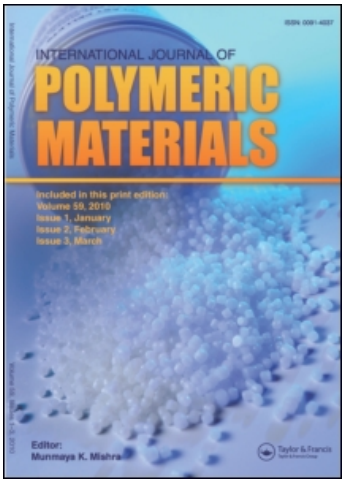

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Thermal Analysis of Metal Poly(Ethyl Methacrylates) Part VII

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The thermal stabilities of metal poly(ethyl methacrylates) (PEMA) have been studied by thermogravimetry (TG) between 25 and 550°C under nitrogen flow. The kinetic data for Pd-PEMA decreases with the lowering of molecular weights fraction. In general, the thermostabilities decrease in the order Cu-PEMA > Ge-PEMA > Pd > PEMA > Au-PEMA > Al-PEMA > Cd-PEMA > In-PEMA > Zn-PEMA > Sn-PEMA > Ag-PEMA > Ga-PEMA suggesting that thermal stability is depending upon the thermal conductivity of the metal incorporated in the backbone polymer. It was observed that metals with higher thermal conductivity exhibit higher thermal decomposition temperature (T_D). 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(ethyl methacrylates) have been determined.

KEY WORDS Thermal analysis, metal, poly(ethyl methacrylate), thermal stability.

INTRODUCTION

Thermogravimetry has been used widely as a means for assessing the thermal stability of polymeric materials.[1] Several investigations were carried out to find a relationship between thermal stability and chemical structure.[2] In general, the systems are too complex to get quantitative information.

On heating a polymer, decomposition takes place in a medium of high viscosity and is possible that chemical and physical control might be present during degradation reactions. But it is clear that high values of activation energy are related with thermally stable materials.[3]

A good knowledge of the kinetic behaviour can give as a good idea of solid state reaction processes during thermal decomposition. The incorporation of metals or

metal clusters in polymers should increase their thermal stability and increase their semiconductor properties.[4,5]

The aim of this report about poly(ethyl methacrylates) with several metals incorporated is to find out a relation between kinetic parameters values and thermal stability. This is the first report of these polymers with metal prepared by codeposition technique at low temperature. Here we report several poly(ethyl methacrylates) containing metals such as Pd, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Ge, Sn, Sb and Bi.

EXPERIMENTAL

Colloid Synthesis

The colloids were prepared by codeposition of the monomer (EMA) with the metals at 77 K using a metal atom reactor.[6,7] Based on metal evaporated and ethyl methacrylate inlet, the approximate concentration could be calculated.

Polymerization

As a typical example, Cu colloid (10 ml) was placed in four polymerization flasks with 0.1, 0.2, 0.5 and 1.0 mol% of azodiisobutyronitrile (AIBN) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 62°C for 40 min. The content of each flask was poured into a beaker containing methanol. The dark blue polymer was filtered off and dried under vacuum (10^{-3} Torr) for 24 h at 35°C. The yield of the polymer was then determined.

Elemental Analysis

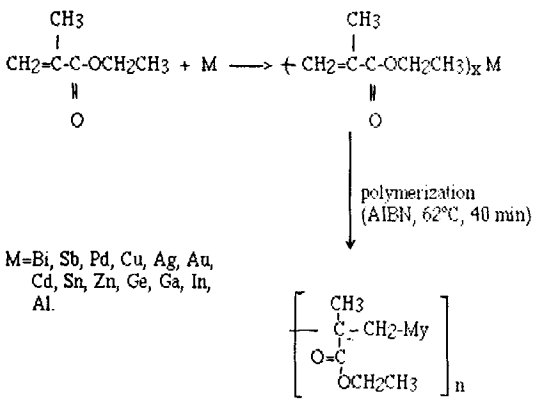
The samples for microanalysis of metals were handled by Inorganic Laboratories. The carbon, hydrogen were performed by the Organic Laboratories, both from the Chemistry Department at the University of Concepción.

Thermogravimetry

The thermogravimetric data were obtained using a Perkin-Elmer TGA-7 thermobalance. Samples (2–5 mg) were placed in aluminum pans and heated under nitrogen flow (50 ml min^{-1}) at 10°C min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of polymers with metal atoms or clusters incorporated in polymeric materials is rather new.[8] Wright has also reported about synthetic approach to obtain metal cluster trapped in polymers based on the clustering of atoms in organic monomers.[9] This approach allowed us to obtain polymer with several colors and a wide range of molecular weight, depending upon the metal. The scheme below summarized the synthesis of this polymer.



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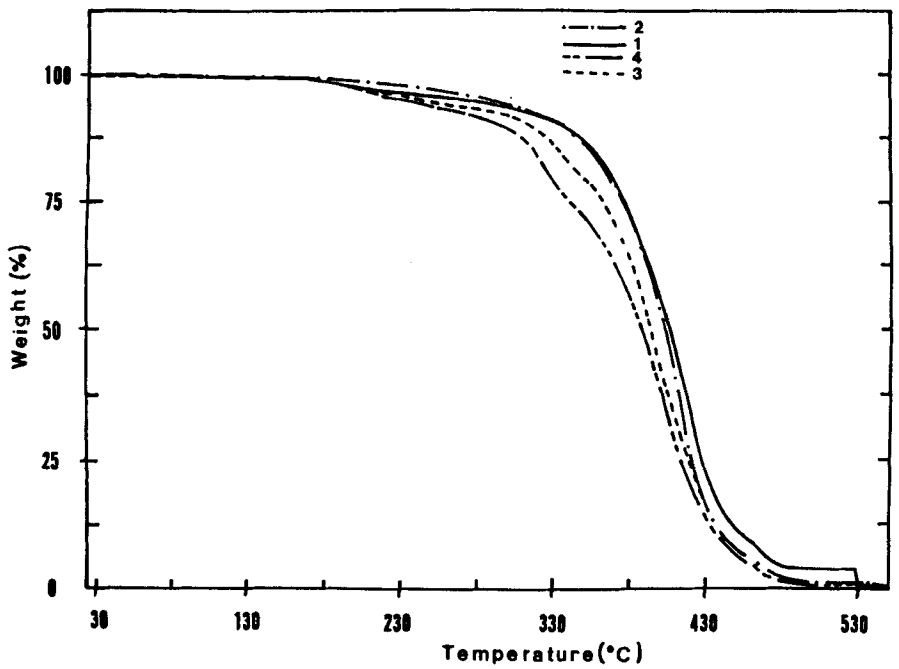


FIGURE 1 Thermogram of Pd-poly(ethyl methacrylates) corresponding to four M.W. fractions (0.1, 0.2, 0.5 and 1.0 mol% AIBN).

From the microanalysis it was possible to compare the different polymers. For example, the 0.1 mol% AIBN exhibit higher metal concentration in the polymer than 1.0 mol% AIBN. This is probably due to the great radical concentration in solution that are able to react with the metal or clusters. The polymers show a low metal incorporation between 0.07% (Cd-PEMA) and 0.72% (Pd-PEMA). These values are even lower than reported previously for poly(methyl methacrylates).[10] The sol concentrations range between 4.5 and 48 $\times$ 10^{-3} M. The viscosimetric molecular weights range between 4.5 and 11.8 $\times$ 10^{5} (g mol^{-1}) for the 1 mol%

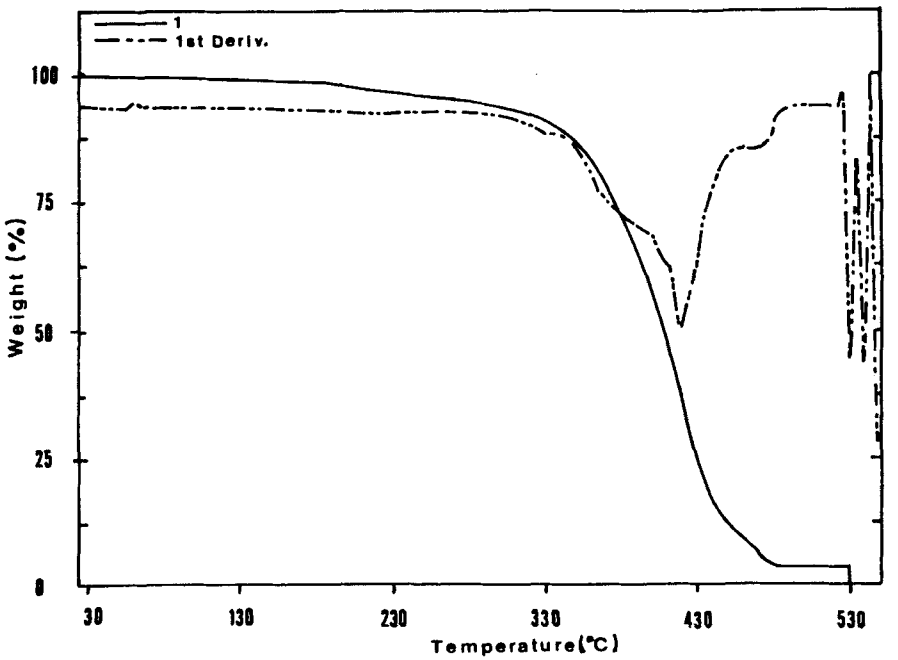


FIGURE 2 Thermogram of Pd-PEMA (0.1 mol% AIBN) and the first derivative. T_D = 420°C.

initiator. In all the metals, these values are higher than the MW reported for PMMA.[11]

In Figure 1 we observe the change in sample weight as a function of time and temperature when the four fractions of Pd-PEMA are heated from 25 to 550°C. We can observe that the higher T_D are consistent with the highest molecular weights. In Figure 2 we have the thermogram of Pd-PEMA; the first derivative shows a T_D at 420°C. Table I summarizes the thermal decomposition temperatures (T_D) for each polymer. These values were taken from the first derivatives of the TG curve.

All the polymers degrade in one stage and exhibit a T_D around 400°C, a little lower than PMMA.[10] The data suggest that the thermal stability of these polymers is strongly influenced by the metal attached to the chain and by the concentration of the sol. Pd-PEMA and Al-PEMA present the highest T_D values (420°C), and also a high activation energy (Ea) values. Cu-PEMA is the most unstable polymer with a T_D of 226°C.

The decomposition reaction is irreversible so that the rate dependent parameters such as activation energy and order of reaction may be calculated from a single experimental curve.[12] The specific rate constant k can be expressed in the Arrhenius equation.

$$k = A \exp(-Ea/RT) \tag{1}$$

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

TABLE I

Kinetic parameters of metal poly(ethyl methacrylates)

POLYMER	M+1 E-3 (g/mol)	REACTION ORDER	Ea (KJ/n)	A (seg^{-1})	THERMAL CONDUCTIVITY (w/cm K)	SPEC.CAPAC. (J/gK)	T_D(°C)
Cu-PEMA(1)	615.4	0	36.41	279.74	4.01	0.38	260
Cu-PEMA(2)	615.4	0	35.16	97.51	4.01	0.38	343
Ge-PEMA(F1)	455.2	0	34.6	19.88	0.599	0.32	410
Ge-PEMA(F4)	79.3	0	20.13	0.18	0.599	0.32	--
Pd-PEMA(F1)	--	0	32.59	9.02	0.718	0.24	420
Pd-PEMA(F2)	--	0	30.86	2.2	0.718	0.24	408
Pd-PEMA(F2)	--	0	26.89	888.91	0.718	0.24	401
Pd-PEMA(F4)	--	0	20.27	0.11	0.718	0.24	400
Au-PEMA	708.40	0	30.28	4.57	3.17	0.128	410
Al-PEMA	--	0	27.9	2.16	2.37	0.9	420
Ga-PEMA	789.2	0	2.50	1.84	0.406	0.37	410
Cd-PEMA	967.4	0	27.08	1.55	0.968	0.23	410
In-PEMA	--	0	26.04	1.55	0.968	0.23	385
Zn-PEMA	--	0	25.55	1.01	1.16	0.39	390
Sn-PEMA	622.9	0	25.23	0.75	0.66	0.227	424
Ag-PEMA	947.2	0	22.96	0.48	4.29	0.235	390

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

$$\frac{-d\alpha}{dt} = k(1 - \alpha)^n \tag{2}$$

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 ($d\alpha/dt$) was calculated using a differential technique with a heating rate, (v) of 10°C min^{-1}. Since $d\alpha/dt = v(d\alpha/dT)$ and after combining and rearranging terms we can establish Equation (3).

$$\beta = \ln\left[-v\frac{d\alpha}{dT}\left(\frac{1}{1-\alpha}\right)^n\right] = \ln A - Ea/RT \tag{3}$$

A computer linear multiple-regression program was used to calculate the kinetics parameters E and A using a linear least-squares fit of the data in a semilog plot of β versus $1/T$. This program is somehow similar to that one reported recently by Ma and coworkers.[13]

For all the metal-PEMA the linear relationship obtained indicated that the order of the reaction is zero. The coefficients of linear correlation vary from 0.986 to

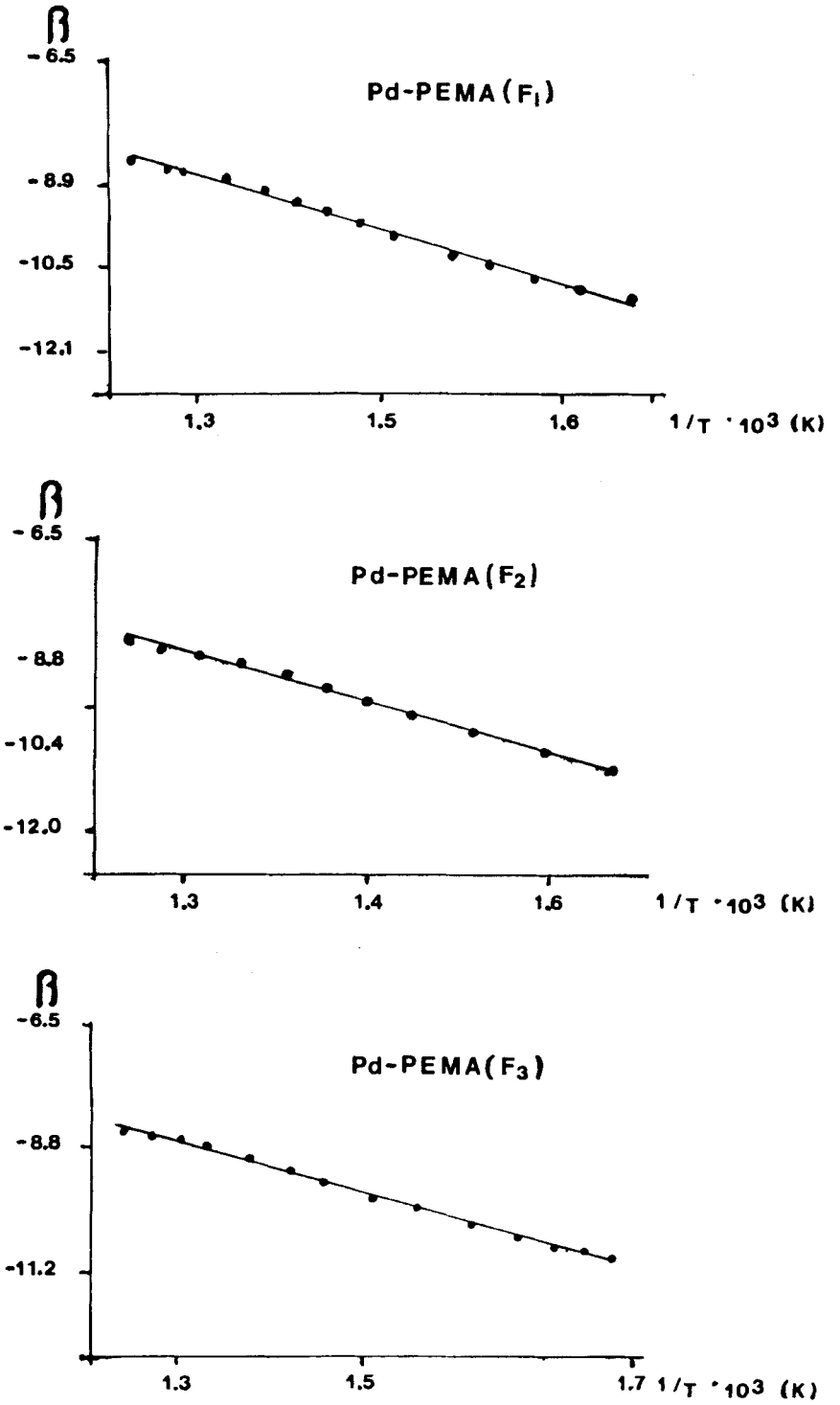
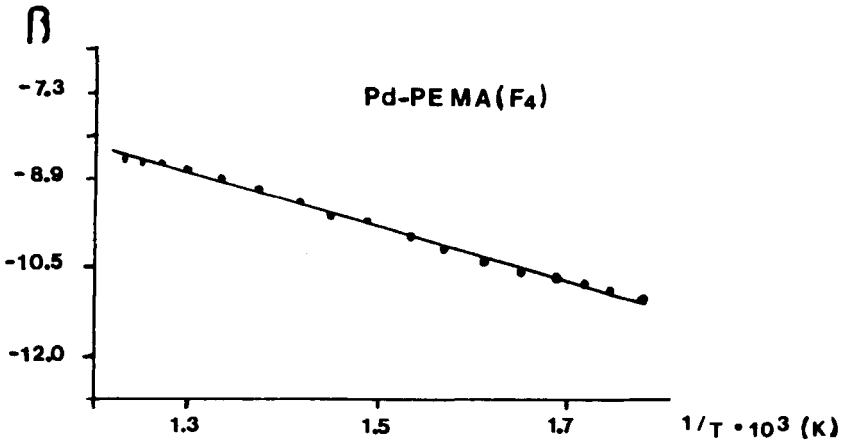
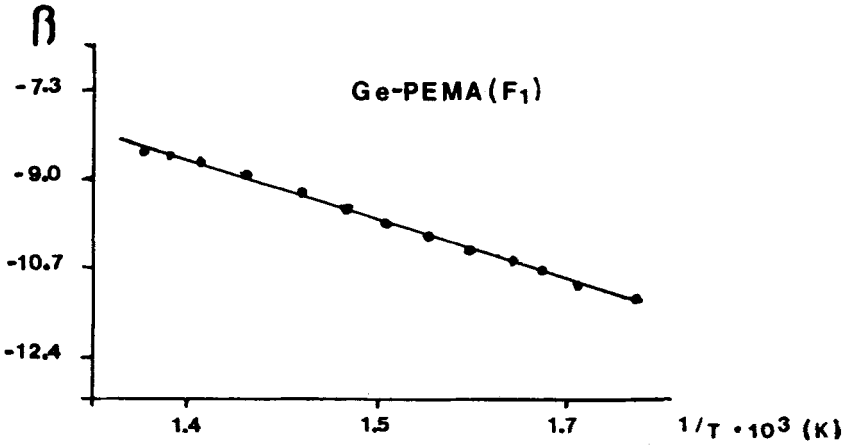


FIGURE 3 Arrhenius plot for the thermal degradation of poly(ethyl methacrylates).





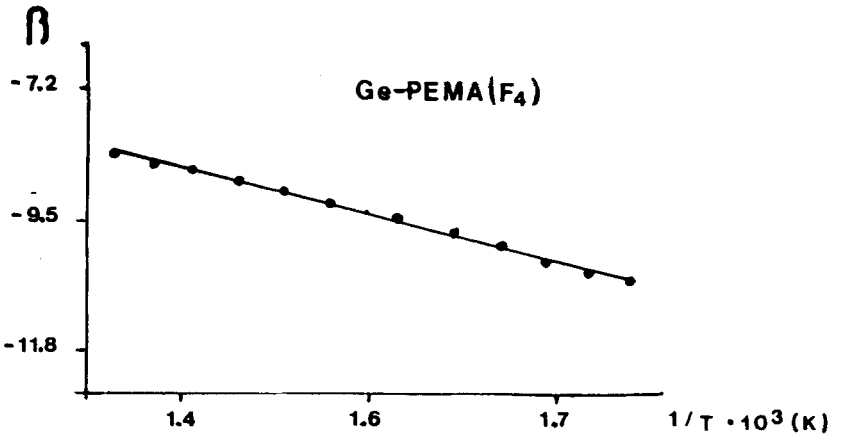


Figure 3 (*Continued*)

0.997. The kinetic parameters *Ea* and *A* calculated from these plots are summarized in Table I.

In general, all the metal-PEMA polymers exhibit lower activation energies than metal-PMMA[10] but higher than poly(dialkylphenyl methacrylates).[14] They range from 36.41 to 22.96 for Cu and Ag, respectively. The lowest *Ea* was Ga-PEMA probably due to a very unstable dispersion and the low redox potential of the metal.

Several parameters are related with the kinetic parameters obtained for the thermal decomposition of these polymers. Apparently, metal nature, dispersion stability, amount of the metal and molecular weight are strongly related. It is easy to observe that activation energy increase with specific capacity of the metals, with the Al and Ga exceptions, probably due to the very unstable dispersions. The T_D is related with the inverse of the thermal conductivity and it is clear that Cu, Ag and Zn showed the lower T_D values and the highest in conductivity.

Another interesting feature is related with metal nature and for Ge and Pd, even if the amount of the metal is less in the first one, the change in *Ea* is more dramatic.[15]

The combination effect of metal amount incorporated and molecular weight is observed in the four fractions of Pd-PEMA. The *Ea* and T_D increases with the increase in molecular weight. Also, for Cd and Sn although their specific capacity and metal amounts are similar a higher molecular weights exhibited a higher *Ea* and T_D.

Pd and Au showed similar activation energy and higher than Ag, probably due to more stable colloids and more stability to oxidation. Figure 3 shows the Arrhenius plot for the Pd-PEMA (F_1), (F_2), (F_3), (F_4) and Ge-PEMA (F_3) and (F_4).

All these values give us a valuable information with respect to quantitative measurements of thermal stability.

By comparison of activation energies from PMMA and PEMA with the same metals incorporated we can conclude that the tacticity of these polymers should be different. The T_D of metal PEMA—are much lower than metal PMMA and this is probably due to the size increase in the monomeric unit.

Acknowledgment

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