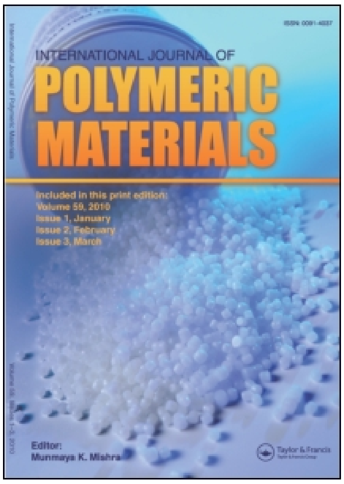

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Cárdenas T. Galo[a]; Acuña E. José[a]
[a] Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

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Synthesis and Properties of Metal Poly(Isobutylmethacrylate)s

GALO CÁRDENAS T.* and JOSÉ ACUÑA E.

Departamento de Polímeros, Facultad de Ciencias Químicas,
Universidad de Concepción, Casilla 3-C, Concepción (Chile)

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Isobutyl methacrylates colloids are obtained by codeposition at 77 K of the monomer with metals such as Cu, Ag and Au. The colloids were polymerized with different amounts of initiator (BPO) at 70°C for 85 min and a wide range of viscosity. Molecular weights ($\bar{M}_v$, 10^4–10^5 g/mol) were obtained depending upon the metal used. The metal colloid concentration and stability are reported. The medium particle size of 162 Å for Au and 33 Å for Ag colloid were obtained. The thermal stability and metal composition are also described. The polymers are stable even at 250°C and from the thermogravimetric curves the kinetic parameters of the decomposition reaction were obtained. The metal constant is ranging between 0.18 and 5.12% w/w for the highest MW fraction and between 0.13 and 0.74% w/w for the lowest MW fraction. Polymers with different colors were obtained depending on the metal used.

Keywords: Metal clusters; metal polymers; cocondensation; low temperature; metal atoms

INTRODUCTION

Several syntheses of colloidal metals dispersed in organic monomers such as styrene [1], methyl [2] ethyl [3] and butylmethacrylate [4] have been reported.

This method, chemical liquid deposition, involves codeposition of metal vapor with organic solvents at low temperature (77 K) followed by clustering of metal atoms. Polymers with higher thermal stability than the undoped and with potential semiconductor properties can be obtained.

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*Author to whom correspondence should be addressed.

EXPERIMENTAL

Colloid Synthesis

The colloids metal-isobutylmethacrylates (IBMA) were prepared by cocondensation of the monomer with the metals at 77 K using a metal atom reactor [5,6]. Two concentrations of metal dispersed in the monomer were used. Different current intensities were used depending upon the metal used and the vacuum. The metals under study were Cu, Ag and Au.

Typical Polymerizations

(i) Colloid Au-IBMA (10 mL) was placed in three polymerization flasks with 0.5, 1.0 and 2.0 mol% benzoyl peroxide (BPO) under nitrogen flow. The flask tubes were closed and placed in an isothermal bath at 70°C for 85 min. The content of each flask was quenched with methanol. The purple polymers obtained were filtered off and dried under vacuum at 10^{-3} Torr for 48 h at 40°C. The yield of each polymer fraction was measured. The molecular weight was determined by dissolving the samples in acetone at 25°C. The viscosity was obtained using an Ostwald viscometer, and from the intrinsic viscosity and the Mark-Houwink equation [7] the molecular weight was obtained; $[\eta] = K \bullet M_v^a$, where K and a are constants ($K = 23.4 \times 10^{-3}$ (mL/g) and $a = 0.66$) [8].

(ii) Similarly, the colloid Ag-IBMA and Cu-IBMA were polymerized with the same BPO concentration under nitrogen at 65°C for 85 min.

Elemental Analysis

The samples for C, H microanalyses were performed in a Perkin-Elmer 2100 Automatic Analyzer and metals in a Perkin-Elmer 3500 Atomic Absorption Spectrometer by the Faculty of Chemical Sciences Laboratories (Universidad de Concepción).

Electron Microscopy

Transmission electron microscopy (TEM) was carried out on a JEOL JEM 1200 EXII. The particle size of the colloids were determined.

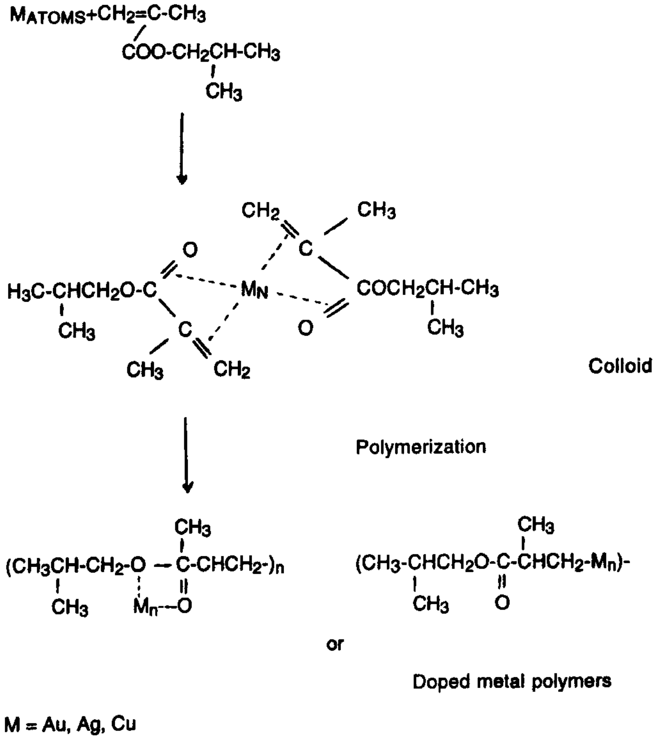
Thermogravimetric Analysis

A Perkin-Elmer Model TGA-7 Thermogravimetric System with a microprocessor driven temperature control unit and a TA data station, was used.

The mass of these samples was generally in the range of 2–5 mg. The sample pan was placed in the balance system equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The mass of the sample pan was continuously recorded as a function of the temperature.

FTIR

KBr pellets were prepared with each sample of the higher and lower MW fractions. The samples were recorded in a Nicolet Magna 550 FTIR Spectrometer with 2 cm^{-1} resolution. An average of 128 scans were accumulated for all the samples.



RESULTS AND DISCUSSION

Previously, metal colloids stabilized by organic monomers styrene [1], methyl methacrylate [2], ethylmethacrylate [3] and butylmethacrylate [4] have been reported. The stabilization process is probably due to the *ligating* action of the unsaturated bonds from the vinyl group of the isobutyl methacrylate, as shown in the above scheme:

In the equation above we propose both possible structures. Au-IBMA are stable for several weeks at room temperature. These properties are similar with previous results on metal polymers [9, 10].

The size of metal clusters increases by aggregation in the monomeric medium, and this took place during the warming process from 77 K to room temperature. The metal clusters are incorporated in the polymers and can be found by TEM and EDAX.

For the higher MW fraction, the undoped polymer exhibits the highest molecular weight, being Ag-IBMA very similar to IBMA. Cu and Au are lower probably due to the less reactivity of gold atoms. It is interesting to observe that Ag-IBMA showed the highest MW values for the other fractions. Au-IBMA is quite similar to the undoped polymer due to their low reactivity.

Elemental analyses were carried out after drying the samples under vacuum at 40°C and 10^{-3} Torr for several days. Table II summarizes the data for metal poly (IBMA).

Table I summarizes yield and molecular weights ($\bar{M}_v$) of metal poly(isobutyl methacrylate)s.

The amount of metal in the polymers is very low, but is enough to change thermal and mechanical properties. The metal incorporation ranges from 0.69 to 4.75% for Ag-IBMA being the highest. On the other hand, Cu-IBMA ranges from 0.33 to 0.18 and Au-IBMA ranges from 0.12 to 0.28% w/w. In general, the higher MW fraction exhibited the more significant content of metal cluster incorporation.

TABLE I Correlation between metal poly(IBMA) and molecular weights

Polymer	*Yield (%)**	$\bar{M}_V \times 10^{-3}$	*Color*
IBMA**	4.6 9.4 59.25	228.3 58.1 44.8	White
Au-IBMA	6.42 25.32 46.82	126.3 68.3 41.6	Purple
Ag-IBMA	12.72 67.69 85.23	200.7 116.9 100.1	Brown
Cu-IBMA	5.36 20.74 38.93	162.4 93.5 83.4	Brown

*Yields correspond to 0.5, 1.0 and 2.0 mol% of BPO.
**IBMA: poly(isobutyl methacrylate).

TABLE II Correlation between IBMA polymers and content composition

Polymer	*%M*	*%C*	*%H*
IBMA-1*			
–		67.67	4.89**
IBMA-4	–	67.80	10.88
Ag-IBMA-1	4.75	66.91	9.92
Ag-IBMA-4	0.69	67.93	10.16
Cu-IBMA-1	0.33	67.93	10.34
Cu-IBMA-4	0.18	68.25	10.25
Au-IBMA-1	0.28	68.01	10.30
Au-IBMA-4	0.12	68.34	10.25

*Fraction 1 and 4 correspond to 0.5 and 2.0 mol% BPO.
**The balance is most likely oxygen.

In this system, it is possible to obtain a linear correlation between $\bar{M}_v$ and $(\mathrm{BPO})^{-1/2}$. This result is in agreement with previous results in other doped polymers [11, 12].

In the transmission electron micrograph (TEM) it is possible to see the spherical shape of the Au clusters in the monomer sols. The average size of the Au-IBMA is around 162Å (see Fig.1) and Ag-IBMA colloid is around 33Å. The bigger particles are due to several clusters.

A complete study of the thermal stability between 25 to 550°C was carried out for the polymers and doped polymers [13].

The thermograms reveal that the polymers IBMA are stable up to 260°C (Fig. 2). A striking improvement in thermal stability for Ag-IBMA with a decomposition temperature (T_D) of 366°C was obtained. Similarly, Au and Cu-IBMA showed T_D at 286 and 287°C, respectively (Fig. 3).

The shapes of the Au and Cu thermograms are similar and all the metal-IBMA polymers degrade in a single step. Ag-IBMA showed two-step degradation process (Fig. 3).

The thermal decomposition kinetics of the thermogravimetric weight loss data were assumed to follow the kinetic equation:

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

where α is the fraction of the sample weight reacted at time t, and k is the specific rate with reaction order n. The reaction rates, $d\alpha/dt$, were calculated using a differential technique with the heating rate (10°C min^{-1}) incorporated directly in the data of temperature versus sample weight fraction, according to the method developed by Wen and Lin [14]. The specific rates, k_n, were

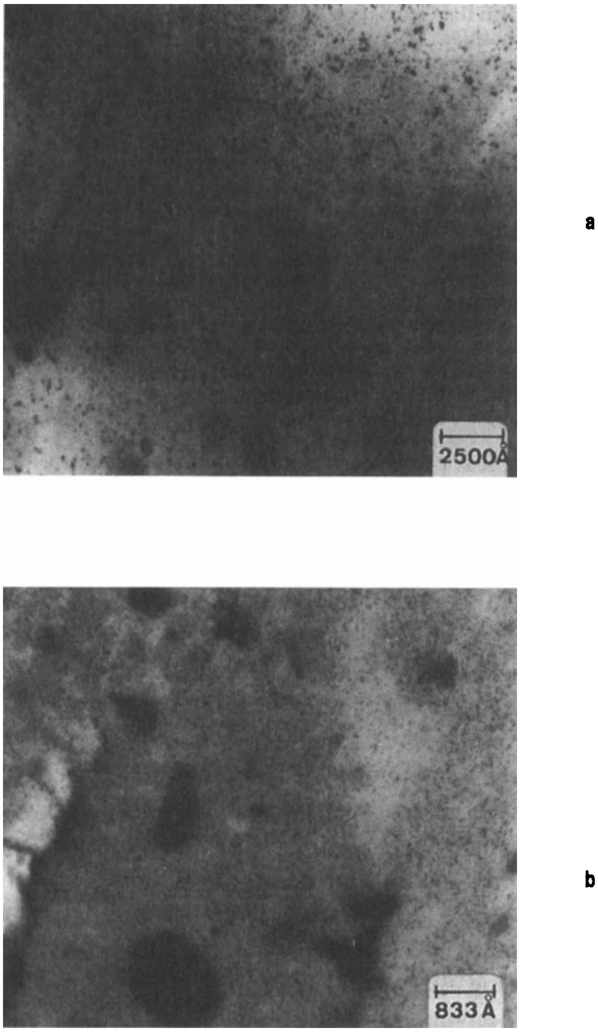


FIGURE 1 Electron micrograph o9f (a) Au-IBMA, 162 Å (40 Kx); (b) Ag-IBMA, 33 Å (120 Kx).

obtained from the Arrhenius equation.

$$k_n = A_{\mathrm{exp}}(-E/RT) \qquad (2)$$

where E is the activation energy, A the pre-exponential factor, T the absolute temperature and R the gas constant. Equations (1) and (2) were

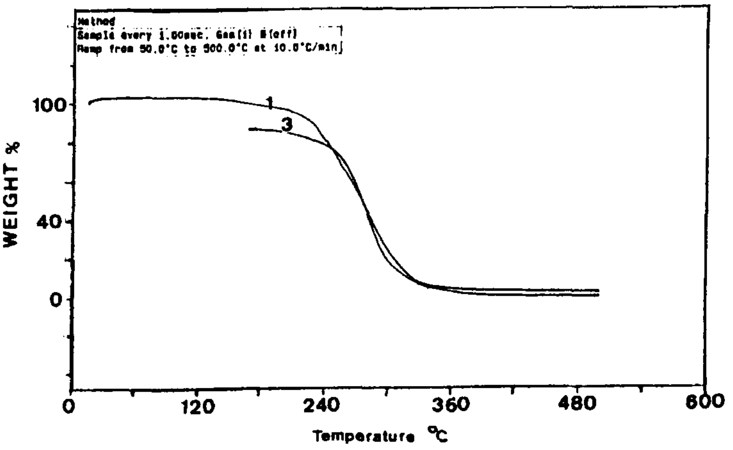


FIGURE 2 Thermogram of pery(isobutyl methacrylate)fractions 1,3 copolymer

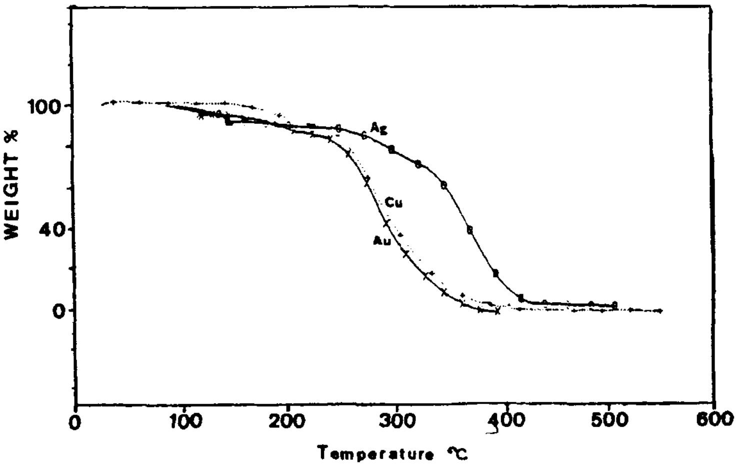


FIGURE 3 Thermogram of (a) Au, (b) Ag and (c) Cu-IBMA fraction 1 copolymers

combined and used in logarithmic form:

$$\beta = \ln\left[-(d\alpha/dT)/6\,(1-\alpha)^n\right] = \ln \mathrm{A} - E/RT \qquad (3)$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from a linear least-square fit of the data in a semilogarithmic plot of β versus $1/T$. The linearity (greater than 0.99) of each plot is good.

Table III shows the kinetic data obtaining according to the above method and the temperature range used to calculate the parameters.

TABLE III Kinetic parameters for metal poly(isobutyl methacrylate)s

Polymer	*n*	*Temp.range* (°*C*)	E_a (*kJ/mol*)	*A*	T_D (°*C*)
IBMA$^{*}_{1}$	0	214–333	52.05	17.29	254.70
IBMA$_3$	0	251–303	59.29	80.16	260.35
Au-IBMA$_1$	0	245–334	41.26	2.08	279.36
Au-IBMA$_3$	0	265–348	46.35	3.11	286.73
Au-IBMA$^{**}_{11}$	0	284–332	29.59	0.108	300.20
Au-IBMA$_{23}$	−0.1	339–395	63.13	25.79	366.42
Au-IBMA$_{23}$	0	251–279	41.93	0.46	301.25
Au-IBMA$_{23}$	−0.2	328–409	69.30	313.41	366.26
Au-IBMA$_1$	−0.5	277–561	87.64	27.77×10^3	289.89
Au-IBMA$_3$	−0.5	247–343	93.10	147.27×10^3	287.12

*Fraction 1(0.5 mol%) and fraction 3(2.0 mol% BPO).
**IBMA : first slope fraction 1.
IBMA^{11}: second slope fraction 1.
IBMA^{23}: first slope fraction 3.
IBMA$^{23}_{23}$: second slope fraction 3.

Metal poly(isobutyl methacrylate) prepared by benzoyl peroxide (Table III) showed a zero reaction order with most of the metals under study. For the highest MW fraction the series exhibit an E_a ranging from 41.26 to 71.52 kJ/mol for Au and Ag, respectively. The IBMA showed an E_a of 52.05 kJ/mol. On the other hand, butyl methacrylates [15] showed lower E_a, most probably due to $n = -0.5$. It is interesting that Cu-IBMA with the same *n*, showed an E_a 87.64 kJ/mol almost three times higher than Cu-IBMA already reported [15]. In fact, Au, Ag and Cu-IBMA exhibit higher E_a than the corresponding PBMA series. The stability is probably due to the different tacticity due to the branched carbon chain. The most relevant result is the increase in thermal stability by the presence of metal clusters in the polymer. In all the polymer fractions, the metal polymers exhibited a higher T_D than the undoped polymers.

Acknowledgements

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