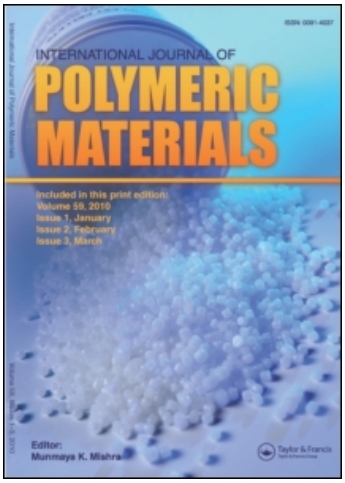

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Thermal Analysis of Metal Poly(4-methylstyrenes). Part XV

Cárdenas T. Galo[a]; Salgado C. Elizabeth[a]; Luis H. Tagle[b]
[a] Departamento de Polimeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile [b] Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile

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Thermal Analysis of Metal Poly(4-methylstyrenes). Part XV.

GALO CÁRDENAS T.* and ELIZABETH SALGADO C.

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

and

LUIS H. TAGLE D.

Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

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The thermal stabilities of metal poly(4-methylstyrenes) have been studied by thermogravimetry (TG) between 278 and 823 K under nitrogen flow. The comparison of two series of metal doped polymers (i) with azobisisobutyronitrile (AIBN) and (ii) with benzoyl peroxide (BPO) as radical initiators will be achieved. From the thermal decomposition temperatures we can establish that in the AIBN series the thermostabilities decrease in the order: Zn-4MeS > Sn-4MeS > Ge-4MeS > Cu-4MeS > Ga-4MeS > Pd-4MeS > Bi-4MeS > In-4MeS > Sb-4MeS > Ag-4MeS > Au-4MeS. On the other hand, in the BPO series the thermostabilities decrease in the order: Bi-4MeS > Ga-4MeS > Sb-4MeS > Cu-4MeS > Sn-4MeS > Zn-4MeS > Ag-4MeS > Ge-4MeS > Pd-4MeS > Au-4MeS > In-4MeS. There are also differences in the activation energies due to the different molecular weight ranges in both series.

KEY WORDS Poly(4-methylstyrene), metal clusters, thermal analysis, kinetics, thermal stability.

INTRODUCTION

The thermal stability of polymers is very important due 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 analysis of the kinetic parameters is also important in the understanding of solid state reactions which could occur during the decomposition processes.

Degradation reactions are initiated or strongly influenced in our case by the metal clusters incorporated into the polymer chain.[2–5] The presence of metal clusters in the polymers produce a strong influence on the degradation reactions.

*Author to whom correspondence should be addressed.

This paper discusses the kinetics of the thermal degradation of metal poly(4-methylstyrenes) to continue our studies to establish a relation between metal presence in the polymers and thermal stability. The aim of the kinetic analysis of thermogravimetric data is to find the most probable kinetic model which gives the best description of the studied process and allows the calculation for the parameters E and A in equation 2 below.

EXPERIMENTAL

Colloid Synthesis

The colloids metal-4-methylstyrenes were prepared by cocondensation of the monomer with the metals at 77 K using a metal atom reactor.[6,7] Two concentrations of metal dispersed in the monomer were used. Different current intensities were used depending upon the metal used and the vacuum.[6,7] The metals under study were Pd, Cu, Ag, Au, Zn, Ga, In, Ge, Sn, Sb and Bi.

Typical Polymerizations

(i) Colloid Sn-4MeS (10 mL) was placed in four polymerization flask with 0.1, 1.0, 2.5 and 5.0 mol% of 2,2'-azoisobutyronitrile (AIBN) under nitrogen flow. The flask tubes were closed and placed in an isothermal bath at 65°C for 9 h. The content of each flask was quenched with methanol. The dark brown 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 toluene at 30°C. The viscosity was obtained using an Ostwald viscometer, and from the intrinsic viscosity and Mark-Houwink equation[8] the molecular weight was obtained: $[\eta] = K \cdot M_v^a$, where K and a are constants.[9]

(ii) Similarly, the colloid Sn-4MeS (10 mL) was polymerized with 1.0, 2.0, 2.5 and 5.0 mol% of benzoyl peroxide (BPO) under nitrogen at 65°C for 8 h.

Thermogravimetry

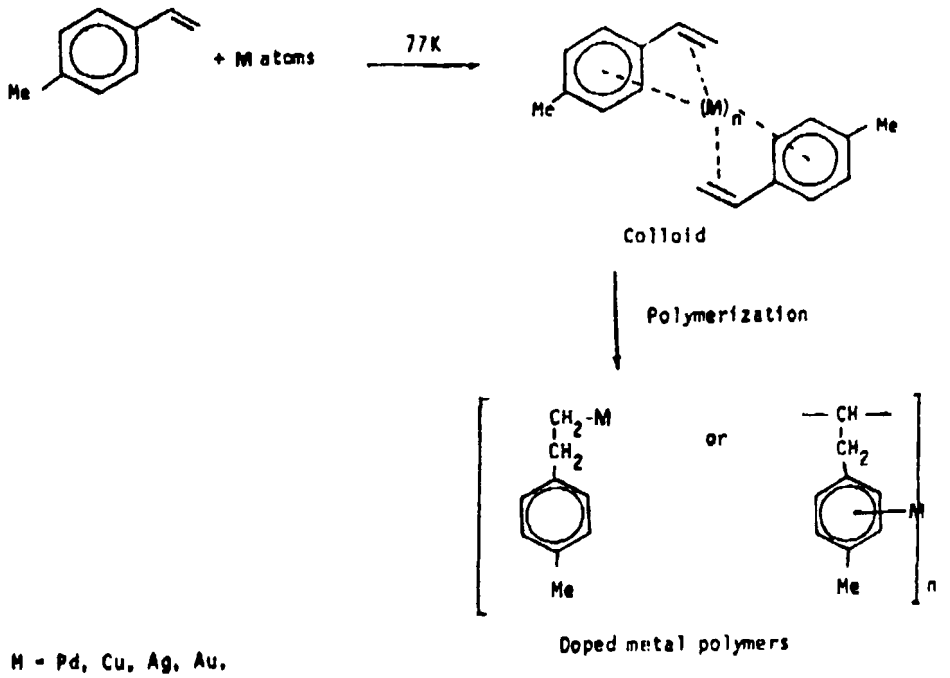
A Perkin-Elmer Model TGS-2 thermogravimetric system, with a microprocessor-driven temperature control unit and a TA data station, was used. The masses of these samples were recorded accurately and were generally in the range 5–10 mg. The sample pan was placed in the balance system and the temperature was raised from 25 to 550°C at a heating rate of 10°C min^{-1}. The mass of the sample was continuously recorded as a function of the temperature.

RESULTS AND DISCUSSION

The synthesis and thermal studies of styrenes with incorporated metal has been previously reported.[10,11] The polymers prepared have a wide range of molecular weight, stability and colors depending on the metal. The amount of metal incor-

porated was very low ranging from 0.01 to 1.74% for AIBN and from 0.05 to 2.92% for BPO.[12] This low amount of metal clusters incorporated in the polymers is just enough to produce some changes in colors and in the physical properties.

These new modified poly(4-methylstyrenes) were prepared by using the process shown in the following scheme:



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

In the equations above we propose both possible structures. The most relevant difference between these two series is the molecular weights. In the Cu, Ag, Au series the AIBN the MW are higher than the BPO series. These feature also for the homopolymer is observed. Ga and In-poly(4-MeS) are also higher for AIBN series.

Sb and Bi, the heavier metals, are also exhibiting higher MW fractions for AIBN. Probably, the more reactive radicals will allow them to grow faster than BPO. The tacticity of the polymer are also different which makes another relevant point.

It is possible to observe a strong relation between the amount of metal incorporated and the thermal stability of the polymers. Pd-poly(4-MeS) shows a good stability around 400°C for both AIBN and BPO (Figure 1) series. Au and Ag-series are also very stable. On the other hand, In and Sb exhibited a lower thermal stability.

In Figure 2 we have plotted the four MW fractions corresponding to the homopolymers of 4-methylstyrenes. The BPO series showed a more consistent regularity of thermal decomposition temperature (T_D).

The T_D are decreasing with the MW, most probably due to the smaller chain

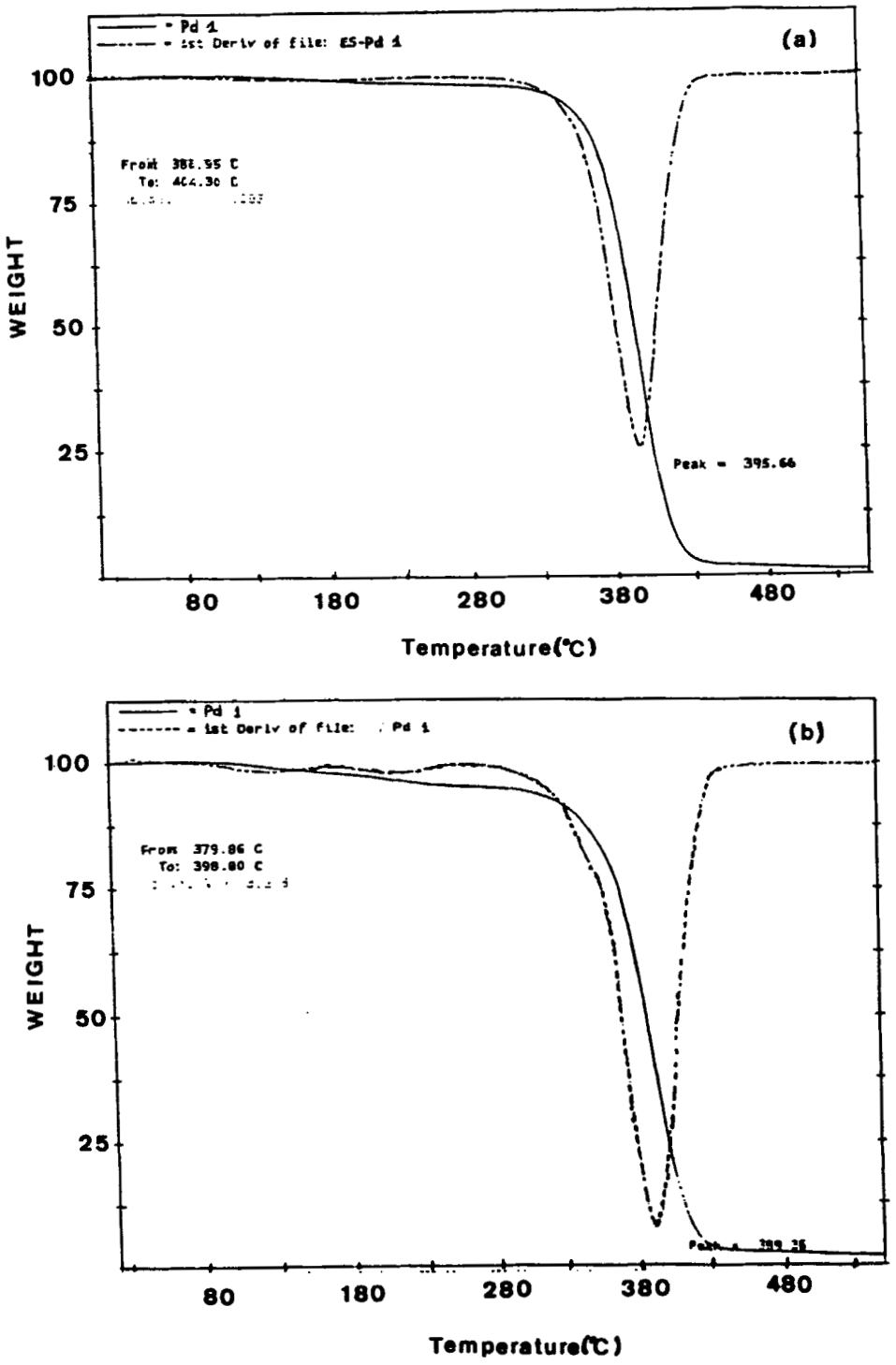


FIGURE 1 Thermogram and first derivative of Pd-poly(4-methylstyrenes) obtained at a heating rate of 10°C min^{-1}. (a) Fraction of 0.1 mol% AIBN, (b) fraction of 0.1 mol% BPO, respectively.

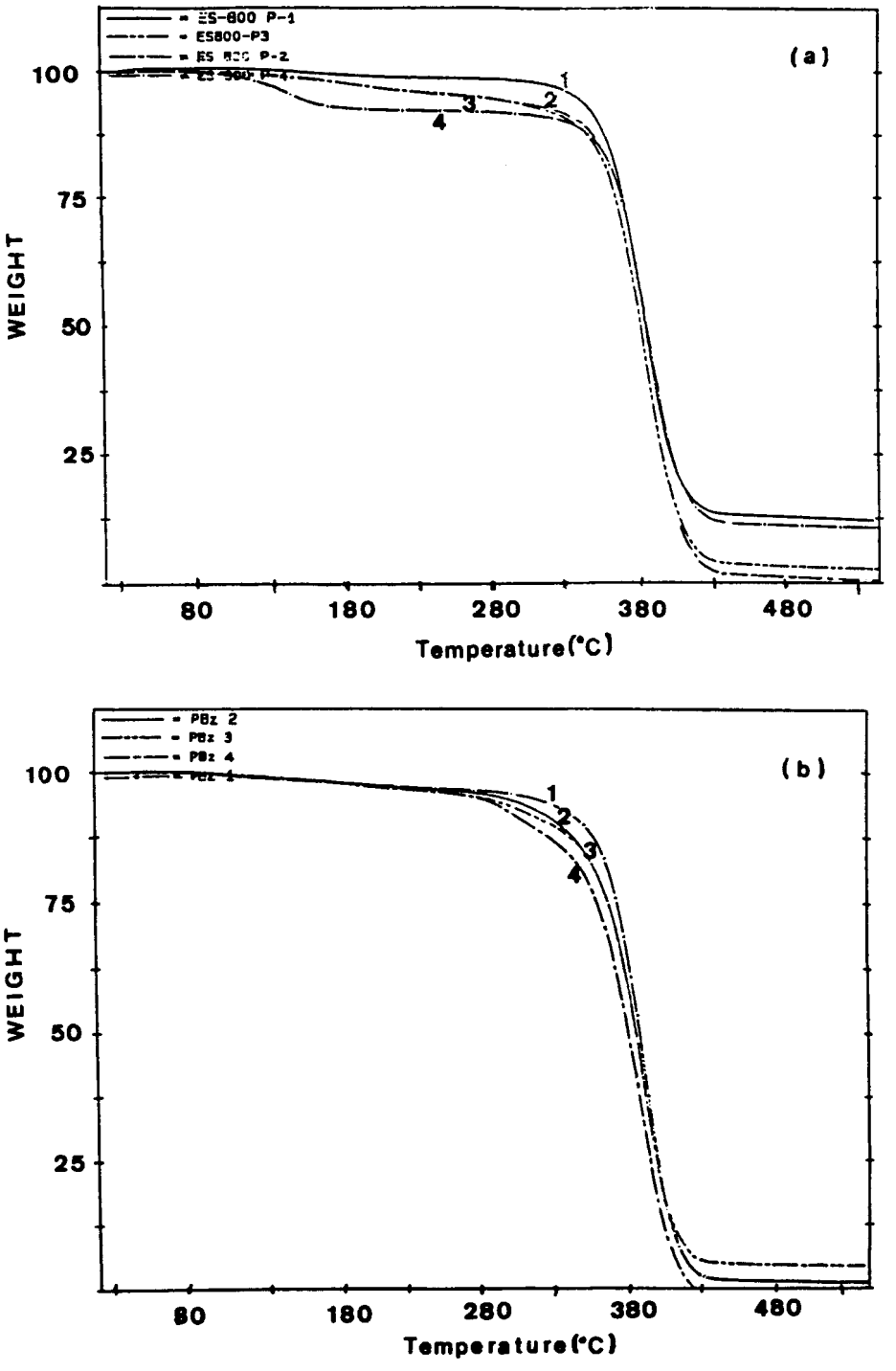


FIGURE 2 Thermogram of poly(4-methylstyrenes) (a) homopolymers from AIBN series, (b) homopolymers from BPO series. The fractions 1, 2, 3 and 4 are corresponding to 0.1, 1.0, 2.5 and 5.0 mol% AIBN and 0.1, 2.0, 2.5 and 5.0 mol% BPO.

size. The AIBN homopolymers are very close, with a few degrees between the MW fractions.

The shapes of the thermograms are similar and all the metal-4MeS polymers degrade in a single-step process which is similar to the thermal decomposition of other metal polymers.[13]

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

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

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 Win and Lin.[14] The specific rates, k_n, were obtained from the Arrhenius equation.

$$k_n = A \exp(-E/RT) \tag{2}$$

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 combined and used in logarithmic form:

$$\beta = \ln[-(d\alpha/dT)/6(1 - \alpha)n] = \ln A - \frac{E}{RT} \tag{3}$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semi-logarithmic plot of β versus $1/T$. The Arrhenius plots for the thermal degradation of the Cu metal poly(4-methylstyrene)s are shown in Figure 3. The linearity (greater than 0.996) of each plot is good, although some scatter is detected at the beginning and end of the decomposition, which can be due to the difficulty in obtaining accurate measurements specially at the beginning of the experiments, as frequently encountered in kinetic measurements.

Tables I and II show the kinetics data obtained according to the above method and the temperature range used to calculate the parameters.

Metal poly(4-methylstyrene)s prepared by benzoyl peroxide (Table II) showed a zero reaction order with all the metals under study. For the higher MW fraction the series exhibit an *Ea* ranging from 95.93 to 144.97 kJ/mol for Au and Bi, respectively. These values are lower than metal poly(styrenes) already reported.[15] On the other hand, the fraction 4 (lower MW) the activation energy values are also lower ranging from 60.61 to 88.36 kJ/mol for Au and Bi, respectively.

Furthermore, the metal poly(4-methylstyrene)s prepared with AIBN (Table I) showed a -0.5 reaction order with most of the metal, with Ge and Sn showing zero reaction order.

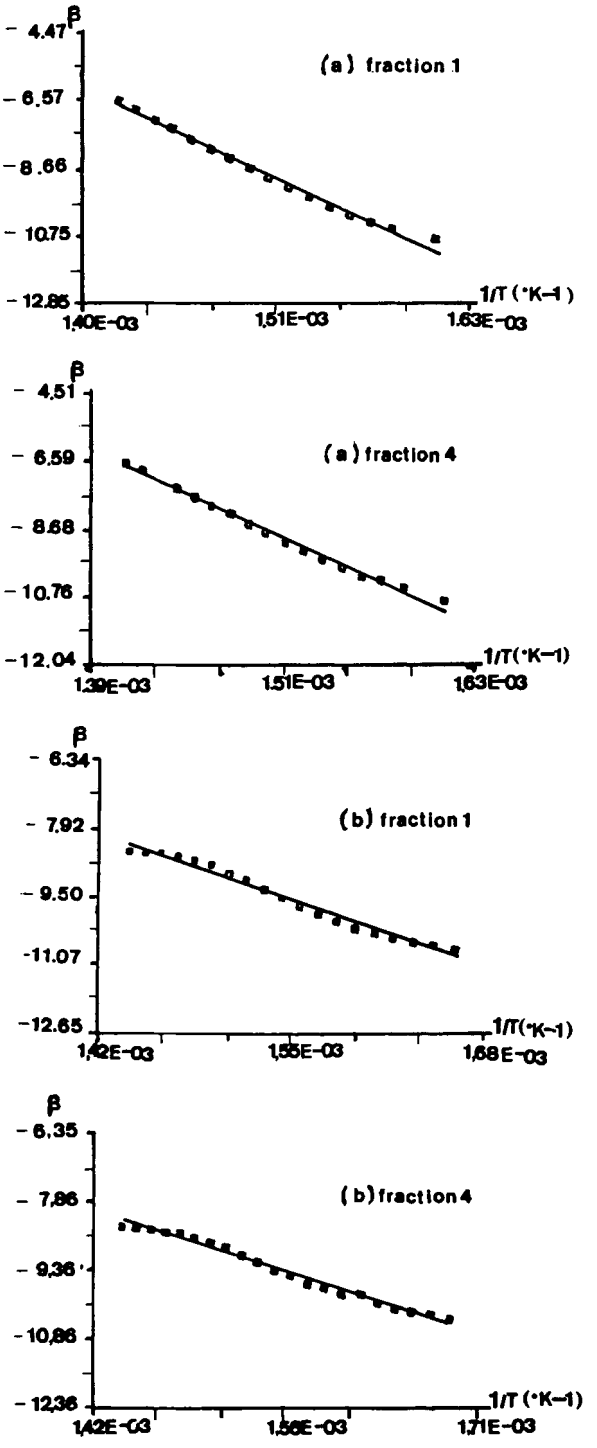


FIGURE 3 (a) Arrhenius plot of Cu-P(4-MeS) (fraction 1 and 4) for AIBN; (b) Arrhenius plots of Cu-P(4-MeS) (fractions 1 and 4) for BPO, respectively.

TABLE I

Kinetic parameters for metal poly(4-Methylstyrenes) with AIBN

Polymer	Ea(kJ/mol)	n	Temp.Range	T_D
P4-MeS-1	193.32	-0.5	330-420	384.23
P4-MeS-2	190.35	-0.5	345-420	387.50
P4-MeS-3	185.44	-0.5	345-420	389.83
P4-MeS-4	167.54	-0.5	340-420	387.09
Pd-4MeS-1	205.84	-0.5	350-430	395-66
Pd-4MeS-4	183.51	-0.5	350-435	392.16
Cu-4MeS-1	210.87	-0.5	350-430	396.36
Cu-4MeS-4	196.74	-0.5	350-435	399.16
Ag-4MeS-1	181.42	-0.5	345-420	385.40
Ag-4MeS-4	154.01	-0.5	340-425	387.50
Au-4MeS-1	181.16	-0.5	345-420	384.46
Au-4MeS-4	178.94	-0.5	335-400	382.83
Zn-4MeS-1	224.23	-0.5	360-445	406.73
Zn-4MeS-4	183.81	-0.5	355-430	395.27
Ga-4MeS-1	207.51	-0.5	345-430	395.90
Ga-4MeS-4	176.45	-0.5	345-430	394.96
Ge-4MeS-1	126.26	0	350-430	404.53
Ge-4MeS-4	87.65	0	330-420	386.10
In-4MeS-1	242.52	-0.5	345-425	391.70
In-4MeS-4	86.27	0	330-420	385.16
Sn-4MeS-1	120.17	0	350-340	405.81
Sn-4MeS-4	116.87	0	330-340	402.90
Sb-4MeS-1	211.84	-0.5	245-420	388.40
Sb-4MeS-4	148.24	-0-5	340-425	385.80
Bi-4MeS-1	186.00	-0.5	350-425	392.01
Bi-4MeS-4	184.89	-0.5	355-440	397.92

P4-MeS = poly(4-methylstyrene)s; T_D = decomposition temperature.

For the higher MW fraction the serie show an *Ea* ranging from 120.17 and 242.52 kJ/mol for Sn and In, respectively. Although, for fraction 4 the *Ea* values are ranging from 148.24 and 196.74 kJ/mol for Sb and Cu, respectively. The similarities in E in the AIBN metal polymers is due to the very low amount of metal incorporated.

Most of the thermograms show a single thermal decomposition which is indicated

TABLE II

Kinetic parameters for metal poly(4-methylstyrene)s with BPO

Polymer	n	Ea(kJ/mol)	T_D(°C)	Temp.Range (°C)
P4-MeS-1	0	125.31	392.40	305-420
P4-MeS-2	0	91.04	391.46	320-420
P4-MeS-3	0	93.74	389.36	335-420
P4-MeS-4	0	81.13	386.33	325-420
Pd-4MeS-1	0	98.95	389.36	330-425
Pd-4MeS-4	0	63.05	383.83	310-420
Cu-4MeS-1	0	102.80	394.00	330-420
Cu-4MeS-4	0	78.53	389.36	320-420
Ag-4MeS-1	0	115.35	392.16	335-415
Ag-4MeS-4	0	86.78	387.50	325-420
Au-4MeS-1	0	95.93	387.96	330-415
Au-4MeS-4	0	60.61	365.10	285-420
Zn-4MeS-1	0	114.52	392.26	340-420
Zn-4MeS-4	0	84.31	385.63	325-420
Ga-4MeS-1	0	124.93	395.43	335-420
Ga-4MeS-4	0	72.76	382.67	310-420
In-4MeS-1	0	103.63	382.35	330-410
In-4MeS-4	0	65.77	377.93	315-410
Ge-4MeS-1	0	98.62	389.83	335-415
Ge-4MeS-4	0	81.50	383.76	320-415
Sn-4MeS-1	0	135.31	393.56	340-415
Sn-4MeS-4	0	82.38	384.26	320-415
Sb-4MeS-4	0	106.98	394.73	330-420
Sb-4MeS-4	0	78.11	386.33	320-420
Bi-4MeS-1	0	144.97	397.76	345-420
Bi-4MeS-4	0	88.36	390.06	325-420

P4-MS = poly(4-methylstyrene)s; T_D = decomposition temperature.

in Tables I and II. Mainly, the high molecular weight fraction exhibits a higher T_D in both series under study. The negative order in the AIBN series is probably due to the different tacticity of the polymers obtained.

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