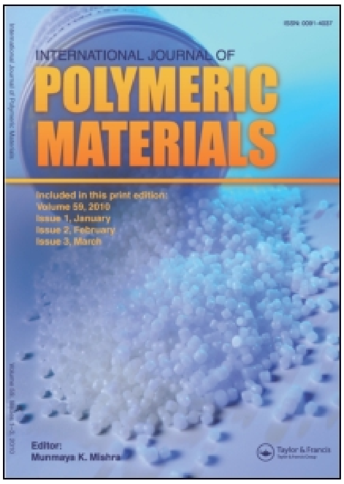

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Thermal Studies of Metal Poly(Styrene-*co*-4-methylstyrene)s Copolymers. Part XVI

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

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Thermal Studies of Metal Poly(styrene-*co*-4-methylstyrene)s Copolymers. Part XVI.

GALO CÁRDENAS T.* and ELIZABETH SALGADO C.

Departamento de Polímeros, Facultad de Ciencias Químicas, 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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Metal poly(styrene-*co*-4-methylstyrene)s copolymers were obtained by radical copolymerization with azobiisobutyronitrile. The monomers were cocondensed simultaneously with the metals: Pd, Cu, Ag, Au, Zn, Ga, In, Ge, Sn, Sb and Bi. The metals were evaporated to produce atoms and with the monomers they can produce a matrix at 77 K. After the warm up process, metal comonomer colloids can be obtained. The colloids were polymerized with azobiisobutyronitrile at 65°C for 3 h. Four different initiator concentrations (0.1, 0.5, 1.0 and 2.5 mol%) were used. The yields are over 30% and the viscosimetric molecular weight ranges from 10^3–10^5 g/mol. The higher $\bar{M}_v$ are Bi, In and Pd-poly(styrene-*co*-4-methylstyrene) copolymers. The thermal stabilities of these metal polymers have been studied by thermogravimetry (*TG*) between 25 and 550°C under nitrogen flow. The decomposition temperature was obtained from the maximum of the first derivative from *TG* curve. The kinetic parameters of the thermal decomposition were determined by the Arrhenius equation. All these copolymers degrade in one stage. The kinetic data thus obtained show the thermostabilities decrease in the order: Zn-(S-4MeS) > Bi-(S-4MeS) > In-(S-4MeS) > Sb(S-4MeS) > Ga(S-4MeS) > Pd-(S-4MeS) > Ag(S-4MeS) > Au-(S-4MeS) > Sn-(S-4MeS) > Ge-(S-4MeS). The thermal stability apparently is dependent upon the metal incorporated in the copolymers. The decomposition reaction order is zero. The pre-exponential factor, the activation energy, the reaction order and the decomposition temperature for all the copolymers have been determined.

KEY WORDS Metal copolymers, co-monomer colloids, metal atom, metal vapor, thermogravimetry, decomposition temperature.

INTRODUCTION

Thermogravimetry (TGA) is used to study the weight loss kinetics at high temperatures and also the stability of polymeric materials. Differential thermogravimetry (DTG) has been used to determine the maximum temperature of polymer

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*Author to whom correspondence should be addressed.

decomposition.[1] In these processes involving polymers and especially copolymers one can distinguish reactions of thermal decomposition, in which solids undergo transformations and evolution of gaseous dissociation products.

The application of thermal dissociation reactions is one of the reasons why a knowledge of the mechanisms and rates of such reactions has become one of the most relevant chemical investigations.[2]

The course of thermal decomposition may depend on the nature of decomposition, in other words, the chemistry of the reaction.[3]

The study of thermal decomposition of solids should begin with a recognition of the dissociation stages of the given compound. A good knowledge of all the intermediate stages enables a better success of the kinetic studies.

The objective of the present study was to obtain decomposition temperatures of metal copolymers in order to improve their physical properties with the incorporation of metal clusters. In this paper, we report the thermal behaviour of the metal poly(styrene-*co*-4-methyl styrenes). The metals used were Pd, Cu, Ag, Au, Zn, Ga, In, Ge, Sn, Sb and Bi.

EXPERIMENTAL

Colloid Synthesis

The metal-co-monomer colloids were prepared by simultaneous codeposition of styrene and 4-methyl styrene with the metals at 77 K using a metal atom reactor.[4,5] As a typical example an Al_2O_3-W crucible was charged with 150 mg of In metal. Freshly distilled styrene(s) and 4-methyl styrene (4-MeS) were separately placed in a ligand inlet tube connected with a Y device to the reactor and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 4–5 μ Hg while the crucible was warmed to red heat. A liquid nitrogen filled Dewar, was placed around the vessel and In (70 mg) and styrene (28 ml) and 4-methyl styrene (25 ml) were cocondensed over 60 min using 25 A at 10 μ of Hg. The matrix was a black color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen Dewar for 1 h. Upon meltdown a black colloid was obtained. After addition of nitrogen up to 1 atm, the colloid was allowed to warm for another 0.5 h to room temperature. The solution was syphoned out under nitrogen into a flask ware. Based on metal evaporated and styrene and 4-MeS inlet, the concentration could be calculated.

Polymerization

As a typical example, indium colloid (10 ml) was placed in a polymerization flask with 0.1 mol% of azobiisobutyronitrile (AIBN) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath (Heidolph) at 65°C for 3 h. The content of the flask was quenched in 100 ml of methanol. The polymer was filtered off and dried under vacuum (10^{-3} Torr) for 48 h at 30°C. The yield of the polymer was determined. Similar procedure was followed for 0.5, 1.0 and 2.5 mol%.

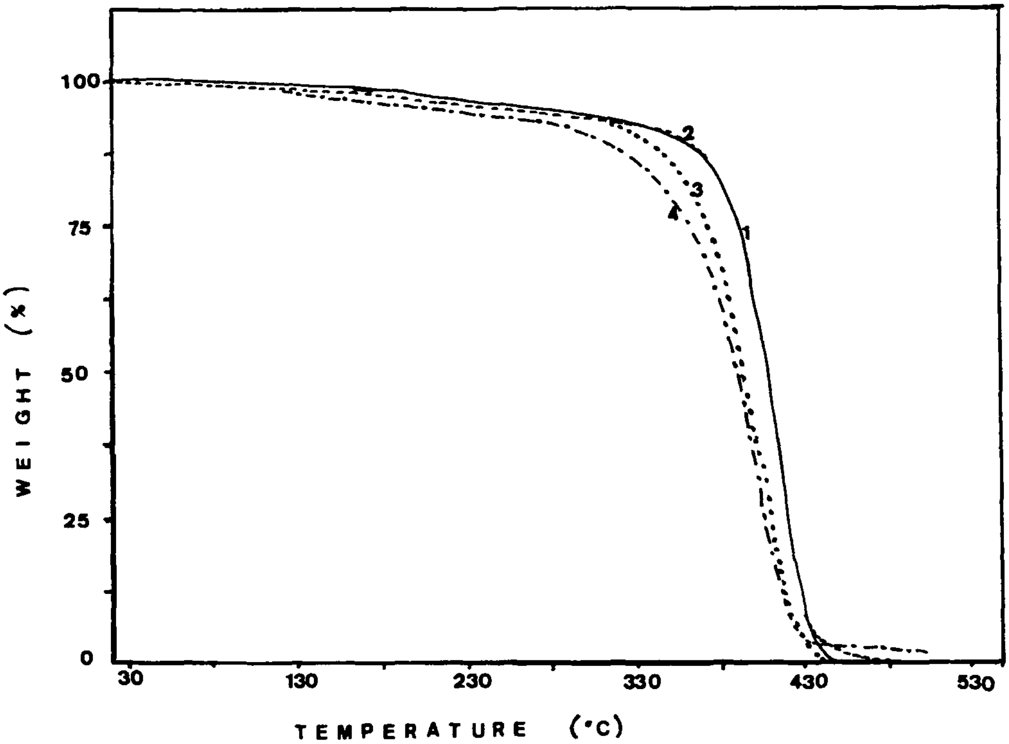


FIGURE 1 Thermogram of poly(styrene-*co*-4-methyl styrene) copolymers obtained by heating the polymers from 25 to 550°C at 10°C min^{-1}. 1 = 0.1; 2 = 0.5; 3 = 1.0 and 4 = 2.5 mol% of AIBN, respectively.

Molecular Weights

The viscosimetric molecular weights ($\bar{M}v$) were determined by using an Ostward osmometer. The samples were dissolved in benzene at 25°C and the parameters $K = 8.11 \times 10^{-3}$ (dl/g) and $a = 0.75$ were used.[6]

Thermogravimetry

A Perkin-Elmer Model TGS-2 Thermogravimetric System, with a microprocessor driven temperature control unit and a TA data station, was used. The weight of these samples were recorded accurately and were generally in the range of 4–10 mg.

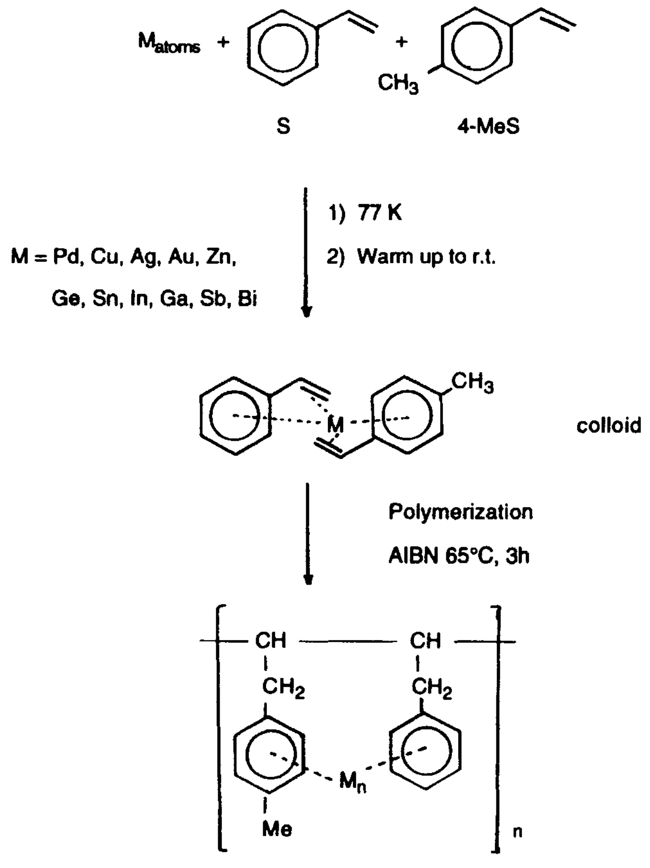
The sample pan was placed in the balance system in equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The weight of the sample pan was continuously recorded as a function of the temperature.

Elemental Analysis

The samples for microanalysis were dried under vacuum (10^{-3} Torr) for 48 hrs. The metals were determined by atomic adsorption and C/H using a Perkin-Elmer 2100 automatic analyzer.

RESULTS AND DISCUSSION

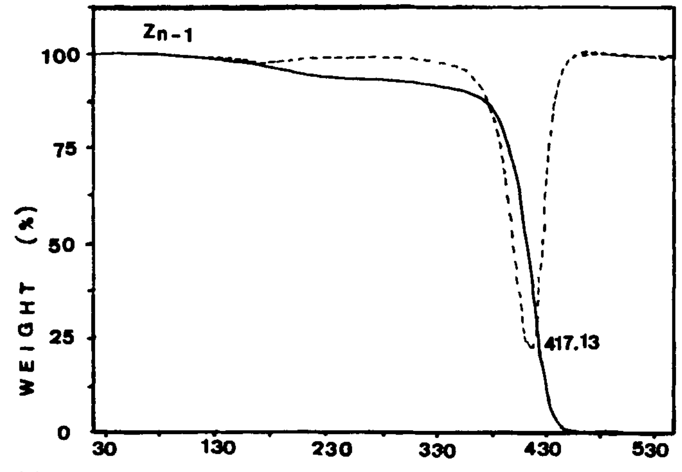
The synthesis of metal poly(styrene-*co*-4-methyl styrene) copolymers with AIBN has been already reported.[7] The polymers exhibited a low-metal content and they can be prepared by codeposition of the metal and the monomers.



Metal Copolymer

Most of the copolymers exhibit a low level of metal incorporation, Sn being the lowest 0.22–0.29, and Zn the highest 1.50–0.18%. The metal clusters in the copolymers are increasing the stability of the non doped analogues. The presence of the methyl group in one of the monomers will increase the reactivity of the aromatic ring allowing a higher metal incoporation, compared with metal polystyrenes reported before.[8]

Nevertheless, the small amount of metal incorporated is able to produce different colors and decomposition temperatures. The molecular weight ($\bar{M}v$) of these copolymers range between 3 × 10^3 and 1 × 10^5. Stable metals such as Pd and Au exhibited similar T_D, being higher than one corresponding to the higher MW fractions. On the other hand, Ga and Ge showed differences due to their suscep-



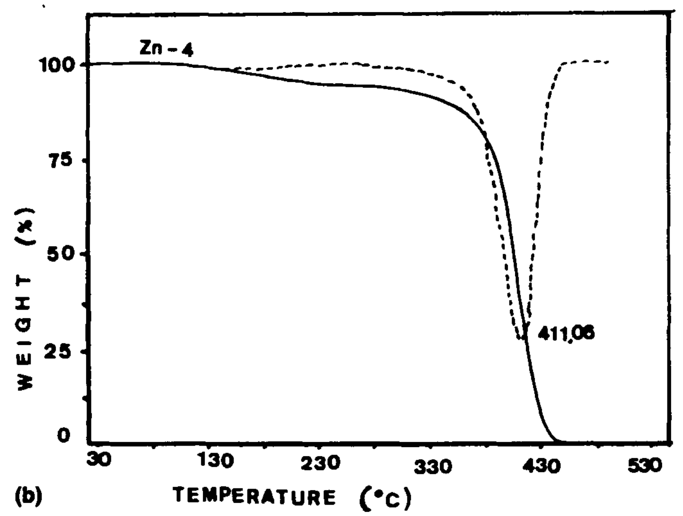


FIGURE 2 Thermogram and first derivative of Zn poly(styrene-*co*-4-methyl styrene)s obtained at a heating rate of 10°C min^{-1}. (a) Fraction of 0.1 mol%, (b) fraction of 2.5 mol% AIBN, respectively.

tibility for oxidation. The shapes of the thermograms are very similar and all the metal poly(styrene-*co*-methyl styrene) degrade in one stage which is similar to the thermal decomposition of metal polystyrenes[9] and other doped copolymers.

In Figure 1 we have summarized thermograms of the four fractions of $\bar{M}v$ corresponding to the copolymer without doping. We have found that in most of the polymers the higher the molecular weight, the higher the decomposition temperature.[11,12,13] The metal copolymers also exhibited similar behaviour.

In general, the thermal decomposition temperatures (T_D) are quite similar ranging from 388 to 417°C. In most cases, the fractions of higher MW show the higher stability.

TABLE I

Kinetic parameters for metal poly(styrene-*co*-4-methyl styrene)s copolymers

Copolymer	n	Temp. Range (°C)	E_a (kJ/mol)	T_D (°C)
(S-4-MeS)-1	0	315 - 430	80.25	407.80
(S-4-MeS)-2	0	350 - 440	103.68	414.25
(S-4-MeS)-3	0	345 - 440	92.80	410.83
(S-4-MeS)-4	0	310 - 430	63.89	401.80
Pd(S-4MeS)-1	0	315 - 420	98.07	404.03
-4	0	325 - 420	76.86	401.93
Cu(S-4MeS)-1	0	310 - 415	75.18	388.27
-4	0	355 - 435	110.54	411.30
Ag(S-4MeS)-1	0	315 - 415	119.53	400.13
-4	0	315 - 415	81.67	396.73
Au(S-4MeS)-1	0	310 - 415	79.95	397.75
-4	0	310 - 415	73.72	396.01
Zn(S-4-MeS)-1	0	355 - 440	111.25	417.13
-4	0	355 - 440	103.72	411.06
Ga(S-4MeS)-1	0	355 - 430	124.51	408.03
-4	0	345 - 435	69.74	405.70
In(S-4MeS)-1	0	355 - 425	169.32	410.83
-4	0	350 - 440	126.39	410.73
Ge(S-4MeS)-1	0	300 - 415	72.67	392.60
-4	0	295 - 415	56.98	388.58
Sn(S-4MeS)-1	0	345 - 420	120.33	393.56
-4	0	335 - 420	102.21	401.21
Sb(S-4MeS)-1	0	345 - 435	129.11	410.60
-4	0	350 - 440	109.20	412.38
Bi(S-4MeS)-1	0	360 - 440	88.15	413.63
-4	0	340 - 435	75.86	403.59

(S-4MeS) = poly(styrene-co-4-methyl styrene)s.
T_D = decomposition temperature.
1,4 = correspond to fraction of highest and lowest molecular weight.

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

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

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 Wen and Lin.[11] The specific rates, k, were obtained from the Arrhenius equation

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

where E is the activation energy, A the pre-exponential factor, T the absolute

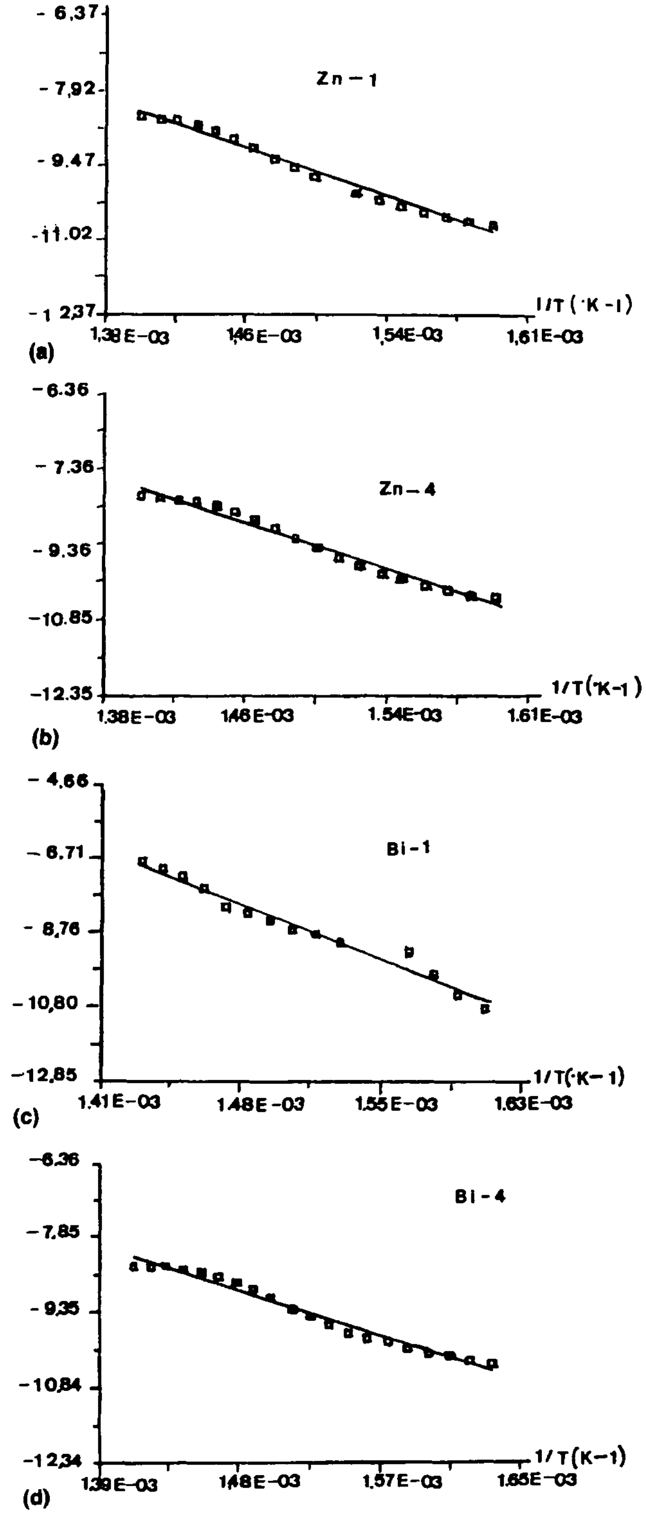


FIGURE 3 Arrhenius plot of Zn-poly(S-4MeS) (fractions 1 and 4) and Bi-poly(S-4MeS) (fractions 1 and 4).

temperature and R the gas constant. After combining equations (1) and (2) and using the logarithmic form we obtained

$$\beta = \ln[-(d\alpha/dT)/6(1 - \alpha)^n] = \ln A - E/RT \qquad (3)$$

A computer linear multiple-regression program was used to calculate the kinetics parameters E and A linear least-squares fit of the data in a semilogarithmic plot of β versus $1/T$. Figure 2 showed the thermogram and first derivative of Zn-poly(styrene-*co*-4-methyl styrene)s. On Figure 2a the higher MW fraction showed a T_D at 417.13°C and Figure 2b, the lower MW fraction showed a T_D at 411.06°C.

Table I summarized the order of decomposition reaction, the temperature range in which the activation energy (E_a) was calculated, the E_a and the T_D for 2 fractions of each copolymer. The highest T_D values were found for In-(S-4MeS) with 169.3 and 126.3 kJ/mol, respectively. At the other extreme, Ge-(S-4MeS) showed 72.67 and 56.9 kJ/mol for the higher and lower MW fractions. If we compare these values with poly styrene, they are very low, Ge-PS for example give 245.6 kJ/mol and In-PS, 319.7 kJ/mol.

On the other hand, metal poly(4-MeS) prepared with AIBN[15] exhibited similarities with the copolymers due to the fact that In-poly(4-MeS) showed also the highest E_a 242.52 kJ/mol which is also higher than the copolymer, the same as in the poly(styrene) case. The only copolymer that is numerically comparable would be Sn-4MeS and Sn-(S-4MeS) with 120.17 and 120.33 kJ/mol for fraction 1, respectively.

Thermal degradation is very useful for analyzing the thermal stability of these metal copolymers and for determining the temperature range in which they can be used, as well as for assessing the influence of the metal clusters in the matrix. Furthermore, the kinetic parameters associated with the total degradation process can be determined.

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