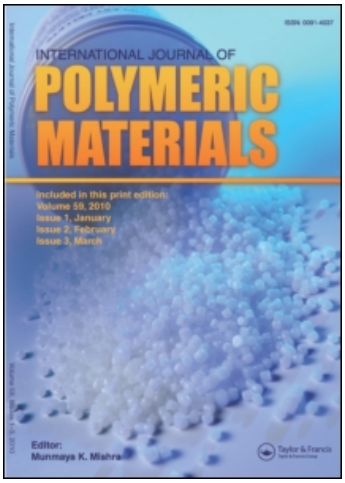

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Thermal Studies of Metal Poly(Styrene-Co-Acrylonitrile). Part 14

Cárdenas T. Galo[a]; Acuña E. José[a]; Carbacho H. Hernán[a]; Rodríguez B. Mario[a]; Luis H. Tagle[b]
[a] Departamento de Polimeros, Facultad de Ciencias Quimicas, Universidad de Concepción, Concepción, Chile [b] Departamento de Quimica Orgánica, Facultad de Quimica, Pontificia Universidad Católica de Chile, Santiago, Chile

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Thermal Studies of Metal Poly(Styrene-Co-Acrylonitrile). Part 14

GALO CÁRDENAS T.,† JOSÉ ACUÑA E., HERNÁN CARBACHO H. and MARIO RODRÍGUEZ B.

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

and

LUIS H. TAGLE D.

Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

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The thermal stabilities of metal poly(styrene-co-acrylonitrile) has been studied by thermogravimetry (TG) between 278 K and 823 K under nitrogen flow. The kinetic data thus obtained indicate that the thermostabilities decrease in the order: Sn-STAN > Ga-STAN > Ag-STAN > Sb-STAN > Cu-STAN > Pd-STAN > Fe-STAN > Au-STAN > Bi-STAN for high Molecular Weight (HMW) and Ag-STAN > Pd-STAN > Fe-STAN > Ga-STAN > Cu-STAN > Sb-STAN > Sn-STAN > Bi-STAN > Au-STAN for low Molecular Weight (LMW) copolymers. The thermal stability seems to be dependable on the nature of the bond established between the copolymer and the metal. Cu-copolymer exhibits the lowest Ea most probably due to their oxidation potential. On the other hand, Ag-copolymer has the highest Ea and similar to the copolymer (fraction 1). The thermal decomposition temperatures were obtained from the DTG curves. The reaction order for the thermal decomposition of these copolymers is zero. In other words, we are dealing with a single step decomposition mechanism. The pre-exponential factor, the reaction order, the decomposition temperature and the activation energy of the decomposition for metal poly(styrene-co-acrylonitrile) have been determined.

KEY WORDS Poly(styrene-co-acrylonitrile), metal, thermal stability, kinetics

INTRODUCTION

Thermogravimetry has been successfully applied to thermal transformation of solids occurring with weight changes because of elimination of volatiles in the degradation processes.[1] By considering that the conversion during these solid-gas equilibrium is related to the accompanying weight changes, thermogravimetry has been used for kinetic investigations mainly for thermal degradation.

It is also important to consider physical factors like sample size, composition and

†Correspondence to G. Cárdenas T.

flow rate of the gaseous products. The heat transfer may influence the course of the reaction specially in high molecular weights polymers.[2]

Nevertheless, the equation rate is used for evaluation of kinetic parameters from the thermogravimetric degradation processes. In non isothermal conditions, we assumed that kinetic parameters are constant. More probably are changes of both the reaction mechanism and the rate determining step with conversion and temperature.[3] However, the calculated values will help to understand the thermal behavior of these copolymers doped with metal clusters.

EXPERIMENTAL

Colloid Synthesis

The colloid metals (styrene-acrylonitrile) were prepared by codeposition of the solvent (1:1 mol ratio) with the metals at 77 K using a metal atom reactor.[4,5] We are assuming that all the metal atoms evaporated are incorporated in the monomers, therefore the approximate concentration could be calculated. Different current intensities were used depending upon the metal and the vacuum used.[6]

Polymerization. As a typical example, gold (styrene-acrylonitrile) colloid was placed in a polymerization flash with 0.1 mol% of azoisobutyronitrile (AIBN) under

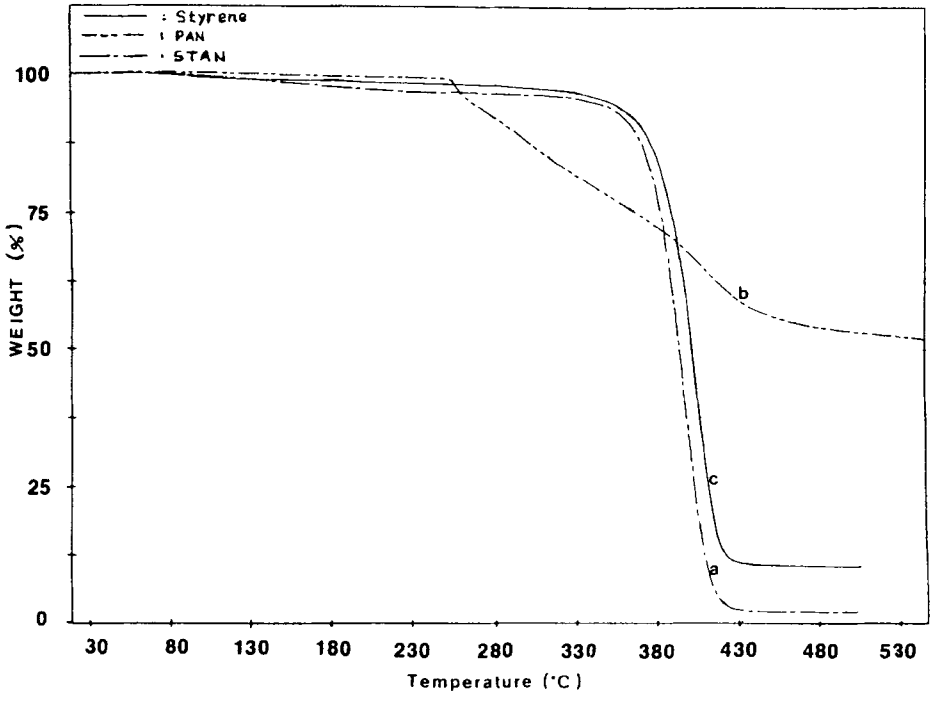


FIGURE 1 Thermogram of (a) polystyrene, (b) poly acrylonitrile and (c) poly(styrene-co-acrylonitrile) obtained by heating the polymers from 25 to 550°C at 10°C min $^{-1}$.

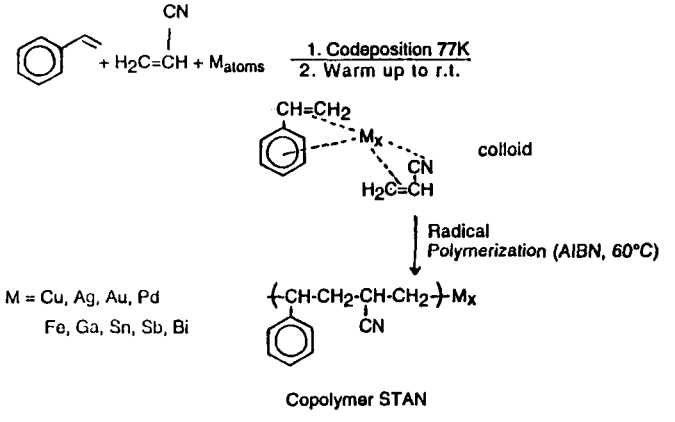
nitrogen atmosphere. The flask was closed and placed in an isothermal bath at 60°C for 2 h. The content of the flask was quenched in 100 ml of methanol. The polymer was filtered off and dried under vacuum (10^{-3} Torr) for 48 h at 35°C. The yield of the polymer was then determined. Similar procedure was followed for 0.2, 0.5, and 1.0 mol% AIBN fractions. Molecular weights were determined by viscosity in toluene at 25°C.

Elemental analysis. The samples were dried under vacuum (10^{-3} Torr) for 48 h. The metals were determined by atomic absorption and carbon, hydrogen by standard methods.

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 5–10 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^{-1}. The weight of the sample was continuously recorded as a function of the temperature.

RESULTS AND DISCUSSION

The synthesis of polymers with incorporated metals from sols or metal dispersed in styrene and acrylonitrile has been reported by us.[7–9] This work is an attempt to prepare copolymers of styrene and acrylonitrile (STAN) as follows:



Copolymer STAN

In this scheme, we have to keep in mind that several conformations are possible. The most probable copolymer is alternating due to the copolymerization ratios and also to the single decomposition temperature denoted in the TG curves (see Figure 1). The copolymer showed a different thermal decomposition (394.73°C) between styrene (405.38°C) and acrylonitrile (257.97 and 408.03°C).

The copolymers prepared have a wide range of molecular weight, stability and colours depending upon metal. The average molecular weight ($\bar{M}_V$) of these copolymers ranges from 1.0 to 7.9 × 10^5.[10] These copolymers exhibit a low amount

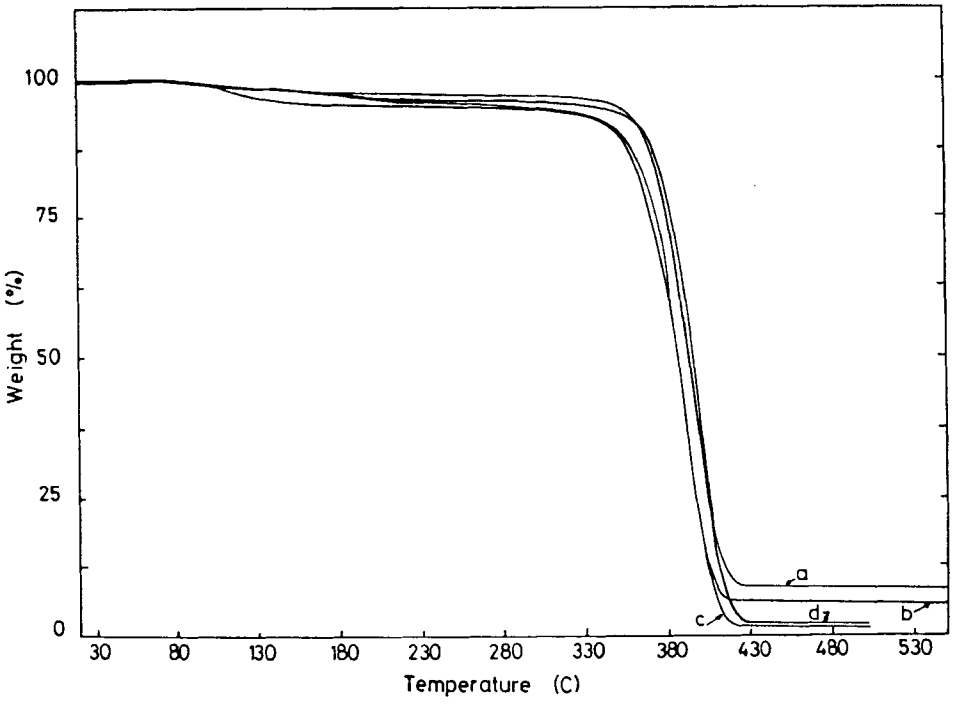


FIGURE 2 Thermogram of poly(styrene-co-acrylonitriles) obtained by heating the polymers from 25 to 550°C at 10°C min $^{-1}$. The fractions are obtained from (a) 0.1, (b) 0.2, (c) 0.5 and (d) 1.0 mol% AIBN, respectively.

of metal incorporated ranging from 0.84 to 2.0% (w/w). The presence of these metal clusters is responsible for the differences in thermal decomposition temperatures and also in the decomposition activation energy values.[11]

Figure 2 shows the change in sample weight as a function of time and temperature when the four fractions of poly(styrene-co-acrylonitrile) are heated from 25 to 550°C. The fraction 1 (the highest MW) exhibits the highest decomposition temperature (T_D) and also the highest activation energy (Ea), 177.8 kJ mol^{-1}. On the other hand, the lowest MW fraction shows 122.9 kJ mol^{-1} (Ea) and T_D at 25°C.

Ag, Pd, Cu, Ga and Sn exhibit high values of activation energy (see Table I).

These copolymers degrade in a single step, loosing most of the weight around 300°C. The decomposition reaction during the heating processes is irreversible so that the rate dependent parameters such as activation energy and order of reaction may be calculated from a single experiment curve.[12] By using the Arrhenius equation we can get some information about specific rate constant (k) and activation energy (Ea).

The thermal decomposition kinetics of the thermogravimetric weight loss data were attributed 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

TABLE I

Kinetic parameters for metal poly(styrene-co-acrylonitrile)

M-Copolymer	n	Ea* (kJ mol^{-1})	A (s^{-1})	Temp. range (°C)	T_D (°C)
$STAN_1$	0	177.8	58.8×10^6	350-415	394.73
$STAN_2$	0	161.7	62.3×10^8	345-415	391.23
$STAN_3$	0	135.7	7.1×10^6	330-415	387.96
$STAN_4$	0	122.9	59.7×10^2	340-420	385.25
Pd-$STAN_1$	0	113.0	11.1×10^2	350-415	390.45
Pd-$STAN_4$	0	109.1	41.4×10^3	330-420	398.93
Cu-$STAN_1$	0	101.2	12.7×10^3	350-420	391.23
Cu-$STAN_4$	0	108.7	49.0×10^3	340-420	390.30
Ag--$STAN_1$	0	167.6	17.1×10^3	350-435	394.03
Ag-$STAN_4$	0	114.1	74.6×10^3	330-420	411.06
Au-$STAN_1$	0	137.4	11.8×10^6	340-405	385.16
Au-$STAN_4$	0	144.2	4.2×10^6	330-403	383.92
Fe-$STAN_1$	0	128.4	2.2×10^6	345-405	386.72
Fe-$STAN_4$	0	134.0	4.5×10^6	355-415	393.56
Ga-$STAN_1$	0	139.0	11.0×10^6	355-415	393.50
Ga-$STAN_4$	0	117.8	27.6×10^2	330-412	390.90
Sn-$STAN_1$	0	147.1	54.8×10^6	340-415	394.73
Sn-$STAN_4$	0	171.8	23.9×10^6	340-410	388.20
Sb-$STAN_1$	0	146.8	43.6×10^6	340-415	391.93
Sb-$STAN_4$	0	124.4	79.1×10^2	330-415	389.36
Bi-$STAN_1$	0	154.2	26.1×10^5	330-403	384.93
Bi-$STAN_4$	0	142.4	24.2×10^6	345-410	387.03

STAN = poly(styrene-co-acrylonitrile)
1,2,3,4 = correspond to different fractions
* = the error of activation energy (molecular weight) is ranging from 5 to 10 (kJ mol^{-1})

rate with reaction order n. The reaction rates, $d\alpha/dt$, were calculated using a differential technique with heating rate of 10°C min^{-1}. The value was incorporated directly in the data of temperature versus sample weight fraction according to the method developed by Wen and Lin.[13] The specific rates, k, were obtained from the Arrhenius equation

$$k = Z \exp\left(\frac{-E}{RT}\right) \tag{2}$$

where Z is the pre-exponential factor, E the activation energy, T the absolute temperature and R the gas constant. Equations (1) and (2) were combined and used in a logarithmic form to obtain Equation (3)

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

A computer linear multiple regression program was developed to calculate the kinetic parameters E and Z from a linear least-squares fit of the data in a semilog

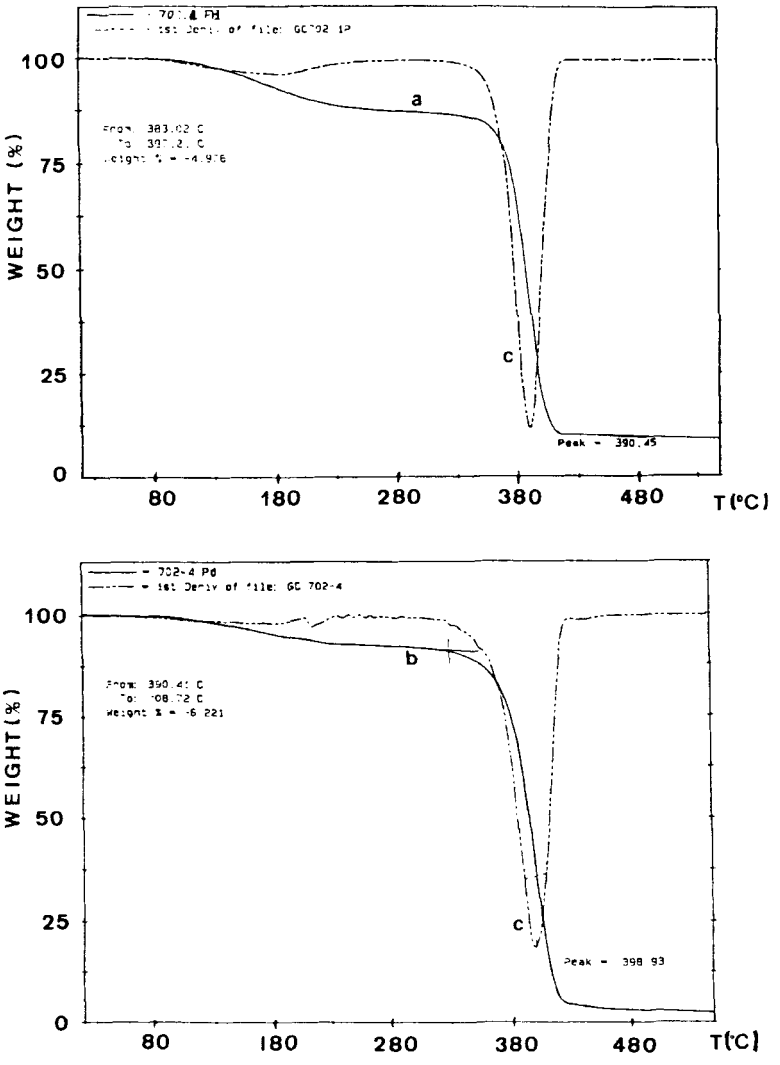


FIGURE 3 Thermogram of Pd-poly(styrene-co-acrylonitrile) obtained by heating the polymer from 25 to 550°C at 10°C min $^{-1}$. (a) fraction 0.1 mol% AIBN, (b) fraction 1.0 mol% AIBN, (c) DTG curves.

plot of β versus $1/T$. The Arrhenius plots for the thermal degradation of the metal copolymers (STAN) are shown in Figure 4. The linearity of each plot is very good (between 0.995 and 0.998), also some scattering was detected at the beginning of the decomposition, which might be attributed to the difficulty in obtaining accurate measurements at the beginning of an experiment, especially in kinetic measurements. Table I summarized the kinetic data obtained according to Equation (3), the temperature range used to calculate the parameters and the decomposition temperatures from the first derivative of the thermograms.

The decomposition temperatures of the copolymers are higher than the acrylonitriles with the same metal doped.[14] For instance, Pd-PAN exhibit a T_D 275°C and Pd-STAN 390°C. Similarly, Ga-PAN showed a T_D 325°C and Ga-STAN 394°C.

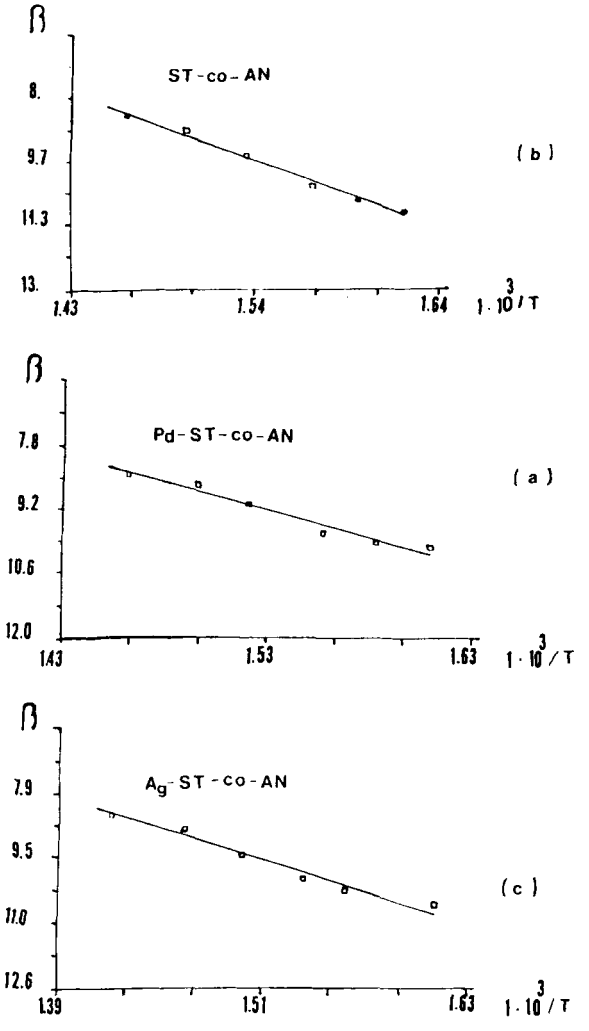


FIGURE 4 Arrhenius plot for the thermal decomposition of (a) Pd-STAN (fraction 1) (b) STAN (fraction 1), (c) Ag-STAN (fraction 1) according to Equation (3).

Furthermore, if we try to compare *Ea* of stable metals such as Pd and Au, in both cases the copolymers exhibit *Ea* higher than polyacrylonitriles already reported.[14] Even though these copolymer activation energies are still lower than M-polystyrenes.[15]

Most of the copolymers showed a zero reaction order, the same as the homopolymers, which means that $d\alpha/dt$ is constant and behaves as a simple evaporation because the concentration of volatile substances at the surface of the sample remains constant.[16] In Figure 3 we observe the thermograms of Pd-poly(styrene-co-acrylonitrile) for the highest (fraction 1) and lowest (fraction 4) molecular weights, respectively.

Similarly, we analyzed the data for 5 and 20°C min^{-1} heating rate. The activation energy values were obtained very close to the calculated data for 10°C min^{-1}.

The most relevant feature of this work was the order of the reaction for the decomposition reaction of metal poly(styrene-co-acrylonitriles) and the decomposition temperatures from the first derivative of the thermograms.

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