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Thermal analysis of metal polyacrylonitriles

G. Cárdenas T. [a,1], C. Retamal C. [a] and L.H. Tagle D. [b]

[a] *Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción (Chile)*

[b] *Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)*

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Abstract

The thermal stabilities of metal polyacrylonitriles (MPAN) were studied by thermogravimetric analysis (TGA) between 25 and 550 °C under nitrogen flowing at 10 °C min^{-1}. The metal contents of the polymers and their molecular weights are also reported. The kinetic data obtained by TGA showed that the thermostabilities of these polymers decrease in the order: Ge-PAN > Ga-PAN > Au-PAN > Sn-PAN > Bi-PAN > In-PAN > Pd-PAN > Sb-PAN. The experimental data suggest that the thermal stability of these polymers depends on the metal and the amount of metal incorporated. The reaction order for the one-step thermal decomposition of the polymers was found to be zero. The pre-exponential factor, the reaction order and the activation energies for the decomposition of the metal polyacrylonitriles were determined.

INTRODUCTION

The thermostability of polymers is a matter of current interest mainly due to their potential application as substitutes for metals and naturally occurring structural materials [1].

Thermogravimetry is used widely for assessing the thermal stability of polymeric materials and, as such, provides valuable technical information [2]. It must be noted that the conclusions drawn with respect to stability are only relevant within the context of loss of weight of the sample. However, there are reactions which can take place on heating a polymer which alter drastically the physical properties of the material without any observed change in weight.

Kinetic parameters such as activation energy, pre-exponential factor and reaction order, give a quantitative measure of thermal stability [3]. We have reported recently on polymers with incorporated metals, prepared by chemical liquid deposition [4,5]. Thermal degradation studies were carried out on

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[1] Author to whom correspondence should be addressed.

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several polyacrylonitriles containing metals such as Pd, Au, Ga, In, Ge, Sn, Sb and Bi.

EXPERIMENTAL

Colloid synthesis

Colloid synthesis using a metal-atom reactor has been previously reported [6–10].

Polymerisation

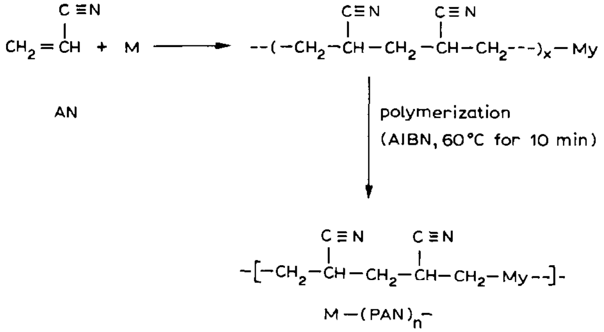
As a typical example, a 10 ml sample of colloid was placed in a polymerisation flask with 0.1 mol. azodiisobutironitrile (AIBN) under N_2 flow. The polymerisation flask was closed and placed in an isothermal bath at 60 °C for 10 minutes. The contents of the flask were poured into a beaker containing methanol. The black polymer was filtered off and dried under vacuum (10^{-2} Torr) for 24 h at 25 °C. The yield of each polymer was then determined.

Thermogravimetry

The thermogravimetric data were obtained using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature-program control. Samples (2–5 mg) were placed in aluminium pans and heated under flowing nitrogen (50 ml $\min^{-1}$) at a rate of 10 °C $\min^{-1}$ between 296 and 623 K.

RESULTS AND DISCUSSION

The synthesis of polymers with incorporated metal from sols or metal dispersed in monomers has been recently reported [11]. The polymers obtained have a wide range of molecular weight and colour, depending on the metal (see Scheme 1).



Scheme 1.

TABLE 1

Correlation between metals [a], microanalyses [b] and molecular weights

Polymer	%M	%N	%C	%N	M.W. ($\overline{M}_v \times 10^{-4}$)
Au–PAN	1.3	66.48	6.53	26.06	131.1
In–PAN	7.0	65.56	6.31	22.50	25.4
Sn–PAN	1.4	66.58	6.40	24.46	167.8
Pd–PAN	0.4	69.63	6.90	24.79	185.0
Sb–PAN	3.9	68.76	7.11	21.97	17.4
Ge–PAN	2.7	65.93	6.35	25.44	68.7
Bi–PAN	1.5	70.19	5.99	26.35	40.9
Ga–PAN	1.9	66.70	8.49	25.61	45.0
PAN	–	68.83	6.26	26.47	72.7

[a] The 0.1 mol.% AIBN is considered.

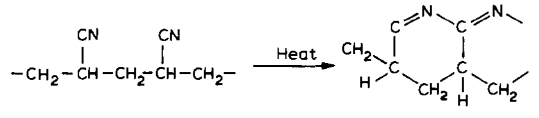
[b] The difference is probably oxygen.

The polymers show a low level of metal incorporation (0.4–7.9), see Table 1; this is due to the sol concentration which is around 10^{-3} M. The viscosimetric molecular weights range between 17×10^4 and 180×10^4 [12].

It is known that polyacrylonitrile is able to produce a chain condensation like that shown in Scheme 2. This cyclisation reaction of the nitrile groups which occurs between 250 and 300 °C (10 °C min^{-1}) is extremely exothermic and causes some fragmentation of the chain due to rapid heat build-up in the sample, because the heat cannot be dissipated at a sufficiently rapid rate [13].

Figure 1 shows the change in sample weight as a function of time and temperature when the eight metal polyacrylonitriles are heated from 298 to 823 K. Table 2 shows the thermal decomposition temperatures (T_D) for each polymer. These values were taken from the first pronounced change in slope of the TG curves. These results are similar to those reported by McNeill [13] for normal polyacrylonitriles.

The polymers degrade in one stage, with T_D being around 550 K. The data suggest that the thermal stability of the polymers reflects the colloid stabililty; Au and In have the most stable colloids. The thermostability depends on the metal attached to the chain. Furthermore, Au, Pd and Sn have the highest molecular weights ($\overline{M}_v$) which may also have some significance. For example, Pd–PAN exhibited a total weight loss of 15% at 673 K.



Scheme 2.

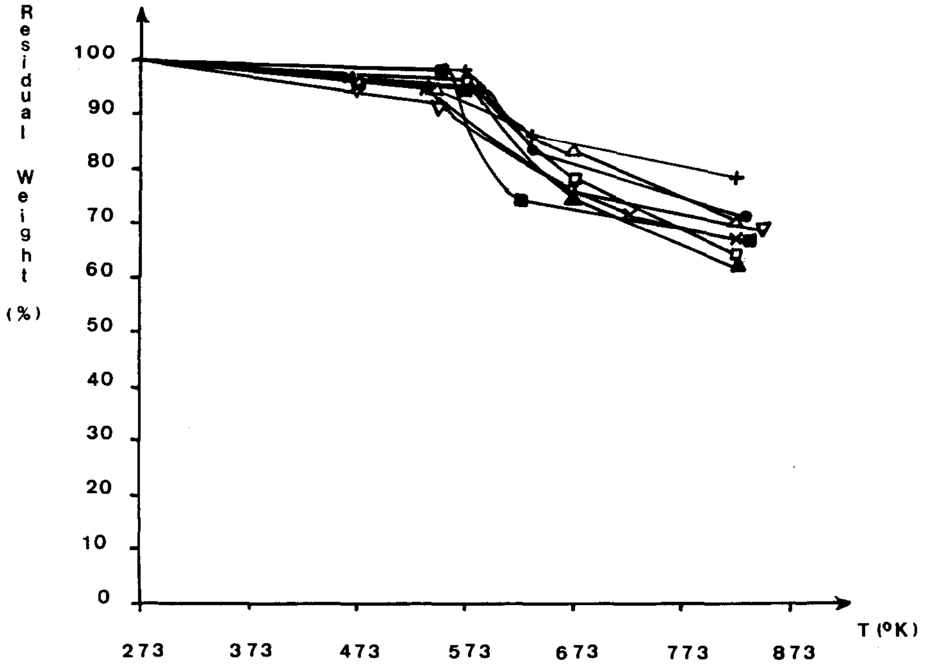


Fig. 1. Thermogravimetric curves of metal polyacrylonitriles measured with a heating rate of 10 °C min^{-1}: +, Ge–PAN; ●, Ga–PAN; ▲, Au–PAN; ×, Sn–PAN; ■, Bi–PAN; ▽, In–PAN; △, Pd–PAN; □, Sb-PAN.

It is interesting to observe that Ge–PAN has the highest T_D (633 K) and also the highest E_a. Bi–PAN is the most unstable polymer with a T_D of 623 K and a low E_a.

In all the experiments, it is possible to obtain a linear correlation between $\overline{M}_v$ and $[\text{AIBN}]^{-1/2}$. This is in agreement with the fact that the molecular weights decrease with increase in initiator concentration.

The cyclisation reaction can also produce changes in the stability due to the bonding of the metals with the carbon or nitrogen atoms.

TABLE 2

Kinetic parameters for metal polyacrylonitriles

Polymer	E_a (kJ mol^{-1})	Z (s^{-1})	n	T_D (K)
Bi–PAN	27.32	6.1×10^{15}	0	563
Sn–PAN	10.23	2.5×10^{3}	0	563
Ge–PAN	72.24	2.7×10^{2}	0	598
Ga–PAN	62.62	3.5×10^{1}	0	598
Au–PAN	58.62	1.8×10^{-1}	0	548
Sn–PAN	35.38	2.0×10^{-1}	0	548
In–PAN	18.55	6.8×10^{-3}	0	548
Pd–PAN	14.08	1.6×10^{-3}	0	548

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 [14]. The specific rate constant (k) can be expressed in the Arrhenius form

$$k = Z \exp(E/RT) \quad (1)$$

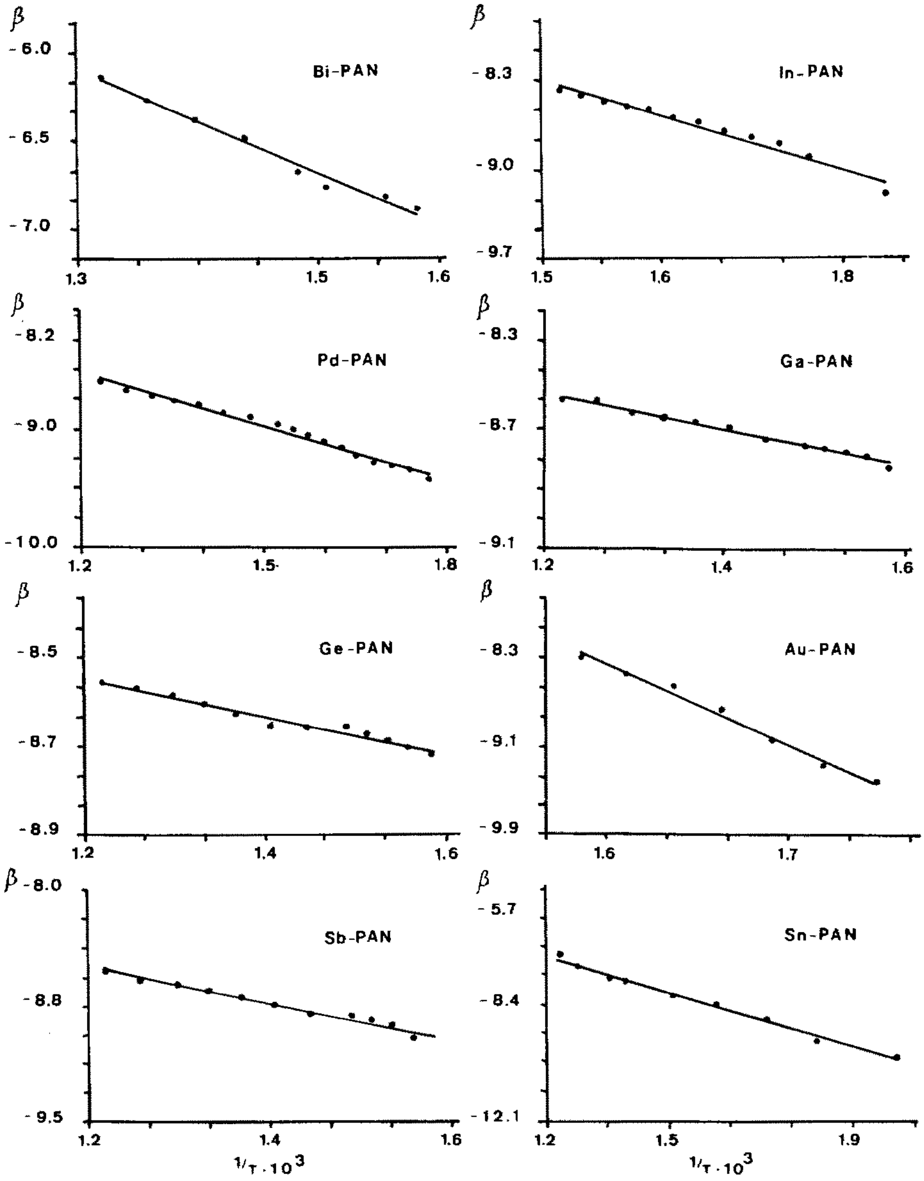


Fig. 2. Arrhenius plot for the thermal degradation of metal polyacrylonitriles according to eqn. (3).

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

The thermal decomposition kinetics of the thermogravimetric weight loss can be described by the kinetic equation

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

where α is the 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 and incorporating the heating rate v (10 °C min^{-1}), using temperature versus sample weight-fraction data [15]. Equations (1) and (2) are combined incorporating v and using the logarithmic form

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

A multiple regression program was used to calculate the kinetic parameters E and Z assuming a first-order reaction model. Plotting β versus $1/T$ should give a straight line (see Fig. 2). From the slope and intercept, E and Z can be determined.

For all the metal polymers, the linear relationship obtained indicated that the reaction order is zero. The coefficients of linear correlation vary from 0.982 to 1.004. The kinetic parameters E and Z calculated from these plots are summarised in Table 2.

In general, all the polymers showed low activation energies, but they are larger than the values for metal poly(methylmethacrylates) already reported [16]. They range from 10.23 to 72.24 for Pd and Ge, respectively. The kinetic parameters obtained for the thermal decomposition of these polymers show a relationship between the metal and activation energy: Ge–PAN has a higher E_a and its thermogram shows lower weight loss (20%).

Another interesting point is that similar metals, such as Ge and Ga, and Sn and Bi, have E_a values within the same range. One of the most important results of this study is that the order of reaction for the decomposition of metal polyacrylonitriles is zero.

ACKNOWLEDGEMENT

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