

## Thermal studies of metal polystyrenes. Part IV

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### Abstract

The thermal stability of metal polystyrene was determined by thermogravimetric analyses (TGA) from 25 to 250°C under nitrogen flow.

The kinetic data obtained by TGA show that the thermostability of these polymers decreases in the following order: Pd-PS > Au-PS > Bi-PS > Cu-PS > In-PS > Ga-PS > Sb-PS > Ge-PS. The data might indicate that the thermal stability of these polymers is related to the metal attached to the polymer chain. The energies of activation of the metal polystyrenes were determined. The order of reaction for the thermal decomposition of these metal polymers was zero. The pre-exponential factor and decomposition temperatures were determined.

### INTRODUCTION

The thermostability of polymers is always of great interest for their industrial applications. Kay and coworkers have reported some interesting properties of gold clusters in fluorocarbon polymer films prepared by plasma methods [1,2]. Andrews and Ozin [3] have also reported studies of metal atoms and clusters in liquid monomers.

Stabilizing polymers are often used in the preparation of colloidal solutions. Very little is known about the interaction between the colloidal particles and the polymers. Poly(vinyl alcohol) and polyphosphate have been used to stabilize PbS [4].

In this report we have developed a new approach to preparing metals trapped in solid, organic polymers, based on our earlier work related to the synthesis of colloidal metals in non-aqueous solvents [5–7]. Only Au and Pd have been previously reported to produce doped polystyrenes [8]. We have

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obtained several polystyrenes with metals such as Pd, Au, Cu, Ga, In, Ge, Sn, Sb and Bi.

## EXPERIMENTAL

### *Colloidal synthesis*

Colloid synthesis using a codeposition technique has been published elsewhere [5,7,8].

### *Polymerization*

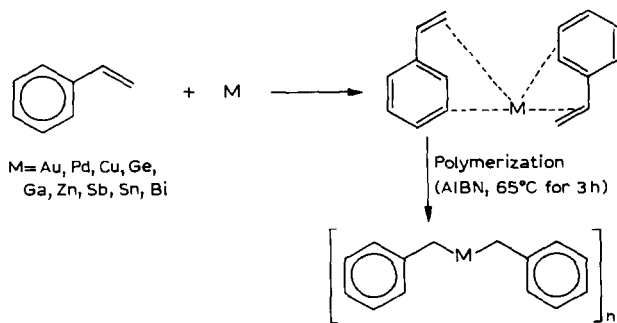
As an example, Pd colloid (10 ml) was placed in a polymerization flask with 0.1 mol.% azodiizobutyronitrile (AIBN) under  $N_2$  flow. The flask was closed and placed in an isothermal bath at  $65^\circ C$  for 50 min. The contents of the flask were poured into a beaker with methanol. The black polymer was filtered off and dried under vacuum for 24 h at  $20^\circ C$ . The yield of the black polymer was determined.

### *Thermogravimetric analysis*

The thermogravimetric data were obtained using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (3.0 mg) were placed in Al pans and heated under dynamic nitrogen at  $10^\circ C \text{ min}^{-1}$  between 298 and 823 K.

## RESULTS AND DISCUSSION

The synthesis of polystyrene with metal incorporated from sols or metal dispersed in monomers has been recently reported [8,9]. The metal polystyrenes have a molecular weight range of between  $5 \times 10^4$  and  $17 \times 10^4$



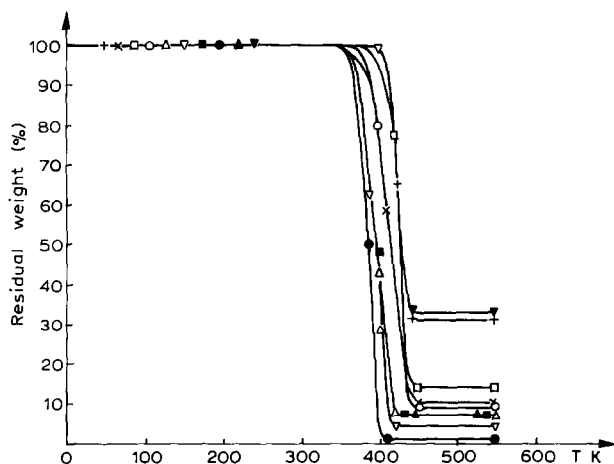


Fig. 1. Thermogravimetric curves of metal polystyrene recorded at a heating rate of  $10^{\circ}\text{C min}^{-1}$  for: +, Au-PS; x, Pd-PS; □, Cu-PS; ○, Ge-PS; △, Ga-PS; ▽, In-PS; ■, Sb-PS; ●, Sn-PS; ▲, Bi-PS; ▼, PS.

( $\bar{M}_v$ ) [10]. The colors and morphology are different depending upon the metal.

The metal content of the polymers is very low, ranging between 0.5% for Au and 2.8% for Pd. The sols obtained were around  $10^{-3}$  M concentration.

Figure 1 shows the change in weight as a function of time and temperature when the metal polystyrenes are heated from 298 to 823 K.

The polymers degrade in one stage with a  $T_D$  around 670 K. The data showing that the thermal stabilities of the polystyrenes are different with different metals bonded to the chain. Cu and Au polystyrene are similar in stability to PS, the only difference being the residual weight. Here there is no clear relation between decomposition temperature ( $T_D$ ) and activation energy. If we examine Table 1, it is easy to see that Pd-PS and Au-PS have the highest  $E_a$ , probably owing to their more stable colloids. Another explanation could relate to the percentage of metal incorporated in the polymer. For example, Pd-PS which is very stable and contains 2.8% metal, gives the highest  $E_a$ ; and Ge-PS has the lowest  $E_a$  and 0.3% metal in the chain [10].

The decomposition reaction is irreversible and the rate-dependent parameters such as activation energy and reaction order can be calculated from a single experimental curve [11].

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

$$-d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

where  $\alpha$  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  $d\alpha/dt$

TABLE 1

Kinetic parameters for metal polystyrenes

Polymer <sup>a</sup>	$E_a$ (kJ mol <sup>-1</sup> )	$Z$ (s <sup>-1</sup> )	$n$
In-PS	319.74	$1.0 \times 10^{21}$	0
Pd-PS	421.32	$1.0 \times 10^{30}$	0
Au-PS	404.38	$5.2 \times 10^{27}$	0
Sb-PS	303.48	$1.9 \times 10^{20}$	0
Bi-PS	402.79	$8.2 \times 10^{27}$	0
Sn-PS	373.71	$5.4 \times 10^{25}$	0
Cu-PS	397.06	$7.7 \times 10^{26}$	0
Ge-PS	245.60	$1.1 \times 10^{15}$	0
Ga-PS	315.64	$7.0 \times 10^{20}$	0
PS	250.00	$1.0 \times 10^{20}$	0

<sup>a</sup> PS = polystyrene. In all these polymers, the 0.1 mol% AlBN fraction was used for comparison.

was calculated using a differential technique, including the heating rate  $\nu$  (10°C min<sup>-1</sup>) and using temperature versus sample weight-fraction data [12]. We can establish from the Arrhenius equation

$$(d\alpha/dt) = \nu(d\alpha/dT) \quad (2)$$

$$k = Z \exp(-E/RT) \quad (3)$$

where  $Z$  is the frequency factor,  $E$  the activation energy,  $R$  the gas constant and  $T$  the absolute temperature; from eqn. (1) after introducing  $\nu$ , we can obtain a logarithmic form

$$\beta = \ln \left[ \frac{d\alpha/dt}{\nu(1-\alpha)^n} \right] = \ln Z - \frac{E}{RT} \quad (4)$$

To calculate the kinetic parameters  $E$  and  $Z$  and assuming a first-order reaction model, a multiple regression program was used plotting  $\beta$  against  $1/T$ ; a straight line should be obtained (see Fig. 2).  $E$  and  $Z$  can be determined from the slope and intercept.

For metal polystyrenes, the linear relationship obtained indicates that, for most of them, the reaction order is zero. The coefficients of the linear correlations fall around 0.988.

The kinetic parameters  $E$  and  $Z$  calculated from these plots are summarized in Table 1.

The metal polystyrenes showed a higher energy of activation than the poly(methyl methacrylates) reported previously [13]. Several authors have already published the activation energy of the thermal decomposition of polystyrenes. The values reported fall between 235 and 250 kJ mol<sup>-1</sup> [14,15]. Table 1 reveals that Pd-PS has the highest  $E_a$  (421.32 kJ mol<sup>-1</sup>) and Ge-PS the lowest (245.60 kJ mol<sup>-1</sup>), Cu-PS and Au-PS are similar in

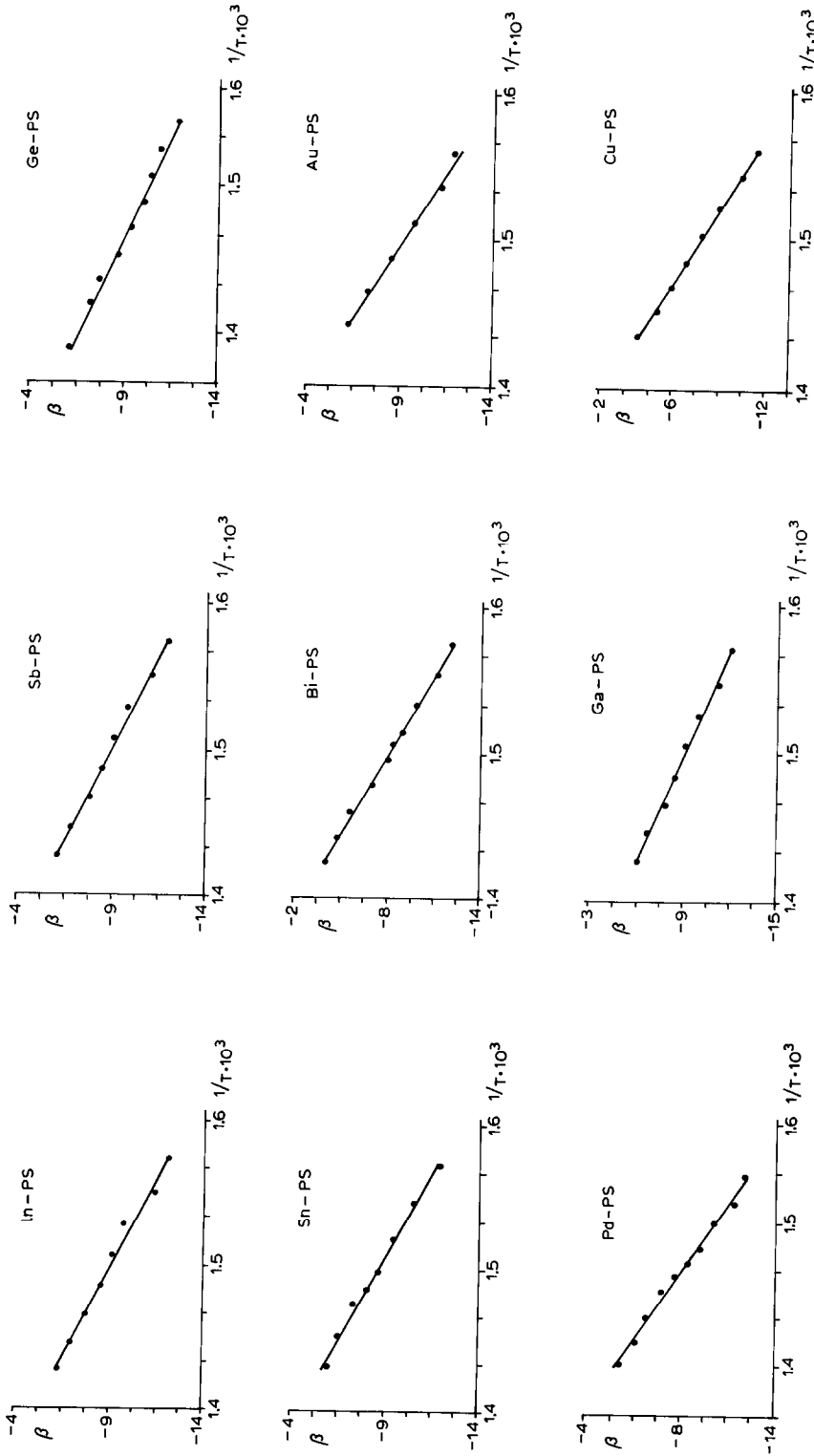


Fig. 2. Arrhenius plot for the thermal degradation of metal polystyrenes according to eqn. (3).

$E_a$ , and Ga-PS and In-PS form another pair. We believe that this is because the metals belong to the same group.

Linear plots are obtained when the molecular weight is plotted against  $(\text{AIBN})^{-1/2}$ , both for pure styrene and for gold-doped styrene [10]; therefore the polymerization process has not been influenced by the metal.

These metal-doped polymers seem very homogeneous. With gold, light to deep purple, transparent solids were obtained. For palladium, several shades of black were obtained.

We can conclude from this study that the reaction order for the decomposition of polystyrene is zero. Thus, the concentration of the volatile substance at the outer surface of the sample remains constant.

#### ACKNOWLEDGEMENTS

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