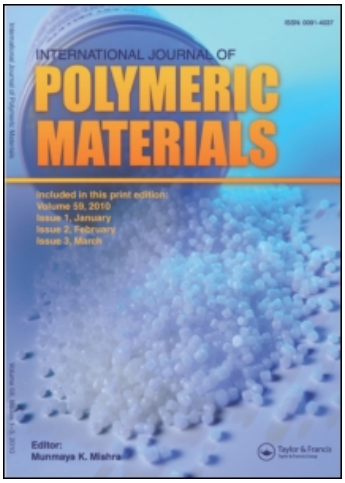

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Thermal Studies of Metal Poly(4-methyl styrene-*co*-styrene) with BPO. Part XVII

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Metal poly(4-methyl styrene-*co*-styrene) copolymers were obtained by radical polymerization with benzoyl peroxide. 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 monomer they can generate a matrix at 77 K. After the warm up process, metal comonomer colloids can be obtained. The colloids were polymerized with benzoyl peroxide at 70°C for 0.5 h at 70°C. Four different initiator concentrations (0.1, 0.5, 1.0 and 2.5 mol %) were used. The yields are around 25% and the viscosimetric molecular weight ranges from 10^4-10^5 g/mol. The higher $\bar{M}v$ are Ag, Ga and Sn-poly(4-methyl styrene-*co*-styrene). 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 a single step around 300°C. The kinetic data thus obtained show the thermostabilities decrease in the order: Ga-(4-MeS-S) > Sb-(4-MeS-S) > Ge-(4-MeS-S) > In-(4-MeS-S) > Zn-(4-MeS-S) > Ag-(4-MeS-S) > Pd-(4-MeS-S) > Cu-(4-MeS-S) > Sn-(4-MeS-S) > Au-(4-MeS-S) > Bi-(4-MeS-S). The thermal stability is depending upon the amount and metal incorporated in the polymer matrix. The decomposition reaction order is zero and we are in the presence of a single decomposition reaction. 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, comonomer colloids, metal atoms, molecular weight, decomposition temperature.

INTRODUCTION

Previous papers of these studies concerning the thermal properties of metal poly(styrene)s, poly(methyl methacrylate), polyacrylonitrile, poly(vinyl acetate),[1-4] have shown that different metals and the reduction potential are important to determine their thermal characteristics, i.e. activation energy and order of the decomposition reaction of these polymers. Based on these investigations, the results of TG and DTG were used to explain some metal polymers and copolymers properties, such as thermal stability.

The domain of applicability of thermal analysis is in the group of processes involving solids in which we can distinguish reactions of thermal decomposition, in

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which solids undergo transformation with evolution of gaseous dissociation products.[5]

During the calculations of activation energy from Arrhenius equation an uncertainty should be produced in extrapolations over temperature.[6] Therefore, the range should be kept as short as in practical measurements.

The objective of the present study was to improve the knowledge of the TG data. This was connected with the presence of metal clusters in the copolymers and the differences depend on the amount and nature of the metal incorporated. In this paper, we report the thermal behaviour of the metal poly(4-methyl styrene-*co*-styrene) copolymers prepared with benzoyl peroxide.

EXPERIMENTAL

Comonomer Colloid Synthesis

The metal comonomer colloids were prepared by simultaneous codeposition of the 4-methyl styrene and styrene with the metals at 77 K using a metal atom reactor.[7,8]

The colloid synthesis and the copolymer properties and parameters has been recently reported.[9]

Polymerization

As a typical example, germanium colloid (10 ml) was placed in a polymerization flask with 0.1 mol % of benzoyl peroxide (BPO) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath (Heidolph) at 70°C for 3 h. The content of the flask was quenched in 100 ml of methanol. The copolymer was filtered off and dried under vacuum (10^{-3} Torr) for 48 h at 35°C. The yield of the copolymer was determined. Similar procedure was followed for 0.5, 1.0 and 2.5 mol % BPO fractions.

Molecular Weights

The viscosimetric molecular weights ($\bar{M}v$) were determined by using an Ostwald viscometer. The samples were dissolved in benzene at 25°C and the parameters $K = 8.11 \times 10^{-5}$ (dL/g) and $a = 0.75$ were used.[10]

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 4–6 mg.

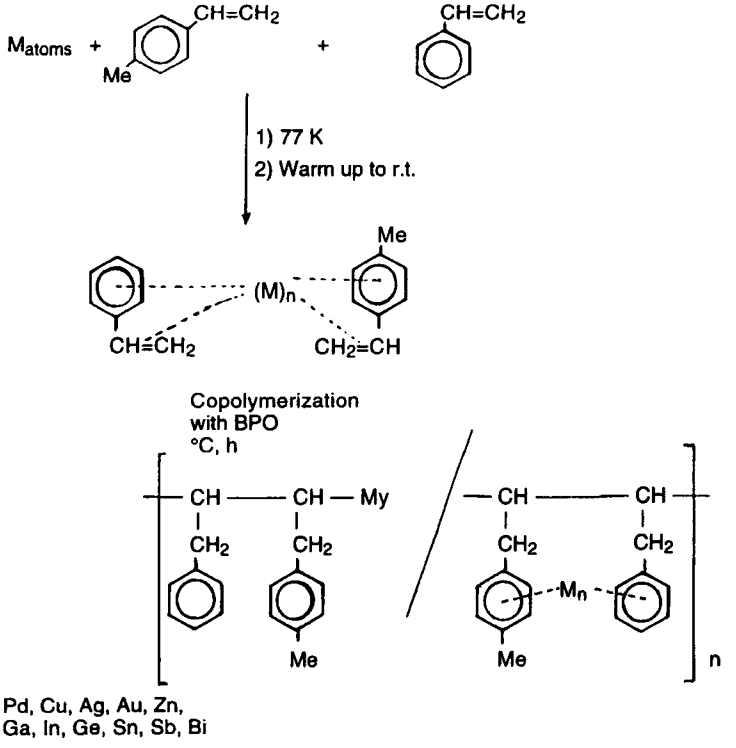
The sample pan was placed in the balance system in equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The weight of the sample pan was continuously recorded as a function of the temperature.

Elemental Analysis

The samples for microanalysis were dried under vacuum (10^{-3} Torr) for 48 h. The metals were determined in a Perkin-Elmer 3100 Model atomic absorption spectrometer. The C/H were obtained in a Perkin-Elmer 2400 Model Automatic Analyzer.

RESULTS AND DISCUSSION

The synthesis of metal poly(4-methyl styrene-*co*-styrene) copolymers with BPO has been recently reported.[9] The copolymers exhibited a low metal content and they can be prepared by cocondensation of the metal and the monomers simultaneously.



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

During the warm up process and later on during polymerization or copolymerization reaction, the small metal clusters tend to grow until the growing polymer chains trap them.

The copolymers show a very low level of metal incorporation, between 0.16–0.74%, Bi being the lowest and Ga the highest (see Table I). The metal clusters in the copolymer are similar in concentration to metal poly (4-MeS)[11] but lower than metal polystyrene.[1,12] Due to the similar reactivities and probably due to the steric effect of the aromatic rings the metal clusters are not able to approach the copolymer. However, the doped copolymers exhibited different colours and in several cases higher decomposition temperatures. The stability of the copolymers is related to the

TABLE I

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

Copolymer	Metal (% w/w)	Temp. Range (°C)	E_a (kJ/mol)	T_D (°C)
(4-MeS-S)-1	—	360–425	77.21	412.26
(4-MeS-S)-2	—	375–435	64.61	409.23
(4-MeS-S)-3	—	365–410	68.40	405.33
(4-MeS-S)-4	—	360–430	41.85	401.21
Sb(4-MeS-S)-1	0.20	274–446	71.95	424.26
Sb(4-MeS-S)-4	0.05	368–438	46.38	413.80
Ga(4-MeS-S)-1	0.74	370–457	73.19	428.53
Ga(4-MeS-S)-4	0.40	355–420	47.37	395.90
Ge(4-MeS-S)-1	0.16	387–447	66.15	420.54
Ge(4-MeS-S)-4	0.14	350–430	57.52	402.51
In(4-MeS-S)-1	0.67	370–430	91.07	418.76
In(4-MeS-S)-4	0.64	365–430	59.34	418.11
Zn(4-MeS-S)-1	0.38	370–430	79.87	416.16
Zn(4-MeS-S)-4	0.16	350–425	50.08	400.34
Ag(4-MeS-S)-1	0.18	361–440	52.51	416.14
Ag(4-MeS-S)-4	0.35	209–443	40.45	412.92
Pd(4-MeS-S)-1	0.35	360–430	43.35	414.65
Pd(4-MeS-S)-4	0.26	360–430	29.05	413.78
Cu(4-MeS-S)-1	0.32	375–420	74.93	408.58
Cu(4-MeS-S)-4	0.11	370–405	55.68	402.95
Sn(4-MeS-S)-1	0.43	370–410	76.26	407.06
Sn(4-MeS-S)-4	0.29	360–400	51.80	398.61
Au(4-MeS-S)-1	0.17	385–415	73.96	406.41
Au(4-MeS-S)-4	0.08	360–405	51.67	395.15
Bi(4-MeS-S)-1	0.16	360–430	62.53	405.26
Bi(4-MeS-S)-4	0.15	350–425	45.74	397.75

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

amount of metal clusters incorporated, i.e. Ga and In exhibited the higher stability (see Table I). It is interesting to observe that the lower MW fraction in most of the copolymers gives lower decomposition temperatures (T_D) (see Figure 2). The T_D values are similar to the AIBN series recently reported.[13] This is also consistent with the fact that the lower MW fraction showed lower metal cluster incorporation in the copolymers.

The shapes of the thermograms are similar with decomposition in one stage, which is another demonstration of the copolymer formation. This behaviour is similar to another metal copolymers already reported,[14,15] and other metal polymers.

The four MW fractions represented in Figure 1 are exhibiting a single-step process. The T_D are increasing from 401.2 to 412.2°C with the increase of the MW. At T = 400°C, at least 50% of the residual weight has decomposed; therefore, this copolymer can be considered stable. They do not lose weight even at 360°C.

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

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

where α is the fraction of the sample weight reached at time t, and k is the specific

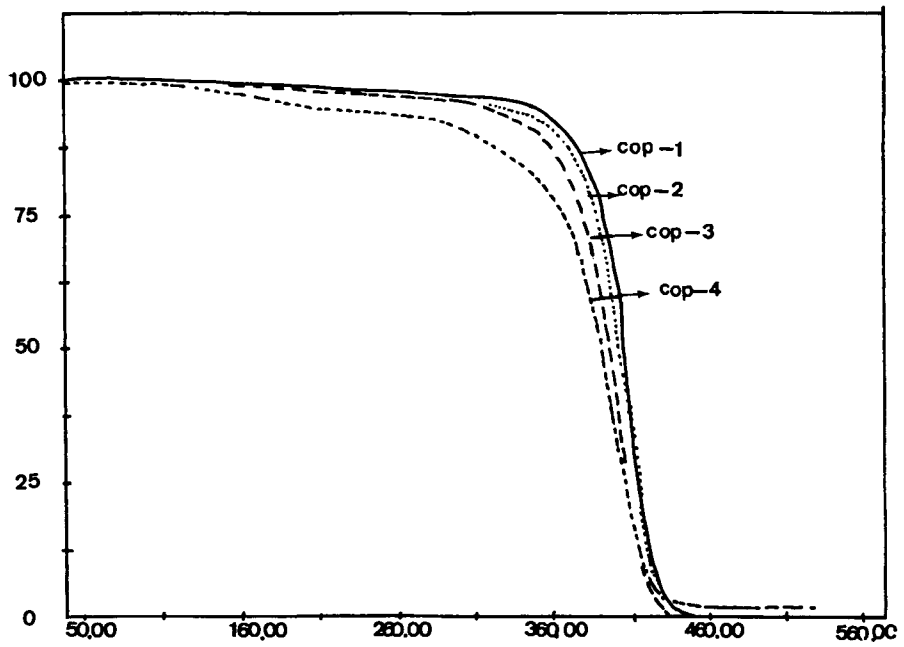


FIGURE 1 Thermograms of poly (4-methyl styrene-*co*-styrene) copolymers obtained by heating the copolymers from 25 to 550°C at 10°C min^{-1}. 1) 0.1 mol %, 2) 0.5 mol %, 3) 1.0 mol %, and 4) 2.5 mol % of benzoyl peroxide, respectively.

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.[16] 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 temperature and R the gas constant. After combining Equations (1) and (2) and using the logarithmic form we obtained:

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

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 $1/T$. The Arrhenius plots of In and Pd, fractions 1 and 4, respectively are exhibited in Figure 2. The plots showed a very good correlation.

The pure copolymer showed E_a between 41.85 and 77.20 kJ/mol (Table I). The highest T_D value was found for In-(S-4-MeS) with 91.07 which is lower than the copolymer already reported with AIBN.[13] Sn, Au, Cu and Ga showed also higher values of E_a (76.26, 73.56, 74.93 and 73.19 kJ mol^{-1}), respectively. The activation energies of these copolymers are lower than that of the homopolymer containing metals.[11,17]

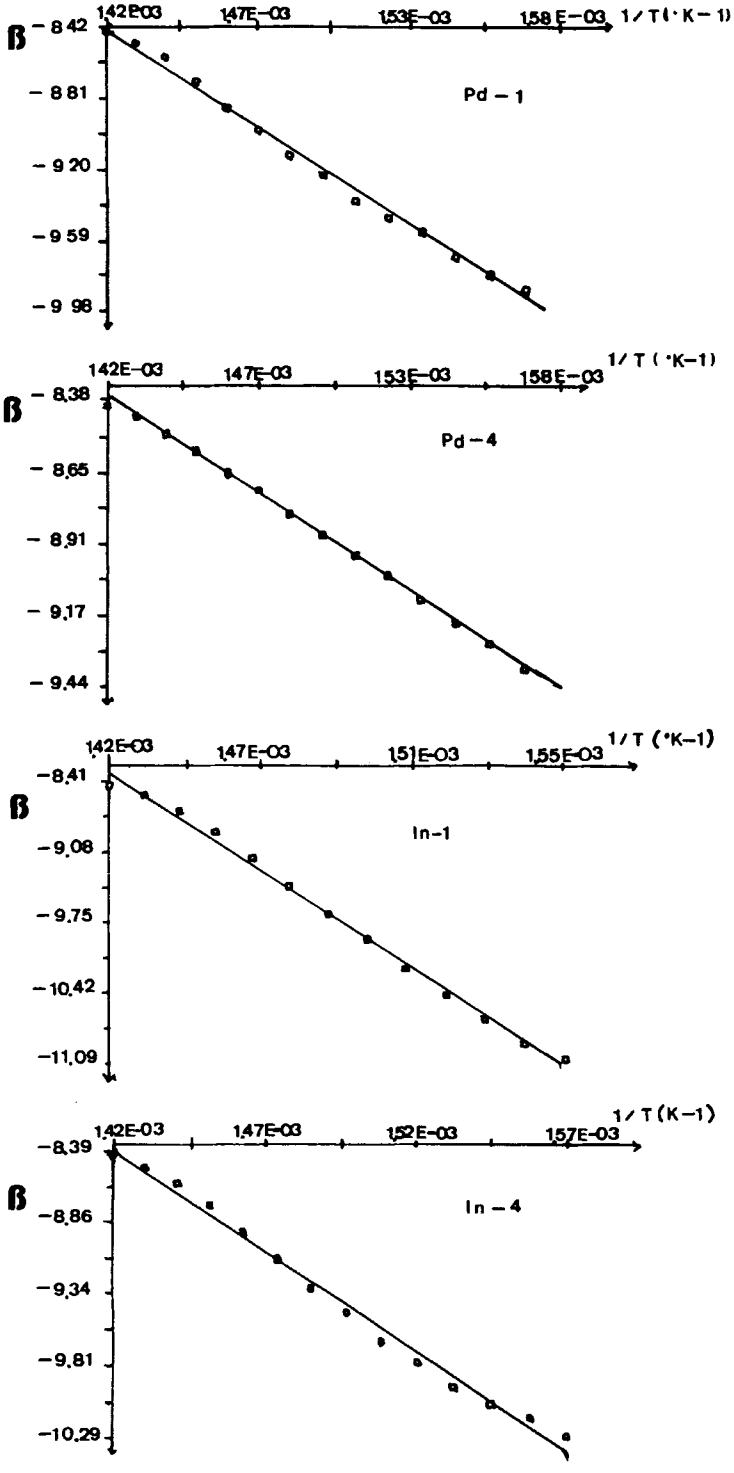


FIGURE 2 Arrhenius plot for the thermal decompositon of (a) Pd-poly(4-MeS-S) fraction 1 and 4, (b) In-poly(4-MeS-S) fraction 1 and 4.

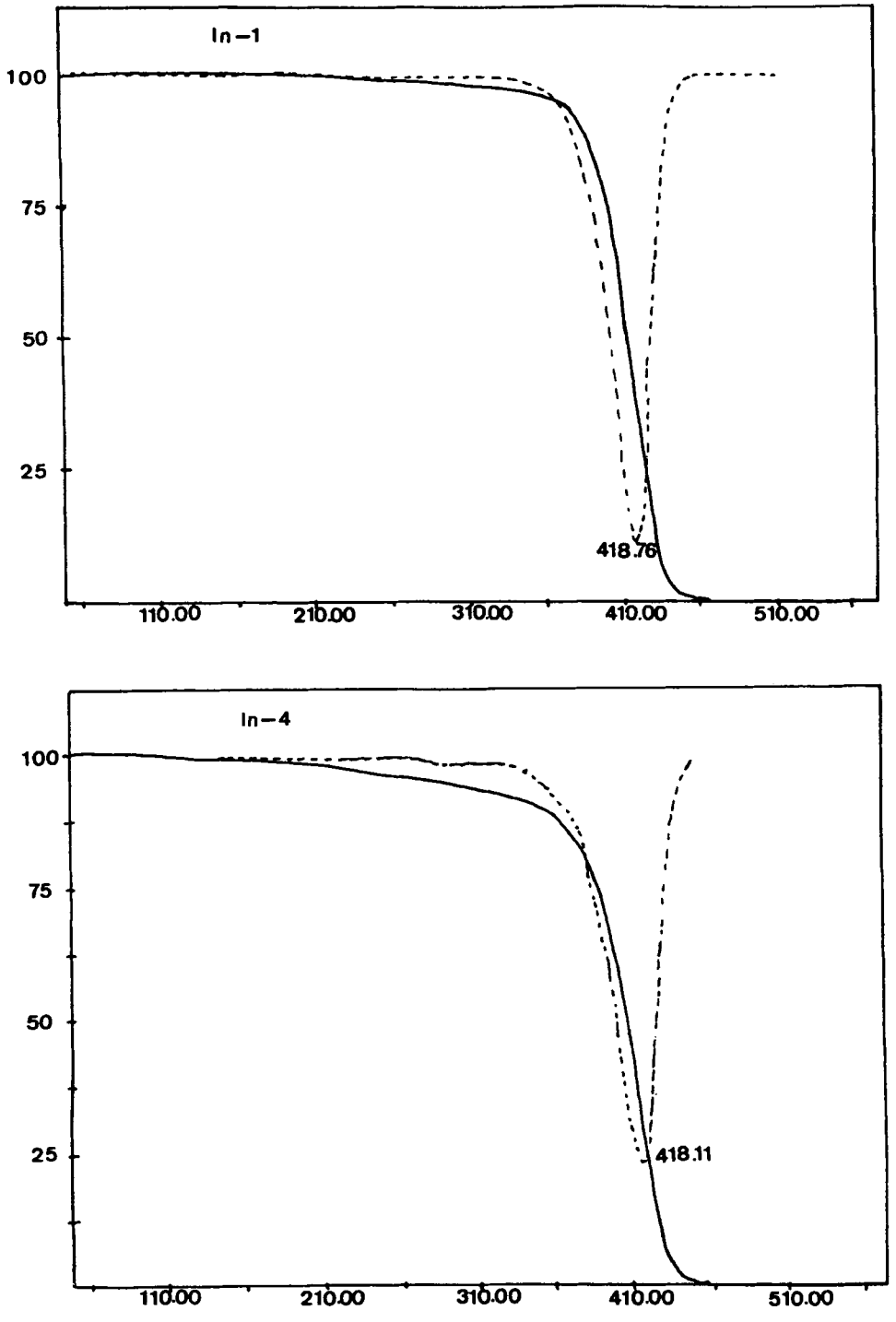


FIGURE 3 (a) Thermogram of In-poly(4-MeS-S) obtained by heating the polymers from 25 to 550°C at 10°C min^{-1} for 0.1 mol % BPO. (b) TG curve of In-poly(4-MeS-S) for 2.5 mol % BPO and their DTG curves.

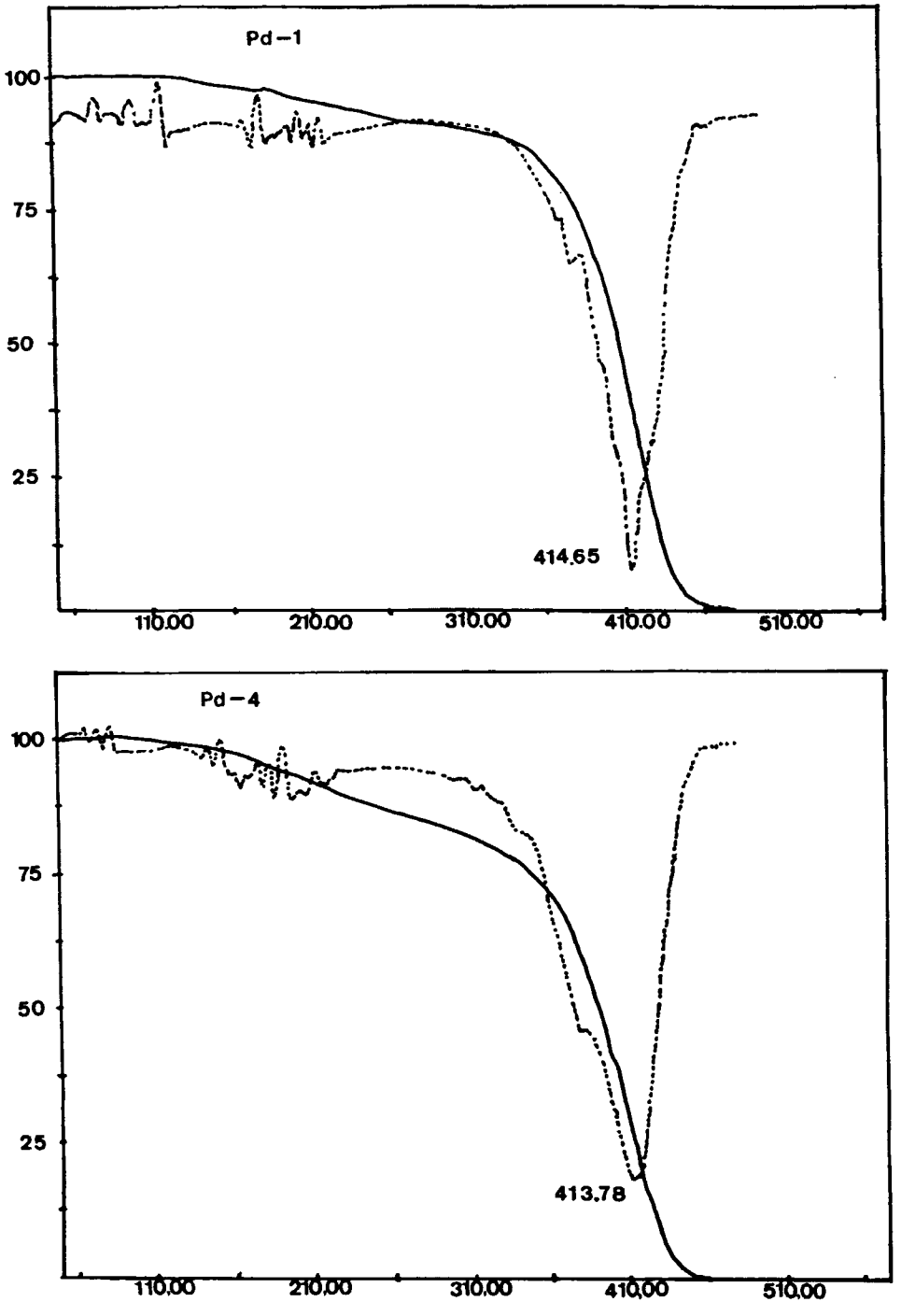


FIGURE 4 (a) Thermogram of Pd-poly(4-MeS-S) obtained by heating the polymer from 25 to 550°C at 10°C min^{-1} for 0.1 mol % BPO. (b) TG curve of Pd-poly(4-MeS-S) for 2.5 mol % BPO and their DTG curves.

Figure 3 shows the thermograms of In (4-MeS-S) (fractions 1 and 4), it is interesting the fact that T_D in both cases, 418.76 and 418.11°C are higher than the copolymers prepared with AIBN.[13] Similar behaviour was found for Pd(4-MeS-S) with T_D 418.76 and 418.11°C for fractions 1 and 4, respectively (Figure 4).

The decomposition temperature has been increased in more than 15°C for In (4-MeS-S) and only Cu and Bi (4-MeS-S) exhibited lower E_a than the undoped copolymer (Table I). This is probably due to the easy oxidation of these metals.

All the copolymers showed decomposition order of reaction zero ($n = 0$), with a single slope in the thermograms. The stability of most of the copolymers is strongly related to the amount of metal clusters on them.

Acknowledgments

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