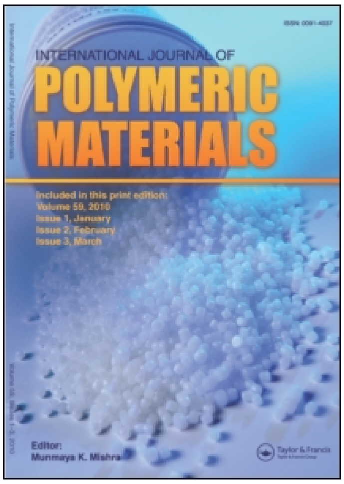

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Thermal Studies of Metal Poly(Styrene-co-Ethyl Methacrylates) Part XVIII

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Metal poly(styrene-co-ethyl methacrylates) copolymers were obtained by radical polymerization with benzoyl peroxide (BPO) and azodiisobutironitrile (AIBN). The monomers were cocondensed with the metals: Pd, Cu, Ag, Au, Zn, Cd, Ga, In, Ge, Sn, Sb and Bi at 77 K. The metals were evaporated to produce atoms and with the monomers they can generate a matrix on the reactor walls at low temperature. During the warm up process, metal-co-monomer colloids can be obtained. The colloids were polymerized with BPO at 65°C for 3.5 h and with AIBN at 65°C for 3.4 h. From different initiator concentrations (0.1, 0.2, 0.5 and 1.0 mol%) were used. The yields are fairly low and the viscosimetric molecular weight range from 10^4–10^5 g/mol. The higher $\overline{M}v$ are Cd, Pd, Ag and Au-poly(styrene-co-ethyl methacrylates) for AIBN series and Ag, Pd, Au and Zn-SEMA for BPO series. The thermal stabilities of these metal polymers have been studied by thermogravimetry (TG) between 25 and 550°C under nitrogen flow. The decomposition temperatures were obtained from 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 process around 300°C. The kinetic data thus obtained show the thermostabilities decrease in the order: In-SEMA > Bi-SEMA > Sn-SEMA > Ga-SEMA > Zn-SEMA > Au-SEMA > Cd-SEMA > Pd-SEMA > Ge-SEMA > Cu-SEMA > Sb-SEMA > Ag-SEMA for AIBN and Cd-SEMA > Sn-SEMA > Pd-SEMA > Ag-SEMA > Bi-SEMA > Ge-SEMA > Au-SEMA > Zn-SEMA > Sb-SEMA > In-SEMA > Cu-SEMA > Ga-SEMA for BPO.

The thermal stability is depending upon the metal incorporated in the polymer matrix. The decomposition reaction order is zero either for AIBN or BPO series of metal copolymers. The pre-exponential factor and the activation energy of the decomposition reaction for all the copolymers have been determined.

Keywords: Poly(styrene-co-ethyl methacrylate); metal clusters; thermal analysis; decomposition kinetics; thermal stability

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INTRODUCTION

The thermodynamics of irreversible processes is based on the hypothesis that thermodynamic changes occur as the consequence of relevant driving forces in the system [1]. In this method each thermodynamic flux is a linear function of all gradients present in the system (e.g. temperature or concentration). The flux of chemical reaction is also named rate of reaction, determining changes in concentration (concentration (α) in time (t)). We are using relatively simple functions of α to find out reaction mechanisms [2–4]. For each mathematical function a certain value of a rate constant is given at constant temperature. Under these conditions the temperature influences rate constant $k(T)$, which is related in the Arrhenius equation [5]. This method reveals rate constants, when changes in the system are obtained experimentally.

From the starting of development of chemical kinetics, people have been working to discover new methods for theoretical evaluation of rate contents.

Several functions for the description of reaction mechanisms in the solid phase, reflect only physical processes and do not consider the chemical nature of them.

Even though we are using the Arrhenius approach; being an extension of one developed for reactions in the gas phase, we will get information about the activation energy and order of reaction of decomposition processes during thermogravimetry.

The values of E_a can give as a better understanding to correlate the presence of different metal clusters in copolymers of styrene-co-ethyl methacrylate.

EXPERIMENTAL

Colloid Synthesis

The colloid metals (styrene-methyl methacrylate) were prepared by cocondensation of the monomers (1:1 mol ratio) with the metals at 77 K using a metal atom reactor [6, 7]. Assuming that all the metal atoms evaporated are incorporated in the monomers dispersion the approximate concentration could be calculated. Different current intensities were used depending upon the metal and the vacuum used [8].

Polymerization

As a typical example, tin colloid (10 mL) was placed in a polymerization flask with 0.1 mol% of AIBN under nitrogen atmosphere. The flask was closed and placed in an isothermal bath at 65°C for 3.5 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 copolymer was determined. Similar procedure was followed for 0.2, 0.5 and 1.0 mol% AIBN fractions). Molecular weights were determined in 2-butanone ($K = 9.3 \times 10^{-5}$ and $a = 0.72$) [9].

Identical method for copolymers prepared with BPO was achieved.

Elemental Analysis

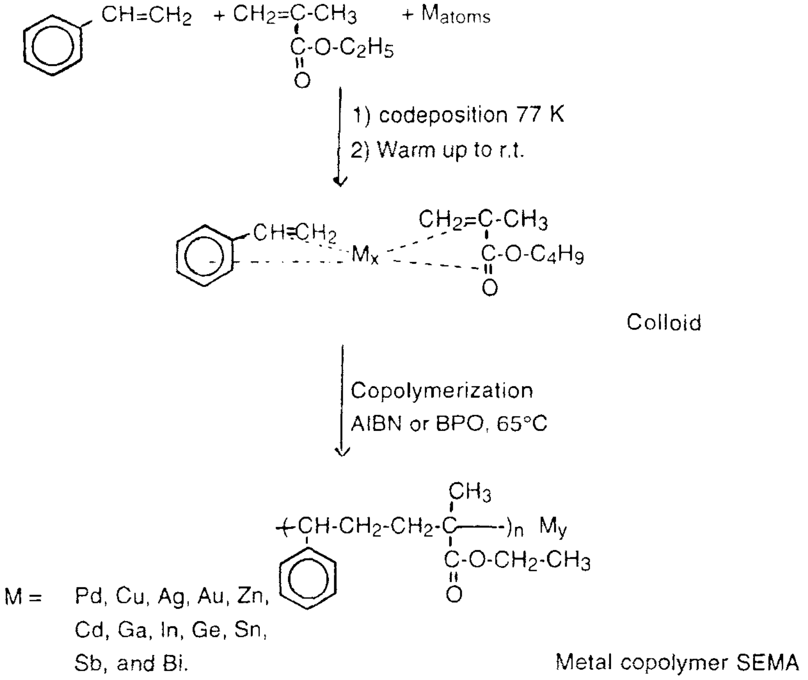
The metals were determined by atomic absorption in a Perkin-Elmer 3100 AA and carbon/hydrogen in a Perkin-Elmer 2100 Automatic Analyzer.

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 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 metal poly(styrene-co-ethyl methacrylates) has been recently reported [10]. The synthesis of polymers with doped metals or metal dispersed in styrene [11] and ethyl methacrylates [12] has



Scheme 1.

been also reported by us. This work is an attempt to prepare alternate copolymers of styrene and ethyl methacrylate (SEMA) as follows.

In the above scheme. we can also obtain other conformations with the metal clusters. The most probable copolymer is alternating due to the copolymerization ratios and also to the single step decomposition curve denoted in the TG (see Figs. 1a, b). The copolymer showed a different thermal decomposition (T_D) (382.85°C) and between styrene (405.30°C) [11] and ethyl methacrylate (300°C) [12]. On the other hand, In-SEMA (423.21°C) showed a higher T_D than the undoped copolymer for AIBN series. Cd-SEMA (412.69°C) is the more stable copolymer for BPO series.

The copolymers have a wide range of molecular weight, stability and colours depending upon the metal. The copolymers show a low amount of metal incorporation. In-SEMA being the lowest 0.12–0.02, and Sn-SEMA the highest 1.22–0.84% (w/w). The amount of metal clusters in the copolymers is similar to PEMA already reported but lower than poly styrene. The presence of these metal clusters is responsible for the differences in thermal decomposition temperatures and also in the decomposition activation energy values [13].

Figure 1 shows the change in sample weight as a function of time and temperature when the four fractions of poly(styrene-co-ethyl

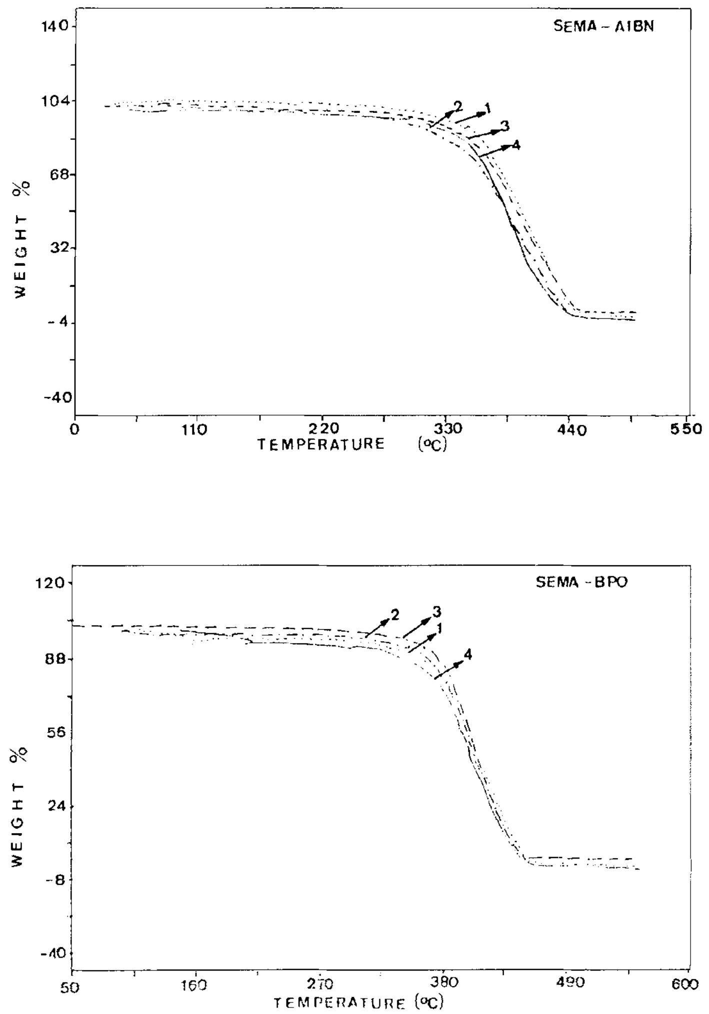


FIGURE 1 Thermogram of poly(styrene-co-ethyl methacrylate) (a) undoped copolymer from AIBN series; (b) undoped copolymers from BPO series. The fractions 1, 2, 3 and 4 are corresponding to 0.1, 0.2, 0.5 and 1.0 mol% radical initiators.

methacrylate) 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 (E_a) of decomposition reaction. Figure 2 shows the thermogram of Au-SEMA and T_D for both series, AIBN and BPO respectively, In the AIBN series (Tab. I) Bi, Sn, Ge, In, Ga, Cd, Zn, and Cu-SEMA showed higher E_a values than the undoped copolymer (46.61 kJ/mol). Only Ag- and Sb-SEMA exhibit lower E_a values, most probably due to their sensibility to air exposure, Bi-SEMA is the highest E_a (54.70 kJ/mol). However, in the BPO series

TABLE I Kinetic parameters for metal poly(styrene-co-ethyl methacrylate) with AIBN

M-Copolymer	E_a *(kJ/mol)*	*n*	*Temp. range*	T_D (°C)
SEMA-1	46.61	0	424–342	382.85
SEMA-2	42.25	0	432–309	387.87
SEMA-3	37.43	0	415–302	403.38
SEMA-4	45.45	0	459–319	381.50
Pd-SEMA-1	40.89	0	435–329	387.98
Pd-SEMA-4	35.60	0	420–308	336.34
Cu-SEMA-1	52.23	0	418–332	387.68
Cu-SEMA-4	54.16	0	402–317	381.55
Ag-SEMA-1	36.39	0	430–323	351.37
Ag-SEMA-4	33.38	0	424–308	382.38
Au-SEMA-1	41.74	0	429–320	405.75
Au-SEMA-4	36.48	0	447–313	382.38
Zn-SEMA-1	52.40	0	434–334	416.22
Zn-SEMA-4	37.84	0	434–327	381.64
Cd-SEMA-1	54.00	0	433–363	402.68
Cd-SEMA-4	47.72	0	445–327	384.91
Ga-SEMA-1	52.19	0	444–360	416.04
Ga-SEMA-4	32.71	0	432–305	404.80
In-SEMA-1	49.21	0	445–360	423.21
In-SEMA-4	36.07	0	440–345	392.24
Ge-SEMA-1	49.22	0	444–360	387.89
Ge-SEMA-4	37.40	0	439–338	382.56
Sn-SEMA-1	53.79	0	435–334	418.41
Sn-SEMA-4	71.07	0	445–354	424.05
Sb-SEMA-1	29.38	0	395–275	365.69
Sb-SEMA-4	26.21	0	385–280	333.52
Bi-SEMA-1	54.70	0	425–338	420.94
Bi-SEMA-4	48.18	0	435–350	403.37

SEMA = poly(styrene-co-ethyl methacrylate)s; T_D = decomposition temperature.

(Tab. II) only Sb-SEMA show a similar value to SEMA (43.48 kJ/mol). Cu-SEMA was the highest E_a (61.89 kJ/mol).

These copolymers degrade in a single step, losing mostly their weight around 350°C. This fact is another evidence that we are in the presence of alternate copolymers.

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 (14). By using the Arrhenius equation [15] we can get some information about specific rate constant (k) and activation energy (E_a).

TABLE II Kinetic parameters for metal poly(styrene-co-butyl methacrylate) with BPO

M-Copolymer	E_a *(kJ/mol)*	*n*	*Temp. range*	T_D *(°C)*
SEMA-1	43.48	0	434–347	378.76
SEMA-2	59.30	0	443–351	375.44
SEMA-3	46.76	0	448–310	473.28
SEMA-4	35.32	0	438–315	396.87
Pd-SEMA-1	49.99	0	447–352	394.01
Pd-SEMA-4	39.83	0	428–337	389.64
Cu-SEMA-1	63.66	0	419–314	373.06
Cu-SEMA-4	50.98	0	432–299	371.56
Ag-SEMA-1	45.51	0	416–312	392.38
Ag-SEMA-4	34.83	0	441–314	454.54
Au-SEMA-1	52.19	0	440–332	386.70
Au-SEMA-4	47.49	0	435–320	383.52
Zn-SEMA-1	47.26	0	444–327	379.25
Zn-SEMA-4	43.95	0	429–328	379.54
Cd-SEMA-1	60.88	0	432–328	412.69
Cd-SEMA-4	51.62	0	436–339	391.64
Ga-SEMA-1	46.96	0	432–350	357.06
Ga-SEMA-4	39.09	0	447–363	384.15
In-SEMA-1	56.45	0	429–341	367.39
In-SEMA-4	40.74	0	437–316	388.45
Ge-SEMA-1	44.66	0	442–319	387.14
Ge-SEMA-4	45.30	0	436–305	383.73
Sn-SEMA-1	53.80	0	439–333	394.83
Sn-SEMA-4	37.91	0	437–298	389.88
Sb-SEMA-1	43.66	0	434–332	370.45
Sb-SEMA-4	37.66	0	424–303	345.58
Bi-SEMA-1	61.89	0	432–325	388.26
Bi-SEMA-4	36.49	0	443–302	379.08

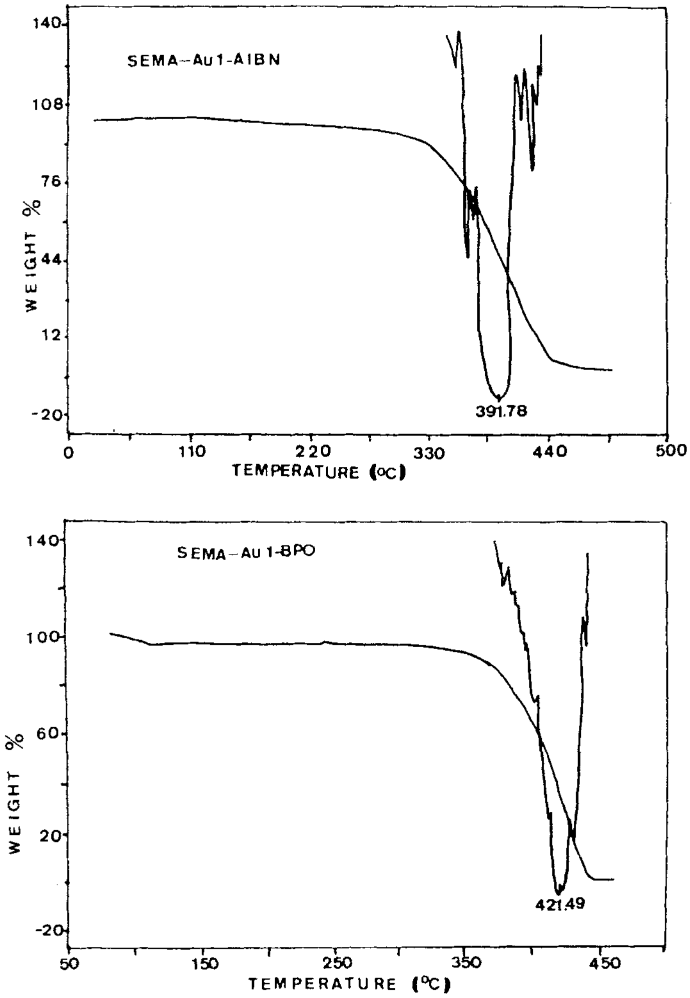


FIGURE 2 Thermogram and first derivative of Au-poly(styrene-co-ethyl methacrylate) obtained at a heating result of 10 C min^{-1}: (a) Fraction of 0.1 mol% AIBN; (b) fraction of 0.1 mol% BPO, respectively.

The reaction rates, $d\alpha/dt$, were calculated using differential technique with heating rate of 10 C min^{-1}. The final equation used in a logarithmic form is

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

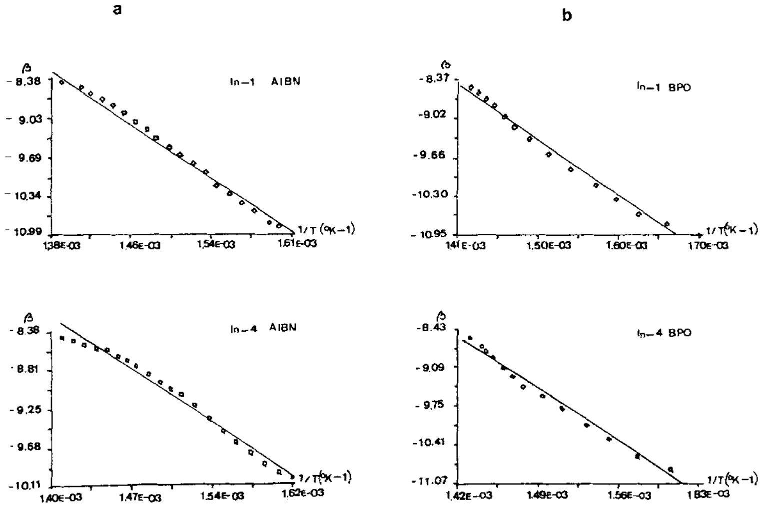


FIGURE 3 (a) Arrhenius plot of In-SEMA (fraction 1 and 4) for AIBN; (b) Arrhenius plot of In-SEMA fraction 1 and 4 for BPO series, respectively.

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 plot of β versus $1/T$. The Arrhenius plot for the thermal degradation of the metal copolymer (In-SEMA) are shown in Figure 3. The linearity of every plot is good (between 0.969 and 0.996) but some scatter is detected at the beginning and end of the decomposition.

Tables I and II show the kinetics data obtained according to the method mentioned above and also the temperature range used to obtain the parameters.

In, Bi, Sn, Ga, Zn and Au-SEMA exhibited T_D over 400°C for fraction 1, which is an improvement in the thermal stability since the undoped copolymer is 382°C. Only Ag- and Sb-SEMA showed lower stability most probably due to their lower metal content in the copolymer for AIBN series (see Tab. I).

Pd, Ag, Au, Cd, Ge, Sn and Bi-SEMA showed T_D over 385°C for fraction 1, a clear increase in thermal stability due to the incorporation of metal clusters in the copolymers prepared with BPO (see Tab. II).

In both series under study the high molecular weight fraction exhibits the higher T_D. The activation energy of the decomposition reaction with differences in 5–10 kJ/mol between the same metals in either AIBN or BPO series.

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