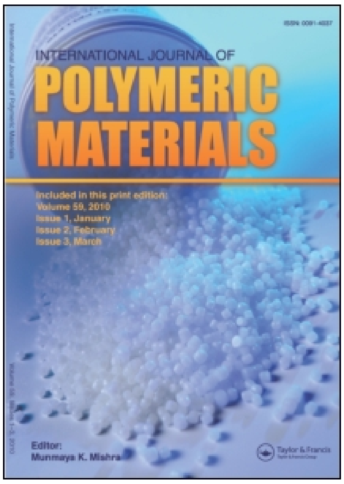

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Thermal Studies of Metal Poly(Styrene-co-Butyl Methacrylates). Part XIX

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Thermal Studies of Metal Poly(Styrene-co-Butyl Methacrylates). Part XIX

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Metal poly(styrene-co-butyl methacrylates) copolymers were obtained by radical polymerization with benzoyl peroxide (BPO) and azodiisobutylonitrile (AIBN). The monomers were codeposited 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-monomers colloids can be obtained. The colloids were polymerized with BPO and AIBN at 65°C for 3.0 h. Four different initiator concentrations (1, 1.5, 3.0 and 5.0 mol%) were used. The yields are fairly low (30–60%) and the viscosimetric molecular weight range from 10^4–10^5 g/mol.

The higher $\overline{M}v$ are Ga-SBMA and Ag-poly(styrene-co-butyl methacrylate) for AIBN series and Sn-SBMA and Pd-SBMA 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: Cu-SBMA > Ge-SBMA > Ag-SBMA > In-SBMA > Zn-SBMA > Bi-SBMA > Ga-SBMA > Cd-SBMA > Sb-SBMA > Sn-SBMA > Pd-SBMA for AIBN series and Ga-SBMA > Ag-SBMA > Au-SBMA > In-SBMA > Ge-SBMA > Zn-SBMA > Sn-SBMA > Bi-SBMA > Cd-SBMA > Pd-SBMA > Cu-SBMA > Sb-SBMA for BPO series.

The thermal stability is strongly dependent on the metal cluster 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-butyl methacrylate); metal clusters; thermal analysis; thermal stability; kinetics

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INTRODUCTION

In solid-state decomposition reactions, we found variations in the kinetic parameters due to the sample and measuring conditions. The variation in the Arrhenius parameters results from a certain change in the overall behavior of the reaction process due to several factors. The variations of kinetic parameters for a series of reactions tend to a result of a mutual dependence of the apparent Arrhenius parameters. Several papers [1–4] showed an historical review dealing with the kinetic compensation effect (mutual dependence of the apparent Arrhenius parameters). It is generally accepted that the experimentally shape of a TG curve changes with the measuring conditions applied, such as sample mass, heating rate, atmosphere and others [5]. Guarini [6] mentioned that non-linearity of the Arrhenius plot increases with the sample mass. Sample mass dependent variation in the apparent Arrhenius has been explained by the effect of gradients in temperature [7]. To avoid this problem we usually used 2–5 mg of sample during the heating process.

The variation in the behavior for a reaction is only detected as changes in the position and shape of the experimentally TG curves. The kinetic parameters calculated from these macroscopic data are projected on the Arrhenius coordinates through the general kinetic equation. The variation in the respective kinetic parameters most probably is produced from the changes in the experimental and physicochemical factors.

It is well known the relationship existing between the TG curves and the general equation.

In this paper, the dependence of the Arrhenius parameters with the increased in the amount of clusters incorporated in styrene-co-butyl methacrylate is discussed. Several metal clusters such as: Pd, Cu, Ag, Au, Zn, Cd, Ga, In, Ge, Sn, Sb were used to prepare copolymers with metals in the matrix.

EXPERIMENTAL

Colloid Synthesis

As a typical example, tin colloid (10 mL) was placed in a polymerization flask with 1.0 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 1.5, 3.0 and 5.0 mol% AIBN fractions). Molecular weights were determined in 2-butanone ($K = 9.3 \times 10^{-5}$ and $a = 0.72$) [10].

Identical method for copolymers prepared with BPO was achieved.

Elemental Analysis

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

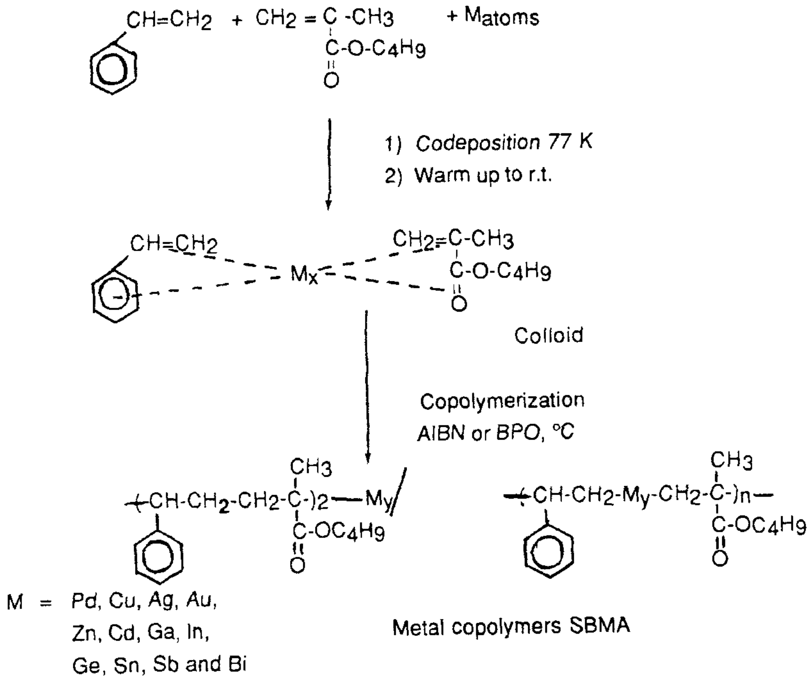
Thermogravimetry

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 and molecular weights of metal poly(styrene-co-butyl methacrylate) has been recently reported [11]. The synthesis of polymers with doped metal in styrene [12] and butyl methacrylate [13], was also reported. The present work is an attempt to study the thermal properties of the alternate copolymers of styrene and butyl methacrylate (SBMA). The following synthesis scheme was followed:

The metal SBMA copolymers might exist in several conformations, but the most probable copolymer is alternating due to their copolymerization ratios. The single step decomposition in the thermograms is also another evidence (see Fig. 1a and 1b). The undoped copolymers showed different thermal decomposition, e.g. for the highest MW fraction SBMA



Scheme 1.

prepared with BPO showed a thermal decomposition (T_D) at 372.16°C, however the SBMA from AIBN exhibited a T_D at 379.87°C (Fig. 1a and 1b respectively). The reported T_D values are between styrene (400°C) [14] and butyl methacrylate (282°C), respectively.

Besides, Cu-SBMA (389.64°C) showed the higher T_D than the undoped copolymer for AIBN series. Ga-SBMA (418.19°C) is the most stable copolymer for the highest molecular weight fraction in the BPO series. In both cases the doped copolymers exhibited higher thermal stability than the corresponding copolymers.

The amount of metal clusters in the copolymers is similar to PBMA [15] already reported but lower than polystyrene series. As we can see, the presence of metal clusters in the copolymers are dealing with the improvement in thermal stability increasing their T_D. Ag, In and Ge-SBMA showed similar T_D in both series (Fig. 2 shows Ag-SBMA fractions 1 and 4). The other metal copolymers showed differences but in general, the AIBN series exhibited higher T_D than the BPO series.

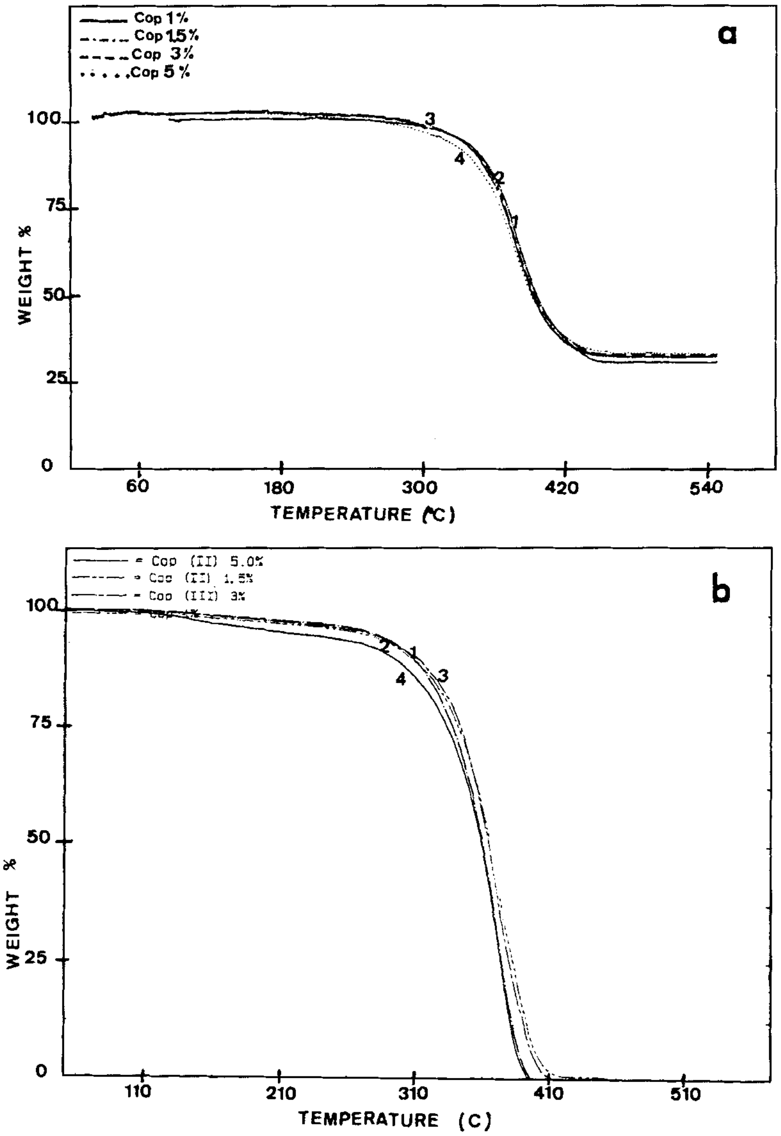


FIGURE 1 Thermogram of poly(styrene-co-butyl methacrylate) (a) undoped copolymers from BPO series; (b) undoped copolymers from AIBN series. The fractions 1, 2, 3 and 4 are corresponding to 1, 1.5, 3.0 and 5.0 mol% initiators.

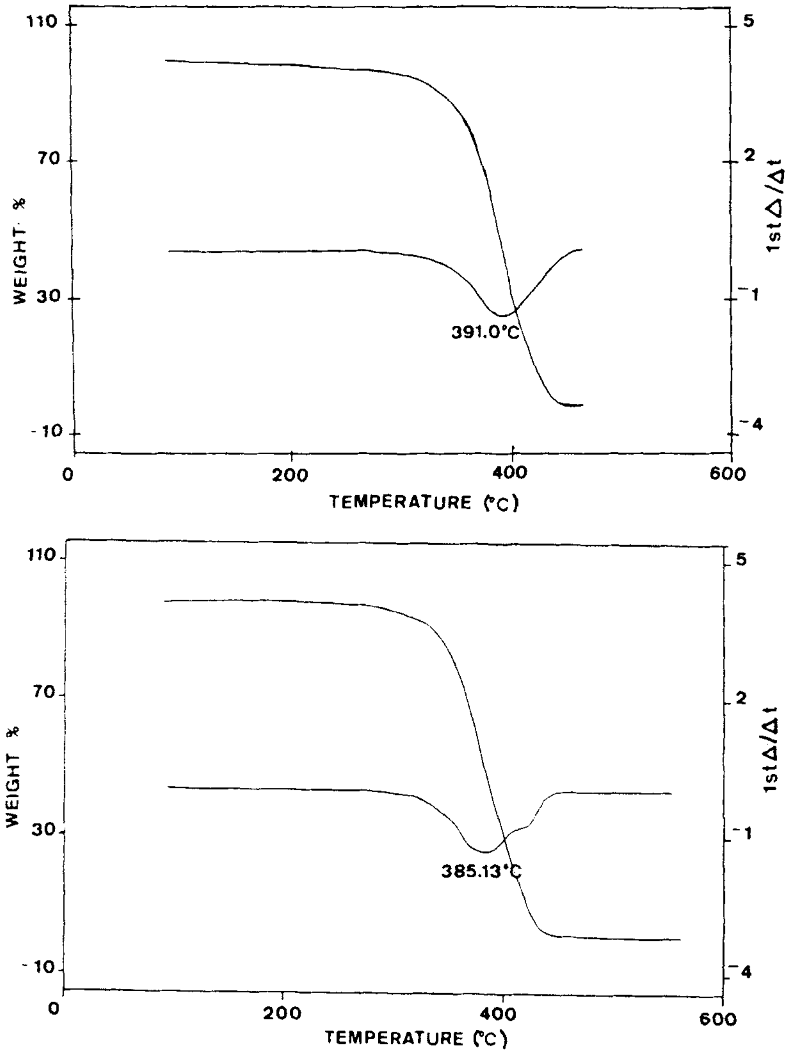


FIGURE 2 Thermogram and first derivative of Ag-poly(styrene-co-butyl methacrylate) obtained at heating rates of 10°C min^{-1}: (a) fraction of 1.0 mol% BPO; (b) fraction of 1.0 mol% AIBN, respectively.

Figure 1 shows the change in sample weight as a function of time and temperature when the four fractions of poly(styrene-co-butyl methacrylates) are heated from 25 to 550°C. The fraction 1 (the highest MW) exhibits the highest decomposition temperature (T_D) in

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

Copolymer	E_a *(kJ/mol)*	n	*Temp. range (°C)*	T_D *(°C)*
SBMA-1	32.28	0	356.62–420.84	379.87
SBMA-2	30.69	0	366.99–425.80	361.20
SBMA-3	20.37	0	367.01–445.33	377.39
SBMA-4	17.34	0	365.94–488.86	379.76
Cu-SBMA-1	36.61	0	355.91–420.50	389.64
Cu-SBMA-4	29.29	0	355.63–435.40	377.99
Ge-SBMA-1	31.43	0	375.53–436.47	385.94
Ge-SBMA-4	27.57	0	356.75–414.82	381.05
Ag-SBMA-1	25.84	0	376.82–437.79	385.13
Ag-SBMA-4	24.77	0	366.94–430.19	374.86
In-SBMA-1	28.26	0	350.42–425.84	385.81
In-SBMA-4	23.94	0	365.76–430.86	385.83
Zn-SBMA-1	34.05	0	355.55–429.66	383.46
Zn-SBMA-4	28.97	0	361.30–422.51	379.89
Bi-SBMA-1	26.81	0	360.23–435.48	381.83
Bi-SBMA-4	26.04	0	350.97–435.90	378.29
Ga-SBMA-1	23.60	0	370.26–433.37	381.05
Ga-SBMA-4	21.55	0	370.30–443.21	374.79
Cd-SBMA-1	31.94	0	353.72–430.10	380.96
Cd-SBMA-4	30.75	0	349.57–429.79	376.06
Sb-SBMA-1	32.28	0	350.60–435.04	379.59
Sb-SBMA-4	27.11	0	340.93–435.23	375.70
Sn-SBMA-1	28.04	0	375.91–440.51	377.61
Sn-SBMA-4	25.25	0	365.98–435.81	375.18
Pd-SBMA-1	30.23	0	369.29–427.33	376.67
Pd-SBMA-4	27.53	0	358.72–425.72	377.56

SBMA = poly(styrene-co-butyl methacrylate)s.
T_D = decomposition temperature.

both BPO (Fig. 1a) and AIBN (Fig. 1b) series. Their activation energies of decomposition reactions are also decreasing with the lower MW (Tabs. I and II).

These copolymers degrade in a single step, loosing mostly their weight around 370°C. It is quite important to observe only one curve in the thermogram which is a good evidence for the presence of alternating copolymers.

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

Copolymer	E_a *(kJ mol)*	*n*	*Temp. range (°C)*	T_D *(°C)*
SBMA-1	44.48	0	351.60–388.00	372.18
SBMA-2	42.48	0	338.16–406.20	372.40
SBMA-3	38.88	0	336.00–400.13	370.88
SBMA-4	40.72	0	335.13–394.93	373.70
Ga-SBMA-1	36.26	0	361.21–420.85	418.19
Ga-SBMA-4	38.77	0	357.41–426.28	411.81
Ag-SBMA-1	42.50	0	361.12–419.96	391.00
Ag-SBMA-4	28.58	0	336.73–414.69	383.34
Au-SBMA-1	40.49	0	360.26–420.06	388.79
Au-SBMA-4	41.30	0	330.36–385.40	363.73
In-SBMA-1	40.67	0	364.78–429.12	388.52
In-SBMA-4	27.59	0	340.80–420.74	381.10
Ge-SBMA-1	35.26	0	355.87–422.97	387.15
Ge-SBMA-4	44.08	0	343.04–411.03	384.80
Zn-SBMA-1	39.76	0	350.30–400.13	376.51
Zn-SBMA-4	32.72	0	366.33–416.16	394.71
Sn-SBMA-1	35.97	0	342.93–397.10	373.05
Sn-SBMA-4	36.69	0	340.33–395.36	374.78
Bi-SBMA-1	36.44	0	325.16–385.40	366.26
Bi-SBMA-4	41.60	0	327.76–390.16	378.68
Cd-SBMA-1	34.25	0	320.40–395.36	366.11
Cd-SBMA-4	28.82	0	325.16–395.36	365.25
Pd-SBMA-1	44.58	0	320.83–380.20	355.50
Pd-SBMA-4	29.63	0	330.36–385.40	353.55
Cu-SBMA-1	27.24	0	344.50–419.31	353.77
Cu-SBMA-4	44.25	0	359.40–425.64	353.77
Sb-SBMA-1	28.53	0	315.20–385.40	347.91
Sb-SBMA-4	30.88	0	330.26–390.16	362.64

SBMA = poly(styrene-co-butyl methacrylates).
T_D = decomposition temperature.

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 [16]. From the Arrhenius equation [17] we can get information of the specific rate constant (k) and activation energy (E_a). The reaction rates, $d\alpha/dt$, were calculated using a differential technique with heating rate of $10^\circ\mathrm{C\,min}^{-1}$.

The final equation used in a logarithmic form is (18):

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

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 (Ag-SBMA) are shown in Figure 3. The linearity of every plot is good (between 0.976 and 0.987) with some scattering at the beginning of the decomposition curve.

Tables I and II summarizes the kinetic data obtained according to the method already mentioned and the temperature ranges used to obtain the parameters.

In the AIBN series most of the doped copolymers (Cu, Ge, Ag, In, Zn, Bi, Ga, Cd and Sb-SBMA) exhibit higher T_d than the undoped copolymers (379°C). The data in Table I is another evidence of the improved thermal stability of those copolymers.

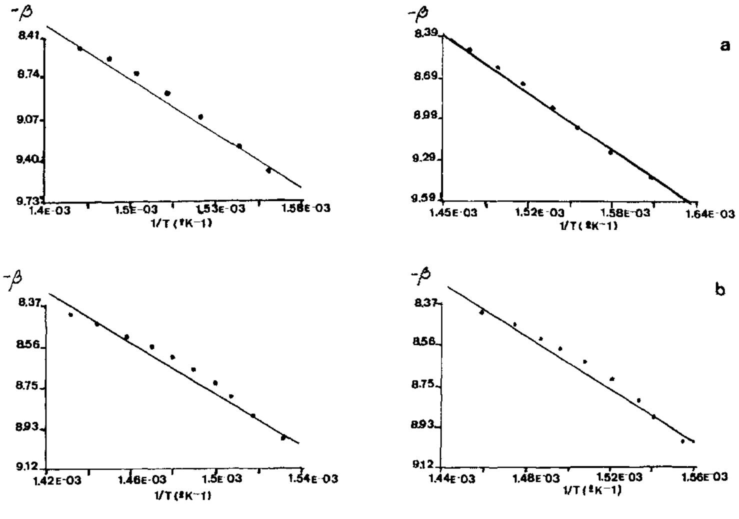


FIGURE 3 (a) Arrhenius plot of Ag-SBMA (fraction 1 and 4) for BPO series; (b) Arrhenius plot of Ag-SBMA (fraction 1 and 4) for AIBN series, respectively.

On the other hand, in the BPO series, Ga, Ag, Au, In, Ge, Zn and Sn-SBMA showed higher T_D than the undoped copolymers (372°C) (see Tab. II).

Both series followed a zero order decomposition reaction with a single decomposition curve.

The activation energies (E_a) are difficult to compare due to the differences in the molecular weights of both series, so the amount of the metal clusters dispersed in the copolymers is different. For example, in the BPO series the E_a is higher for the undoped copolymers than the AIBN series, probably due to the higher MW [19]. For BPO, only Pd and Ag-SBMA are similar to the undoped copolymer. However, in the AIBN series Cu, Zn and Sb-SBMA are similar to the undoped copolymers. In general, the BPO series showed higher values than AIBN series.

Finally, it is important to observe that in both series the fraction of higher molecular weight exhibits the higher T_D. The activation energies of the decomposition reactions showed differences between 4–13 KJ/mol for the same metals in the BPO with AIBN series.

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