Thermal Studies of Metal Poly(Butyl Methacrylates) Part XIII

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Thermal Studies of Metal Poly(Butyl Methacrylates) Part XIII

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Metal poly(butyl methacrylates) polymers were obtained by radical polymerization with benzoyl peroxide. The monomer was cocondensed with the metals: Cu, Ag, Au, Pd, Zn, Cd, 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-monomer 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 (0.5, 1.0, 1.25 and 5.0 mol%) were used. The yields are over 50% and the viscosimetric molecular weight range from 10^4–10^5 g/mol. The higher $\bar{M}v$ are Sb, In, Ag and Ge-poly(butyl methacrylates). 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 polymers degrade in a single step around 300°C. The kinetic data thus obtained show the thermostabilities decrease in the order: Pd-PBMA > Au-PBMA > In-PBMA > Sn-PBMA > Ag-PBMA > Sb-PBMA > Bi-PBMA > Ge-PBMA > Zn-PBMA > Ga-PBMA > Cu-PBMA > Cd-PBMA. The thermal stability apparently is depending upon the metal incorporated in the polymer matrix. The decomposition reaction order is -0.25 or -0.5 which means that we are in the presence of a complex single decomposition reaction. The pre-exponential factor, the activation energy, the reaction order and the decomposition temperature for all the polymers have been determined.

KEY WORDS Metal polymers, monomer colloids, metal vapor, molecular weight, thermogravimetry, decomposition temperature.

INTRODUCTION

The application of solid polymer materials requires information concerning their thermal degradation.[1] Thermogravimetry has been used to study the weight loss kinetics at high temperatures and therefore the lifetime of a polymeric material. This method is simple and accurate due to the sensitivity and stability of the electrobalances. The test mathematical approximation for the dependence of ther-

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mal degradation on temperature is given by the Arrhenius equation. The only condition to get valuable results is that the activation energy should be constant over the degradation range being studied. Most of the materials behave as mentioned, but there are examples of change of activation energy with degree of thermal degradation.[3,4]

We have reported on colloidal metals in organic monomers such as styrene,[5-7] methyl methacrylate[8] and ethyl methacrylate.[9] This method, chemical liquid deposition, involves deposition of metal vapor with organic solvents at low temperature (77 K) followed by controlled accretion of metal atoms. Polymers with metal dispersed and potential semiconductors and photoconduction properties can be obtained.

In this paper, we report the thermal behaviour of the metal poly(n-butyl methacrylates). The influence of the metal was observed for some polymers.

EXPERIMENTAL

Colloid Synthesis

The metal-monomer colloids were prepared by codeposition of the n-butyl methacrylate with the metals at 77 K using a metal atom reactor.[5,10] As a typical example an Al_2O_3-W crucible was charged with 0.25 g of Ag metal (lumps). Freshly distilled n-butyl methacrylate (BMA) was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 4–5 μ Hg while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and Ag and BMA (50 ml) were cocondensed over 60 min using 26 A at 5 μ of Hg. The matrix was a black color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen Dewar for 1 h. Upon meltdown a black colloid was obtained. After addition of nitrogen up to 1 atm, the colloid was allowed to warm for another 0.5 h to room temperature. The solution was syphoned out under nitrogen into a flask ware. Based on metal evaporated and BMA inlet the concentration could be calculated.

Polymerization

As a typical example, silver colloid (10 ml) was placed in a polymerization flask with 0.5 mol% of benzoyl peroxide (BP) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath (Heidolph) at 70°C for 60 min. The content of the flask were quenched in 100 ml of methanol. The polymer was filtered off and dried under vacuum (10^{-2} Torr) for 48 h at 30°C. The yield of the polymer was determined. Similar procedure was followed for 1.0, 1.25 and 5.0 mol% BP fractions.

Molecular Weights

The viscosimetric molecular weights ($\bar{M}v$) were determined by using an Ostwald osmometer. The samples were dissolved in 2-butanone at 25°C and the parameters $K = 9.7 \times 10^{-5}$ (dl/g) and $a = 0.68$ were used.[11]

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 4–10 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 hrs. The metals were determined by atomic absorption and C/H by standard methods.

RESULTS AND DISCUSSION

The synthesis of metal poly(n-butyl methacrylates) with AIBN has been already reported.[12] The polymers exhibited a low metal content and they can be prepared by codeposition of the metal and the monomer.
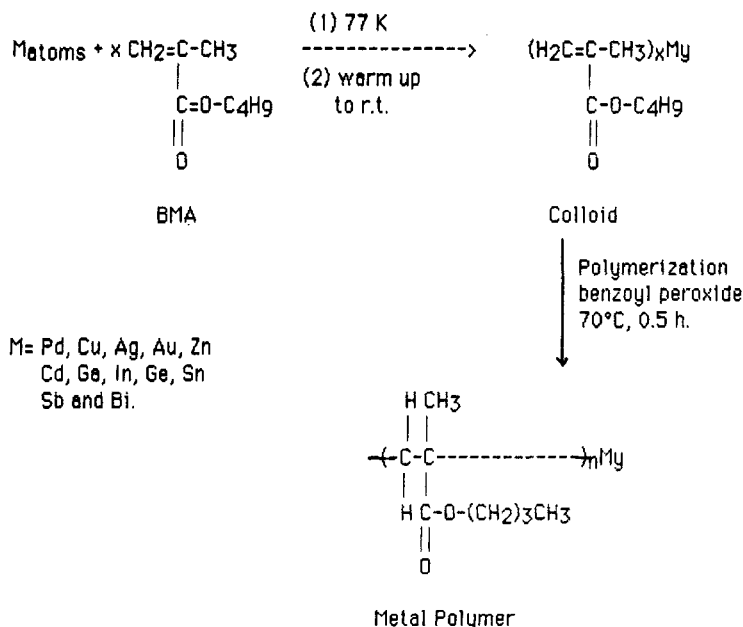
Metal Polymer

The polymers show a low level of metal incorporation, Ga being the lowest 0.02–1.65, and Pd the highest 0.24–0.72. The metal clusters in the polymer are less than the poly(methyl methacrylates) already reported.[7] Probably, the steric effect of the longer side chain is avoiding the approach of the metal clusters in the polymer backbone. Nonetheless, the small amount of metal incorporated is giving different
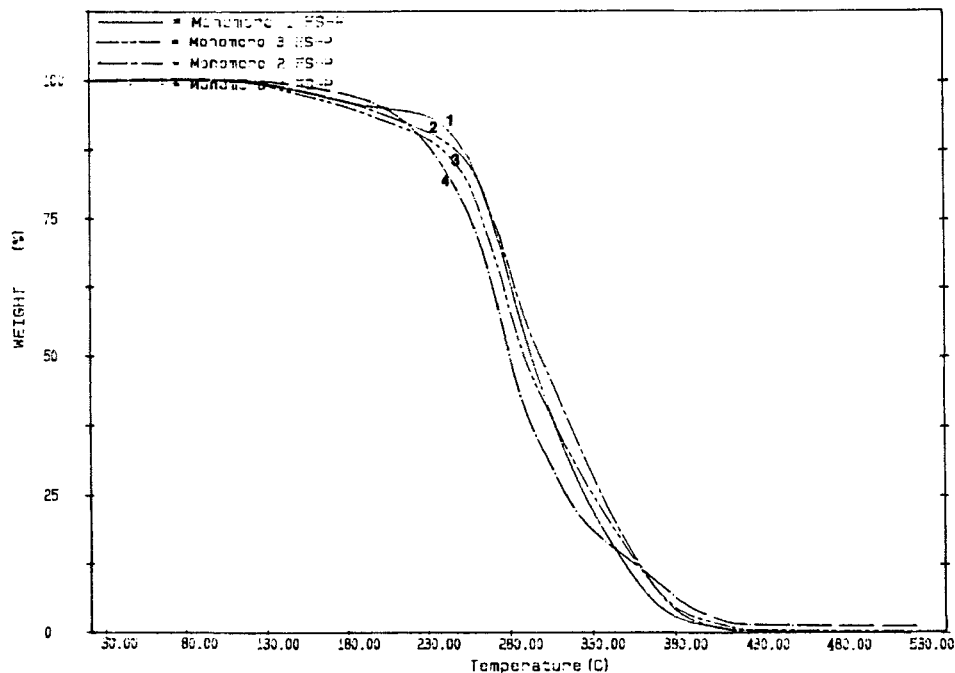
FIGURE 1   Thermogram of poly(butyl methacrylates) homopolymers obtained by heating the poly-mers from 25 to 550°C at 10°C min⁻¹: 1.—0.5 mol%, 2.—1.0 mol%, 3.—1.25 mol% and 4.—5.0 mol% of benzoyl peroxide, respectively.

colours and decomposition temperatures. The stability of the polymers is strongly related to the metal attached, i.e., Pd and Au-PBMA exhibited the higher stability. Those metals are very stable and on the other hand, Ga and Ge are more susceptible for oxidation.

The shapes of the curves are very similar and all the metal poly(butyl methac-rylate) degrade in a single-step process which is similar of the thermal decomposition of many metal polymers[13,14] and other macromolecular compounds reported al-ready.[15,16]

In Figure 1 we have summarized thermograms of the four fraction of MW, corresponding to the homopolymer butyl methacrylate. The thermal decomposition temperatures (T_D) are similar and in the range of 281 and 276°C. The fractions of higher MW are showing also higher stability.

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

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

where α is the fraction of the sample weight reacted at time t, and k is the specific 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
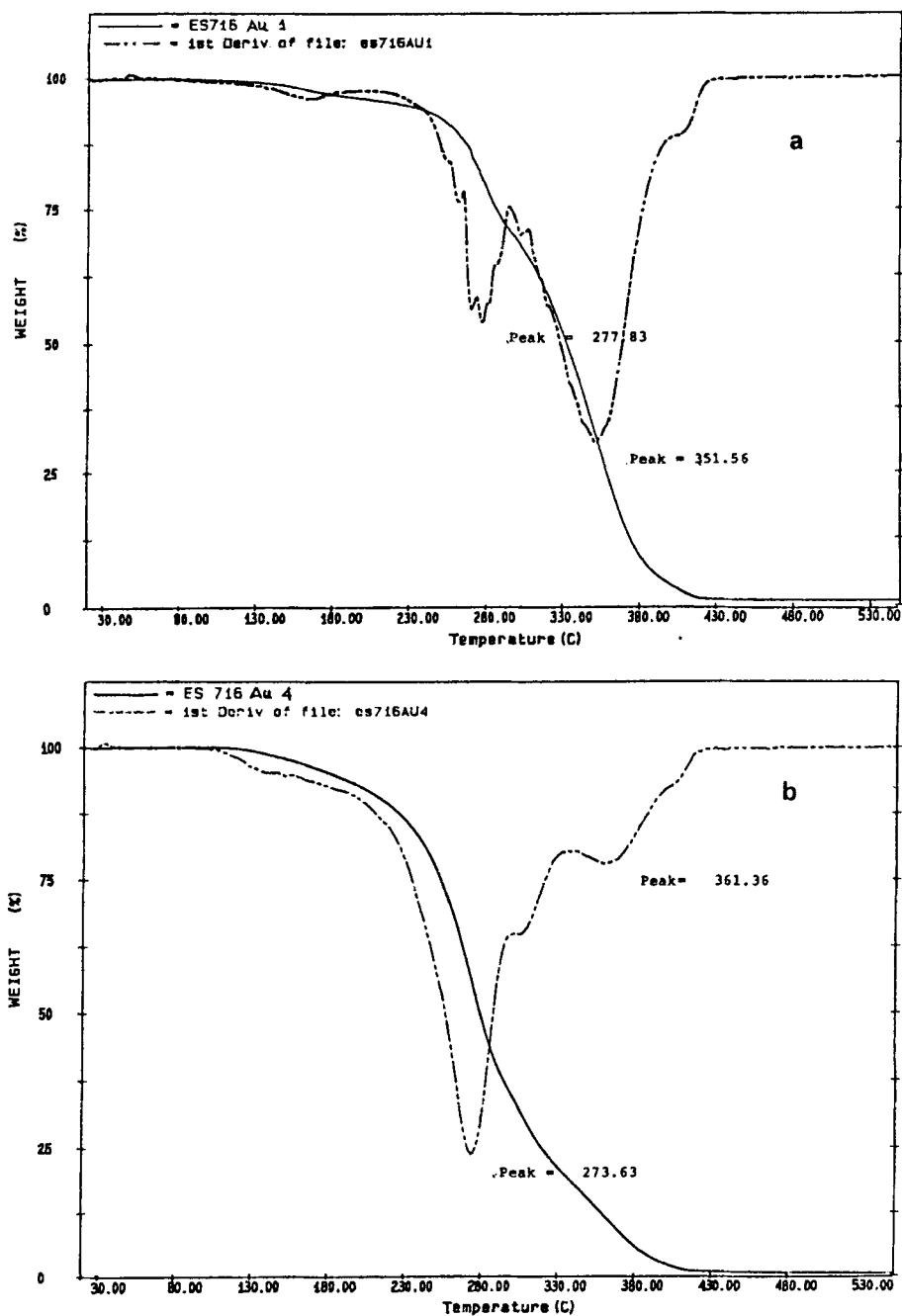
FIGURE 2   Thermogram and first derivative of Gold butyl methacrylates obtained at a heating rate of 10°C min⁻¹ (a) Fraction of 0.5 mol%, (b) fraction of 5.0 mol% benzoyl peroxide, respectively.
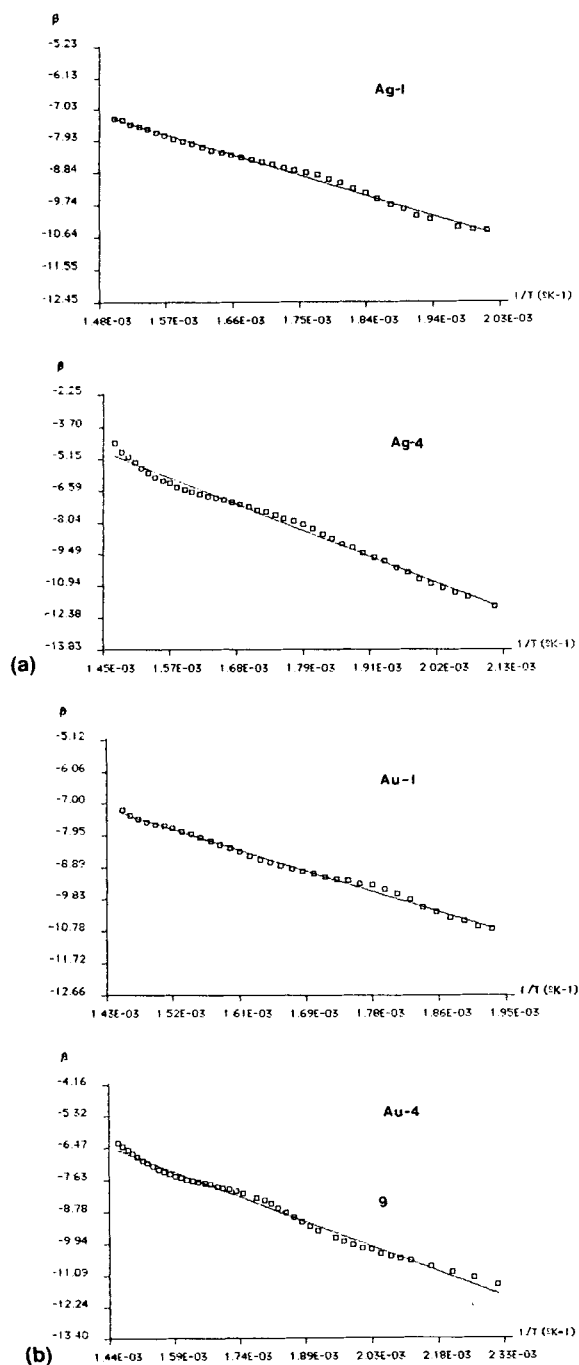
FIGURE 3   Arrhenius plots of Ag-PBMA (fraction 1 and 4); Arrhenius plots of Au-PBMA (fractions 1 and 4).

TABLE I

Kinetic parameters for metal poly(butyl methacrylates)

Polymer	n	Temp.Range (°C)	Ea (kJ/mol)	ln A	TD (°C)
PBMA-1	-0.5	230-395	38.24±0.59	7.48	280.94
PBMA-2	-0.25	230-400	27.47±0.51	2.67	281.56
PBMA-3	-0.5	230-420	31.84±0.44	4.88	276.90
PBMA-4	-0.5	180-410	30.37±0.45	4.43	276.43
Pd-1	0	250-430	30.68±0.40	-1.25	389.60
Pd-4	-0.5	200-410	29.28±0.74	13.95	264.40
Cu-1	-0.5	195±415	31.48±0.61	4.76	276.43
Cu-4	-0.5	210-415	30.40±0.61	4.50	275.03
Ag-1	-0.25	225-395	21.64±0.38	2.30	280.15
Ag-4	-1.0	200-405	45.56±0.71	11.23	272.70
Au-1	-0.25	245-515	29.96±0.38	3.20	351.56
Au-4	-0.5	160-240	26.06±0.39	2.68	277.83
Zn-1	-0.25	230-405	26.97±0.74	2.37	280.15
Zn-4	-0.25	195-405	27.87±0.51	1.23	282.73
Cd-1	-0.50	240-410	33.53±0.54	5.28	272.70
Cd-4	-0.50	220-400	32.74±0.64	5.19	272.46
Ga-1	-0.5	225-390	33.99±0.74	3.09	277.36
Ga-4	-0.5	180-395	28.50±0.43	3.84	282.50
In-1	-0.25	245-410	25.47±0.44	1.44	283.66
In-4	-0.5	185-400	27.47±0.34	3.44	271.76
Ge-1	-0.25	230-405	26.47±0.37	2.26	278.06
Ge-4	-1.0	210-400	47.95±0.85	12.36	272.23
Sn-1	-0.25	230-425	25.54±0.67	1.17	282.03
Sn-4	-0.5	220-410	28.26±0.92	3.29	264.76
Sb-1	-0.5	235-400	34.02±0.50	5.75	280.43
Sb-4	-0.5	195-420	28.23±0.49	3.36	277.36
Bi-1	-0.5	240-410	37.37±0.60	6.92	280.63
Bi-4	-0.5	205-400	32.93±0.79	5.76	271.30

PBMA = poly (butyl methocrylate)
TD = decomposition temperature

the data of temperature versus sample weight fraction, according to the method developed by Wen and Lin.[17] 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

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

A computer linear multiple-regression program was used to calculate the kinetics

parameters E and A linear least-squares fit of the date in a semilogarithmic plot of β versus $1/T$. The Arrhenius plots of Ag-PBMA and Au-PBMA fractions 1 and 4, respectively are exhibited in Figure 3. They show a very good correlation.

Bi, Sb, Ga, Cd show the highest ΔEa (26.97, 26.47, 25.54 and 25.47 kJ mol^{-1}), respectively. It is interesting to observe that Au-PBMA (Figure 2) and Pd-PBMA exhibit the highest T_D (351.56 and 389.60°C), respectively. These values are even higher than already reported MMA.[13] This is in agreement with the fact that these are stable metals with low oxidation potential. Since the amount of metal in the polymers is small they should behave in a way similar to the homopolymer.

Most of the thermogram show a single thermal decomposition which is indicated in Table I. Mainly, the high molecular weight fraction exhibits a higher T_D with only a few exceptions. This pattern was also found in the homopolymer (Figure 1). The negative order of reaction is completely different than MMA ($n = 0$), probably due to the side reactions and complicated decomposition due to the large side chains in the polymer backbone (Table I).

Acknowledgment

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