Thermochimica Acta, 230 (1993) 259–267
Elsevier Science Publishers B.V., Amsterdam
SSDI 0040-6031(93)01167-2

Thermal studies of metal poly(*n*-butyl methacrylates). Part 10

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(Received 11 February 1993; accepted 18 March 1993)

Abstract

Metal poly(*n*-butylmethacrylates) polymers were obtained by radical polymerization with azodiisobutyronitrile (AIBN). The thermal stabilities of the metal polymers (M-PBMA) have been studied by thermogravimetry (TG) between 25 and 550°C under nitrogen flow. The decomposition temperature was obtained from the first derivative of the TG curve. The kinetic parameters of the thermal decomposition were determined by the Arrhenius equation. All these polymers degrade in a single step. The kinetic data thus obtained show that the thermostabilities decrease in the order Pd-PBMA > Ga-PBMA > Cu-PBMA > Ag-PBMA > Au-PBMA > Al-PBMA > Cd-PBMA > Ge-PBMA > Zn-PBMA > Sb-PBMA > In-PBMA > Sn-PBMA. In fact, the thermal stability is dependent upon the metal incorporated in the polymer, the highest being stable up to 389°C and the lowest up to 260°C. The order of reaction from the thermal decomposition of these metal polymers was found to be −0.25 for the homopolymers, Pd, Au, Ag, Cd, Zn, Ga, Ge and Sn but −0.5 for Bi, Sb and Al. The pre-exponential factor, the reaction order and the activation energy of the decomposition reaction for M-PBMA have been determined.

INTRODUCTION

Studies of the thermal stability of polymers are very important due to the increasing demand for polymers with high resistant temperature properties. The analysis of the kinetic parameters is also important in the understanding of solid state reactions which could occur during the decomposition processes. Several programmes are available to calculate the kinetic parameters from non-isothermal thermogravimetric data [1, 2]. Taylor and Khanna have described a programme for the kinetic evaluation of thermogravimetric data for a single non-isothermal experiment [3]. For the polymer industry it is also interesting to find new materials with better mechanical and physical properties. Our contribution deals with the

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synthesis of polymers with potential photoconductive and thermal stability properties.

In previous papers [4–7] several studies were made of the thermal decomposition of different polymers containing metals. The metal and/or metal clusters present in the sample produce a strong influence on the degradation reactions. In this paper, we investigated the kinetics of the thermal degradation of metal poly(*n*-butyl methacrylates) in order to find a relation between metal presence in the polymers and thermal stabilities, as well as activation energy.

EXPERIMENTAL

Colloid synthesis

The colloids metal–*n*-butyl methacrylate were prepared by codeposition of the solvent with the metals at 77 K using a metal atom reactor [8, 9]. By assuming that all the metal evaporated is incorporated into the monomer, the approximate concentration could be calculated. Different current intensities were used depending upon the metal used and the vacuum [10].

Polymerization

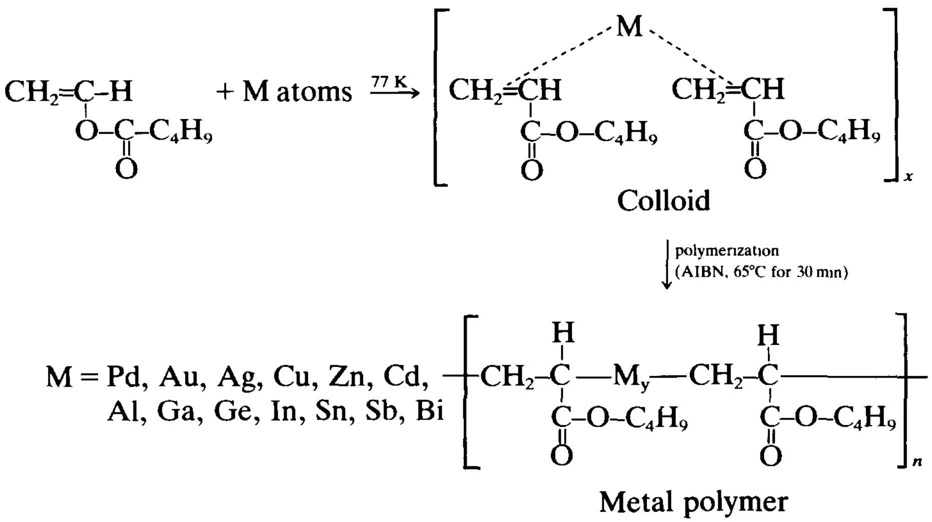
As a typical example, zinc colloid (10 cm^3) was placed in a polymerization flask with 0.5 mol% of azodiisobutyronitrile (AIBN) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath at 65°C for 25 min. The contents of the flask were quenched in 100 cm^3 of methanol. The polymer was filtered off and dried under vacuum (10^{-2} Torr) for 48 h at 35°C. The yield of the polymer was then determined. A similar procedure was followed for 1.0, 1.25 and 5.0 mol% AIBN fractions. Molecular weights were determined by viscosity in 2-butanone at 25°C.

Thermogravimetry

A Perkin-Elmer Model TGS-2 thermogravimetric system, with a microprocessor-driven temperature control unit and a TA data station, was used. The masses of these samples were recorded accurately and were generally in the range 5–10 mg. The sample pan was placed in the balance system and the temperature was raised from 25 to 550°C at a heating rate of 10 K min^{-1}. The mass of the sample was continuously recorded as a function of the temperature.

RESULTS AND DISCUSSION

The synthesis of polymers with metal incorporated from colloids and with metal dispersed in methyl and ethyl methacrylates has been previously reported [9, 11]. The polymers prepared have a wide range of molecular weight, stability, morphology and colours according to the metal. The



Scheme 1.

amount of metal incorporated was very low ranging from 0.063 to 0.86%. This small amount of metal incorporated is enough to change some physical properties of the polymers.

These new modified polymers were prepared by using the process shown in Scheme 1.

In Scheme 1 we propose one of the possible structures of the polymer. Another possibility is that the metal can be complexed through the oxygen in a similar manner to some polymers described by Chatterjee [12]. The average molecular weight ($\bar{M}_v$) of these polymers ranges between 10^4 and 10^5 [13]. These polymers exhibit $\bar{M}_v$ similar to the PMMA [9] but lower than the PEMA [14] series already reported.

Figure 1 shows the change in sample weight as a function of time and temperature when the four fractions of poly(*n*-butyl methacrylates) homopolymer are heated from 25 to 550°C. Table 1 summarizes the percentage weight loss as a function of time and temperature when the thirteen metal polymers are heated in the same range as that of the homopolymer. The thermal decomposition temperatures (T_D) were taken from the first large change in the slope of the TG curve. These values were corroborated by taking the first derivative of the curve.

These polymers degrade in one step, losing most of the weight at around 300°C. The decomposition reaction is irreversible so that the rate dependent parameters such as activation energy and the order of reaction may be calculated from a single experimental curve [15]. From the Arrhenius equation we can get information about the specific rate constants (k) and activation energy (E_a).

The thermal decompositon kinetics of the thermogravimetric weight loss

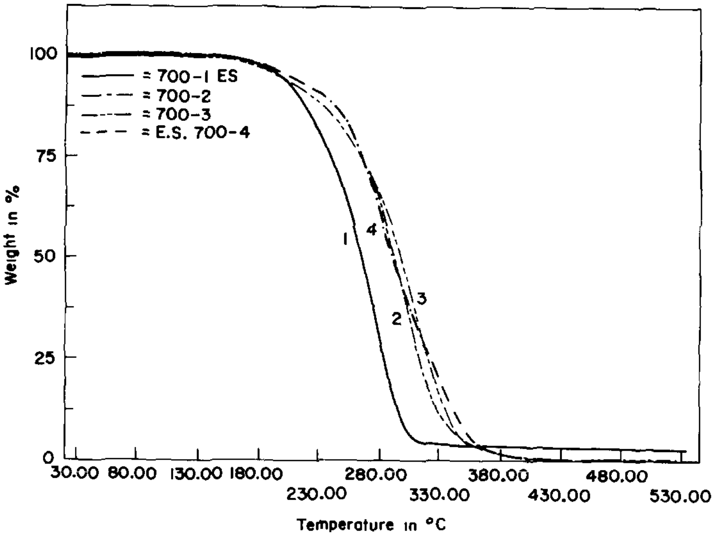


Fig. 1. Thermogram of poly(*n*-butyl methacrylates) obtained by heating the polymers from 25 to 550°C at 10°C min^{-1}. The fractions are obtained from curve 1, 0.5; curve 2, 0.75, curve 3, 1.0 and curve 4, 5.0 mol% AIBN.

can be expressed in tems of the kinetic equation $-\mathrm{d}\alpha/\mathrm{d}t = \mathrm{d}(1-\alpha)^n$, where α 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 ($\mathrm{d}\alpha/\mathrm{d}t$) was calculated using a differential technique with a heating rate, v.

We can establish that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = v\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{1}$$

After combining the relationships mentioned before, we obtain in the logarithmic form

$$\beta = \ln\left[-\frac{v(\mathrm{d}\alpha/\mathrm{d}T)}{(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \tag{2}$$

In eqn. (2) by incorporating $v = 10\,\mathrm{K\,min}^{-1}$, and expressed in $\mathrm{K\,s}^{-1}$ we obtain

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

A computer linear multiple regression program was used to calculate the kinetic parameters from the semilogarithmic plot of β against $1/T$ (see Fig. 2). A straight line should be obtained and ΔE and A calculated from the slope and intercept, respectively. This method is similar to that reported recently by Ma [16].

The thermograms of the four fractions of the homopolymer are shown in

TABLE 1

Kinetic parameters for metal poly(*n*-butyl methacrylates)

Polymer[a]	ΔE_a[b]/kJ mol^{-1}	*n*	Z/s^{-1}	Temp. range/°C	T_D/°C
PBMA-1	37.3	−0.25	2.9×10^3	185–314	282
PBMA-2	27.2	−0.25	1.5×10^1	182–380	316
PBMA-3	28.5	−0.25	2.9×10^1	180–380	307
PBMA-4	29.1	−0.25	3.5×10^1	180–380	282
Pd-PBMA-1	40.6	−0.25	6.6×10^2	277–430	389
Pd-PBMA-4	33.7	−0.50	2.2×10^2	240–415	276 350
Au-PBMA-1	26.6	−0.25	8.9	240–400	294 345
Au-PBMA-4	26.2	−0.25	7.9	205–405	298 350
Ag-PBMA-1	27.3	−0.25	1.0×10^1	245–420	296 361
Ag-PBMA-4	34.7	−0.5	5.2×10^2	225–370	277 341
Cd-PBMA-1	29.4	−0.25	2.5×10^1	200–410	291 340
Cd-PBMA-4	25.2	−0.25	4.9	235–415	287 331
Zn-PBMA-1	35.2	−0.25	2.7×10^2	230–395	286 347
Zn-PBMA-1	31.2	−0.25	6.3×10^1	230–390	275
Ga-PBMA-1	31.9	−0.25	5.8×10^1	260–410	306
Ga-PBMA-4	24.5	−0.25	3.9	230–390	280 342
Ge-PBMA-1	26.9	−0.25	11.9	180–390	289 332
Ge-PBMA-4	25.7	−0.25	6.0	230–415	300 352
In-PBMA-1	21.5	0	0.5	245–405	271 376
In-PBMA-4	39.3	−1	6.4×10^3	220–375	261 322
Sn-PBMA-1	32.2	−0.25	7.6×10^1	225–415	269 340
Sn-PBMA-4	31.7	−0.5	1.7×10^2	200–390	259 319
Bi-PBMA-1	38.7	−0.5	1.7×10^3	235–390	269 332
Bi-PBMA-4	34.1	−0.5	3.7×10^2	230–385	265 320
Sb-PBMA-1	35.3	−0.5	4.3×10^2	230–395	276 326
Sb-PBMA-4	33.4	−0.5	3.2×10^2	220–405	270 249
Al-PBMA-1	34.4	−0.5	4.0×10^2	240–410	284 337
Al-PBMA-4	34.5	−0.5	1.9×10^2	225–385	292 353
Cu-PBMA-1	48.7	−0.5	4.7×10^4	270–395	299 343
Cu-PBMA-4	38.8	−0.5	2.3×10^3	230–395	281 336

[a] PBMA = poly(*n*-butyl methacrylate); 1, 2, 3, 4 correspond to different molecular weight fractions. [b] Errors range from 0.41 to 1.0 kJ mol^{-1}.

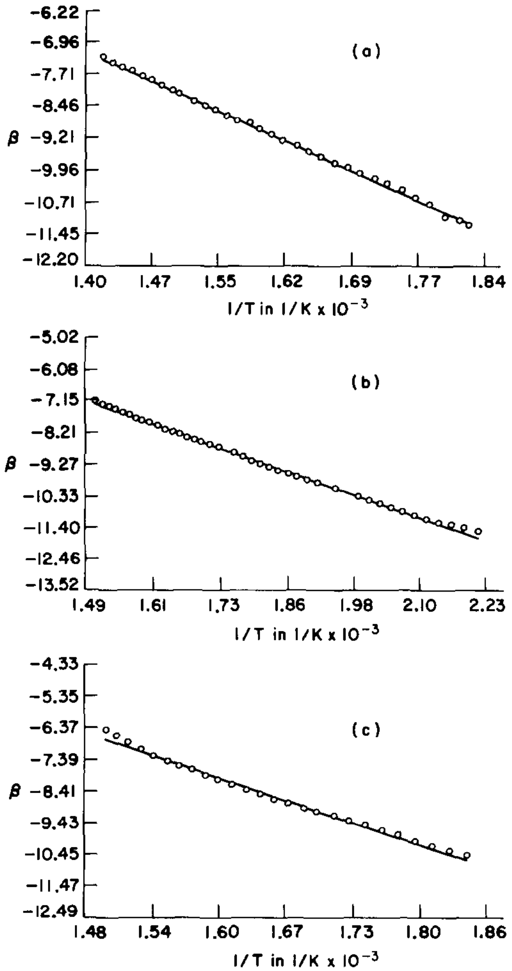


Fig. 2. Arrhenius plot for the thermal decomposition of, (a) Pd-PBMA (fraction 1) (b) Ge-PBMA (fraction 1), (c) Cu-PBMA (fraction 1).

Fig. 1. Their decomposition temperatures (T_D) are in the same range, but fraction 2 is a little higher than fraction 1. Furthermore, Fig. 3 shows the TG of Pd-PBMA and also the first derivative of the curve ($T_D = 388°C$). In contrast Fig. 4 compares the thermograms of Ag-PBMA and we can see that both T_D are lower for fraction 4 than for fraction 1. Both curves exhibit two decomposition step with the first the more important.

We obtain coefficients of linear correlation which ranged from 0.985 to 0.999 for fraction 1 and 0.981 and 0.997 for fraction 4.

Table 1 summarizes all the kinetic data obtained for fraction 1 (higher MW) and fraction 4 (lowest MW). We observe that the activation energies are in the range of 21.5–48.7 for the higher MW polymers and 24.5–39.3 kJ mol^{-1} for the lower. The temperature range over which these

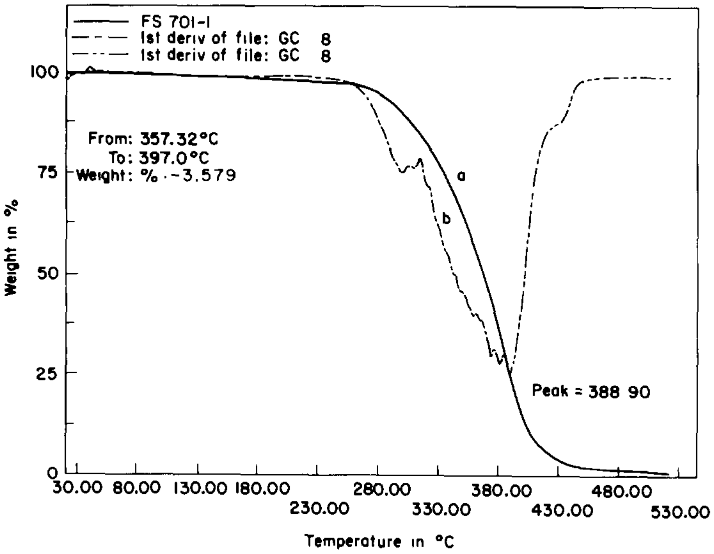


Fig. 3. (a) Thermogram of Pd-poly(*n*-butyl methacrylates) obtained by heating the polymers from 25 to 550°C at 10 K min^{-1} for 0.5 mol% AIBN. (b) DTG curves.

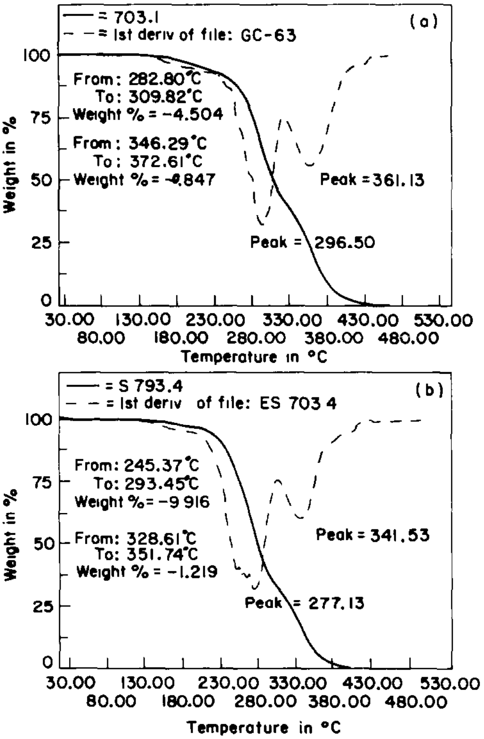


Fig. 4. (a) Thermogram of Ag-poly(*n*-butyl methacrylates) obtained by heating the polymers from 25 to 550°C at 10°C min^{-1} for 0.5 mol% AIBN. (b) TG curves of Ag-PBMA for fraction 4 (5.0 mol% AIBN) and their DTG curves.

values were obtained in order to get the best straight line in the plot β vs. $1/T$ are indicated. The ΔE_a values are similar to those reported for metal poly(ethyl methacrylates) [14, 17], and are even lower than for metal poly(methyl methacrylates) [9]. We also notice that in general, fraction 1 exhibits the higher ΔE_a which corresponds to the higher MW polymer fraction. However, from elemental analysis it was established that fractions with higher metal content, have higher ΔE_a values.

Pd and Cu-PBMA show the highest ΔE_a (40.6 and 48.7 kJ mol^{-1}) and Au and In-PBMA the lowest ΔE_a (26.6 and 21.5 kJ mol^{-1}), respectively. The low ΔE_a value for Au can be explained by the very low amount of metal incorporated into the polymer (0.040%). This was similar to Ge polymers. Since the amount of metal in the polymers is small they should behave in a way similar to the homopolymer and in fact, both exhibited ΔE_a values similar to fractions 2 and 3.

Most of the thermograms show a second thermal decomposition which is also indicated in Table 1. The kinetic order of this reaction is −0.25 in most of the cases with the exception of Sn, Bi, Sb, Al and Cu in which it is 0.5. These negative values are probably due to multistep decompositon due either to loss of CO_2 or hydrocarbons. Some formation of metal complexes might occur between the metal clusters and CO which would inhibit the normal decomposition reaction.

In Fig. 2, we can observe the linear correlation obtained for the Arrhenius plot of Pd-, Ga- and Cu-PBMA fraction 1, corresponding to the highest MW.

We conclude that in most of the polymers there is a change in the properties which depends upon the metal and the amount incorporated.

ACKNOWLEDGEMENTS

The financial support of Fondo Nacional de Ciencia (grant Fondecyt 92/0244) is gratefully acknowledged.

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