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THERMAL STUDIES OF METAL POLY(VINYL ACETATES). IX

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Abstract

Metal poly(vinyl acetates) polymers were obtained by radical polymerization with azodiisobutyronitrile. The thermal stabilities of the metal polymers (M–PVAC) 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 mainly in a single step with a very small second step, probably via a complex reaction. The kinetic data thus obtained show that the thermostabilities decrease in the order:
$\mathrm{Sb{-}PVA_C \sim Ge{-}PVA_C > Bi{-}PVA_C \sim Cd{-}PCA_C > Ag{-}PVA_C \sim PVA_C > Zn{-}PVA_C >}$
$\mathrm{Au{-}PVA_C > In{-}PVA_C > Sn{-}PVA_C > Ga{-}PVA_C > Pd{-}PVA_C}$.

Again, the thermal stability is dependent upon the metal incorporated in the backbone polymer. They loose weight after 320°C. The order of reaction from the thermal decomposition of these metal polymers was found to be –0.5 for the first step and 0 for the second. The pre-exponential factor, the reaction order and the activation energy of the decomposition for metal ($\mathrm{PVA_C}$) have been determined in most of them.

Keywords: kinetics, metal poly(vinyl acetates), polymers, TG, thermal stability

Introduction

The study of the kinetic behaviour is very important for the comprehension of solid state reaction processes. The kinetic parameters of a decomposition process can be calculated from the non-isothermal thermogravimetric data, and many kinetic programs are available [1, 2]. Elder [3] has developed a FORTRAN program for the kinetic analysis of transported non-isothermal TG data

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based on the Arrhenius analysis. More recently, Taylor and Khonna have described a program for the kinetic evaluation of TG data from a single non-isothermal experiment by using the method of Skvara and Šestak [4].

The thermal stability of polymers is very important at the present time due to the demand for polymers specially in high temperature applications. There are several studies that have been investigating the relationship between chemical structure and stability [5].

In polymer industry parts, it is very important to know the thermal stability of the polymeric materials because this information gives the temperature range over which the material can be used without degradation.

In previous papers [6–9], several studies concerning the thermal decomposition of different polymeric materials carried out in a thermobalance under nitrogen atmosphere have been published.

Degradation reactions are probably initiated or strongly influenced by impurities in the sample (in this case, the metals), especially if they are incorporated into the polymer chain.

The objective of the present study was to report the TG data of poly(vinyl acetates) in order to establish a correlation between metals in the polymer, activation energies and thermal stabilities.

Experimental

Colloid synthesis

The colloids (metal-monomer) were prepared by co-condensation of the solvents with the metals at 77 K using a metal atom reactor [10]. From the weight of metal evaporated on solvent added, the approximate concentration could be calculated. Different current intensities were used depending upon the metal used [11, 12].

Polymerization

As a typical example, silver colloid (10 ml) was placed in a polymerization flask with 0.25 mol% of azodiisobutyronitrile (AIBN) under nitrogen atmosphere. The flask was closed and placed in an isothermal bath at 65°C for 10 min. The content of the flask was 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 then determined. Similar procedure was followed for 0.5, 0.75 and 1 mol% AIBN fractions.

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.

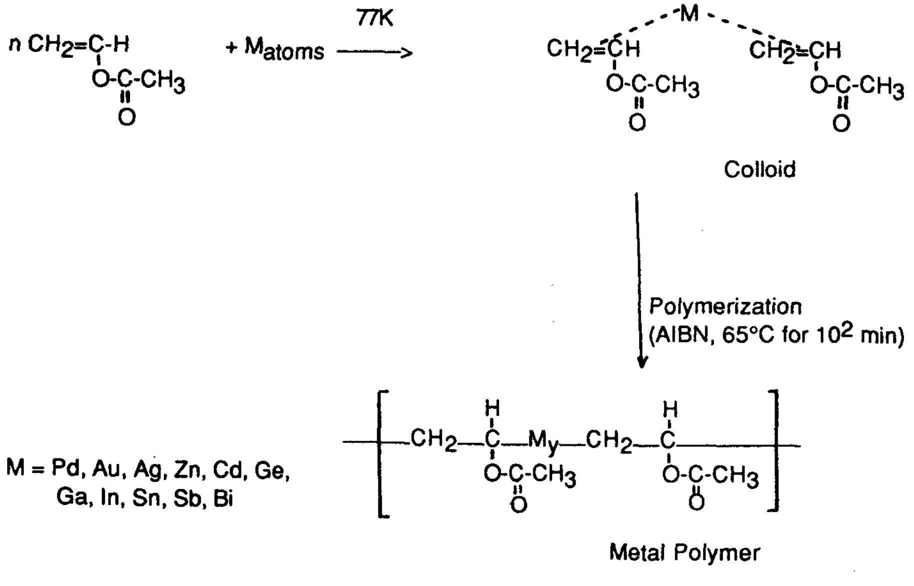
The sample pan was placed in the balance system in equipment and the temperature was raised from 25 to 550°C at a heating rate of 10 deg·min^{-1}. The weight of the sample pan was continuously recorded as a function of the temperature.

Results and discussion

The synthesis of polymers with metal incorporated from colloids or with metal dispersed in the monomers and/or polymers, has been recently reported by us [13, 14].

The polymers obtained have a wide range of molecular weight, stability, morphology and colour according to the metal. The amount of metal incorporated was very low ranging from 0.01% and 0.32%. Even though this small amount, the colour and some physical properties were affected.

These modified polymers were prepared by using the following scheme:



In this scheme we proposed one of the probably structure of this polymer. The average molecular weights ($\overline{M}_v$) range between 10^4 and 10^5 [12]. These polymers exhibit $\overline{M}_v$ similar to the styrene [7] series already reported, but lower than methyl methacrylates [6].

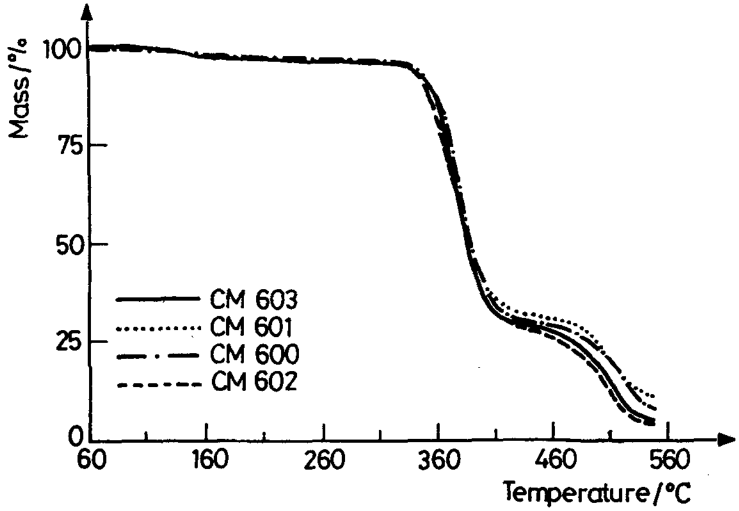


Fig. 1 TG curves of poly(vinyl acetates) obtained by heating the polymers from 25 to 550°C at 10 deg·min^{-1}: 0.25 mol%; 0.5 mol%; 0.75 mol% and 1.0 mol% AIBN, respectively

Figure 1 shows the change in sample weight as a function of time and temperature when the four fractions of poly(vinyl acetates) are heated from 25 to 550°C. Furthermore, the percentage weight loss as a function of time and temperature when the eleven metal polymers are heated in the same range as mentioned above is summarized in Table 1. The thermal decomposition tem-

Table 1 Kinetic parameters for metal poly(vinyl acetates)

Polymer		E_a /kJ·mol^{-1}	n	Z /s^{-1}	T range/ °C	T_D / °C
PVA–1	a	85.6	–0.5	$5.0 \cdot 10^{10}$	300–400	348.0
	b	7.4	0.0	$2.3 \cdot 10^{-3}$	430–490	461.7
PVA–2	a	74.8	–0.5	$1.2 \cdot 10^{9}$	280–400	335.0
	b	4.9	0.0	$1.0 \cdot 10^{-3}$	400–490	450.5
PVA–3	a	71.0	–0.5	$2.2 \cdot 10^{8}$	280–400	333.4
	b	5.4	0.0	$1.1 \cdot 10^{-3}$	410–500	464.9
PVA–4	a	72.5	–0.5	$4.5 \cdot 10^{8}$	290–400	345.03
	b	4.6	0.0	$8.9 \cdot 10^{-4}$	420–500	468.23

Table 1 Continued

Polymer		E_a /kJ·mol^{-1}	n	Z /s^{-1}	T range / °C	T_D / °C
Au–PVA$_1$	a	78.8	–0.5	$5.1\cdot10^{9}$	285–395	341.8
	b	4.4	0.0	$8.6\cdot10^{-4}$	410–500	464.03
Au–PVA$_4$	a	69.6	–0.5	$1.7\cdot10^{8}$	280–300	327.6
	b	4.1	0.0	$7.9\cdot10^{-4}$	395–480	447.0
Ag–PVA$_1$	a	85.2	–0.5	$4.7\cdot10^{10}$	290–400	350
	b	4.0	0.0	$7.5\cdot10^{-4}$	400–500	467
Ag–PVA$_4$	a	80.3	–0.5	$5.8\cdot10^{9}$	300–400	353
	b	4.9	0.0	$9.8\cdot10^{-4}$	425–510	469
Zn–PVA$_1$	a	79.8	–0.5	$3.5\cdot10^{9}$	295–410	356
	b	8.3	0.0	$1.0\cdot10^{-3}$	445–510	482
Zn–PVA$_4$	a	73.8	–0.5	$5.7\cdot10^{8}$	290–400	347
	b	5.5	0.0	$1.2\cdot10^{-3}$	420–495	470
Cd–PVA$_1$	a	88.3	–0.5	$2.1\cdot10^{11}$	295–390	336
	b	4.8	0.0	$9.9\cdot10^{-4}$	410–495	464
Cd–PVA$_4$	a	87.1	–0.5	$1.2\cdot10^{11}$	295–340	335
	b	6.5	0.0	$1.7\cdot10^{-3}$	425–500	465
Pd–PVA$_1$	a	60.0	–0.5	$3.7\cdot10^{6}$	280–395	327
	b	4.4	0.0	$8.6\cdot10^{-4}$	425–505	447
Pd–PVA$_4$	a	50.1	–0.5	$97.6\cdot10^{3}$	285–390	326
	b	4.3	0.0	$7.7\cdot10^{-4}$	440–525	448
Ga–PVA$_1$	a	64.2	–0.5	$5.0\cdot10^{7}$	260–375	311
	b	3.0	0.0	$5.9\cdot10^{-4}$	410–480	462
Ga–PVA$_4$	a	61.1	–0.5	$1.2\cdot10^{7}$	260–375	316
	b	3.9	0.0	$7.6\cdot10^{-4}$	410–490	449
Ge–PVA$_1$	a	86.4	–0.5	$1.4\cdot10^{11}$	285–380	330
	b	4.6	0.0	$9.3\cdot10^{-4}$	405–485	457
Ge–PVA$_4$	a	92.2	–0.5	$1.9\cdot10^{12}$	285–370	325
	b	4.5	0.0	$9.4\cdot10^{-4}$	400–480	453
In–PVA$_1$	a	76.6	–0.5	$3.8\cdot10^{9}$	285–370	338
	b	4.8	0.0	$9.8\cdot10^{-4}$	415–490	454
In–PVA$_4$	a	70.2	–0.5	$2.5\cdot10^{8}$	285–390	330
	b	4.2	0.0	$8.0\cdot10^{-4}$	400–490	461

Table 1 Continued

Polymer		E_a /kJ·mol^{-1}	n	Z /s^{-1}	T range / °C	T_D /°C
Sn–PVA$_1$	a	74.0	–0.5	$8.7\cdot10^{8}$	290–400	325
	b	3.9	0.0	$7.4\cdot10^{-4}$	400–500	462
Sn–PVA$_4$	a	69.8	–0.5	$1.8\cdot10^{8}$	280–400	322
	b	5.1	0.0	$1.1\cdot10^{-3}$	400–475	452
Sb–PVA$_1$	a	92.3	–0.5	$1.4\cdot10^{12}$	300–380	330
	b	4.5	0.0	$8.9\cdot10^{-4}$	400–490	450
Sb–PVA$_4$	a	85.5	–0.5	$1.1\cdot10^{11}$	290–380	329
	b	4.9	0.0	$1.1\cdot10^{-3}$	410–490	453
Bi–PVA$_1$	a	87.1	–0.5	$1.3\cdot10^{11}$	300–390	340
	b	4.7	0.0	$9.3\cdot10^{-4}$	420–500	476
Bi–PVA$_4$	a	80.4	–0.5	$1.1\cdot10^{10}$	295–395	334
	b	4.3	0.0	$8.2\cdot10^{-4}$	410–500	468

PVA = poly(vinyl acetate); 1,2,3,4 = correspond to the molecular weight fractions

peratures (T_D) were taken from the first large change in the slope of the TG curve. This value was corroborated by taking the first derivative of the curve.

These polymers degrade in two steps but being the first one the more important, because in most of them the second degradation exhibits a very low activation energy of the decomposition reaction.

The decomposition reaction is irreversible so that the rate dependent parameters such as activation energy and order of reaction may be calculated from a single experimental curve [15]. From the Arrhenius equation we can get information about specific rate constant (k) and activation energy (E).

The thermal decomposition kinetics of the thermogravimetric weight loss can be expressed in terms of the kinetic equation $-\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n$ 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 relationship mentioned above, we obtain in the logarithmic form

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

In the Eq. (2) by incorporating $v = 10$ deg·min^{-1}, and expressed in K we obtain

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

A computer linear multiple regression program was used to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semilog plot of against $1/T$ (Fig. 2). A straight line should be obtained, and E and A can be calculated from the slope and intercept, respectively. This is a similar method to that one used by Ma *et al.* [16]. The coefficients of linear correlation are ranging from 0.992 to 0.997.

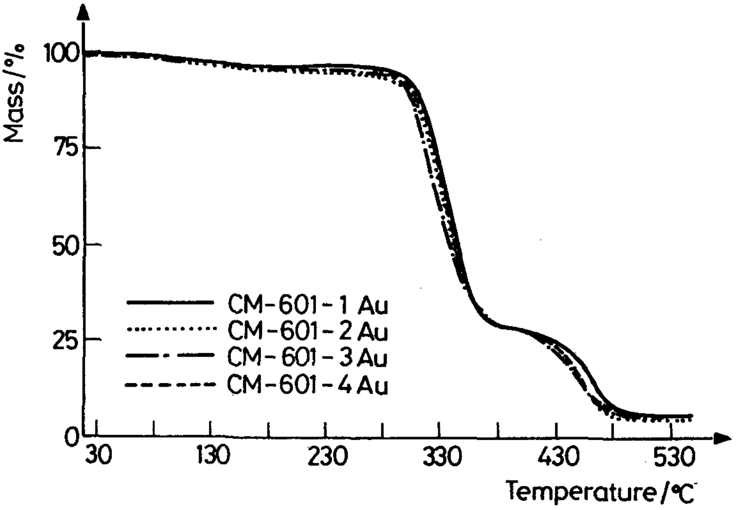


Fig. 2 TG curves of Au-poly(vinyl acetates) obtained by heating the polymers from 25 to 550°C at 10 deg·min^{-1}: 0.25 mol%; 0.5 mol%; 0.75 mol% and 1.0 mol% AIBN, respectively

The values of activation energy are very similar between 60 and 92 kJ·mol^{-1} for the first slope and around 5 kJ·mol^{-1} for most of the second one. The most stable metals like, Ag, Pd, Au exhibit the highest E_a. It is interesting to notice that in general we can observe a correlation between molecular weight (*MW*) fraction polymers and activation energy (*E*). The higher *MW* exhibits also the highest *E*, this can be observed either homopolymer or metal polymer. In the rest of the metal polymers under study only fraction 1 (higher *MW*) and fraction 4 (lower *MW*) were considered.

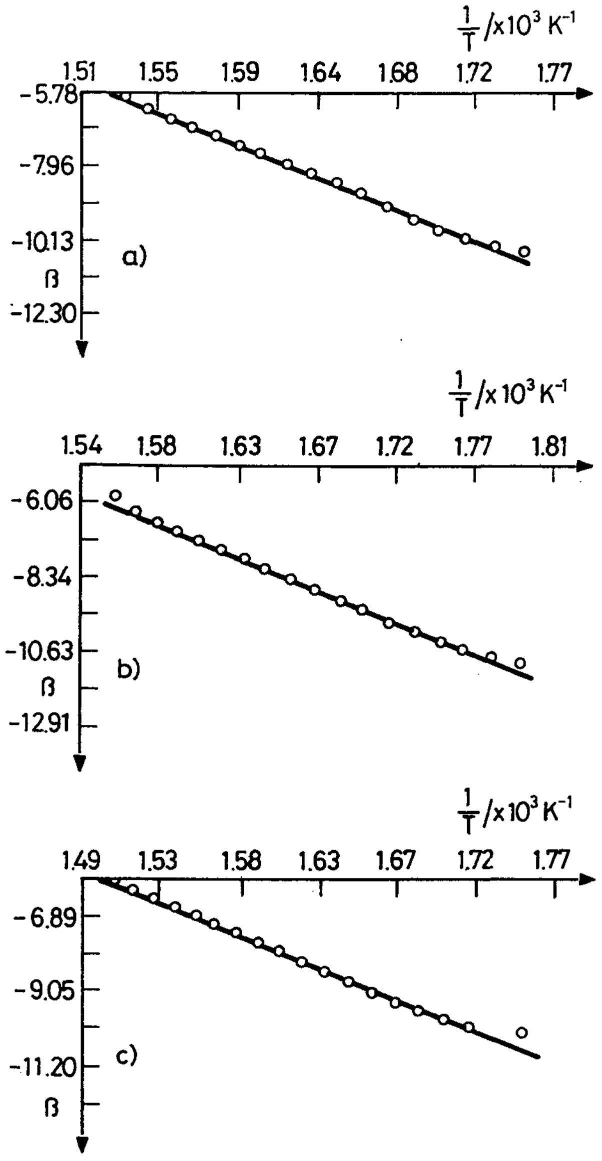


Fig. 3 Arrhenius plot for the thermal decomposition of (a) Sb–PVAc (fraction 1), (b) Ge–PVAc (fraction 1) and (c) Bi–PVAc (fraction 1)

The second degradation is very small and generally is in the same range (4–5 kJ·mol^{-1}). Since this is a very small value, from the kinetic point of view is irrelevant.

The order of reaction was –0.5 in all the higher *MW* fractions of metal PVAc and also in the four fractions of the homopolymer. This is probably due to the multistep decomposition; CO, CO_2 and the hydrocarbon loss. Some of this process could be inhibited by the metal presence with formation of carbonyl compounds.

Figure 2 exhibits the thermoanalytical curves of the four fractions of Au-poly(vinyl acetates) for comparison. Also, fraction 1 shows higher T_D than fraction 4, the same as the homopolymer.

On Fig. 3, we can observe the linear correlation obtained from the Arrhenius plot for Sb-, Ge- and Bi-polyvinyl acetates fraction 1, corresponding to the highest *MW*. All the polymers behave similarly.

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Zusammenfassung — Metallpoly(vinylacetat)polymere werden durch radikalische Polymerisation mit Azodiisobutyronitril erhalten. Mittels TG wurde die thermische Stabilität der Metallpolymere (M–PVAc) im Temperaturbereich von 25 bis 550°C in Stickstoffstrom untersucht. Die Zersetzungstemperatur wurde aus dem Maximum der ersten Ableitung der TG-Kurve ermittelt. Die kinetischen Parameter der thermischen Zersetzung wurden mittels der Arrhenius'schen Glei-

chung ermittelt. All diese Polymere zersetzen sich in erster Linie in einem einzelnen Schritt und einem sehr kleinen zweiten Schritt, wahrscheinlich über eine Komplexreaktion. Anhand der kinetischen Daten nimmt die thermische Stabilität in folgender Reihenfolge ab: Sb–PVAc~Ge–PVAc–Bi–PVAc~Cd–PVAc > Ag–PVAc~PVAc > Zn–PVAc > Au–PVAc > In–PVAc > Sn–PVAc > Ga–PVAc > Pd–PVAc.

Die thermische Stabilität hängt von dem im Hauptpolymer integrierten Metall ab. Gewichtsverlust tritt ab 320°C ein. Die Reaktionsordnung in der thermischen Zersetzung dieser Metallpolymere betrug -0,5 für den ersten und 0 für den zweiten Schritt. In den meisten Fällen wurden präexponentieller Faktor, Reaktionsordnung und Aktivierungsenergie der Zersetzung von Metall-PVAc bestimmt.