Nonisothermal Decomposition Kinetics of Chromium–Polyacrylate Complexes Prepared from Aged Cr(III) Solutions

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ABSTRACT: Thermogravimetric studies of poly(acrylic acid) (PAA) and its chromium–polyacrylate complexes prepared from Cr(III) solutions aged for different times were undertaken. Six kinetic methods were used to investigate the thermal decomposition behavior of these materials. The applied methods were the Coats–Redfern, Horowitz–Metzger, MacCallum–Tanner, van Krevelen, Madhusudanan–Krishnan–Ninan, and Criado methods. The activation energy values obtained with the Coats–Redfern, Horowitz–Metzger, and MacCallum–Tanner methods were in good agreement with one another, and those obtained with the van Krevelen and Madhusudanan–Krishnan–Ninan methods were found to be 10–20 kJ/mol larger. The apparent activation energies increased for the complexes prepared from Cr(III) solutions aged for longer times. An analysis of the experimental results suggested that the actual decomposition mechanisms of PAA and the metal–polymer complexes were a D_n deceleration type. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1129–1134, 2007

Key words: activation energy; degradation; metal-polymer complexes

INTRODUCTION

Polymeric metal chelates are of great significance in different fields of chemistry, such as catalytic reactions, mining separation, biochemistry, medicine, and environmental chemistry.[1–5] Among these, polyacrylate complexes have received special attention as precursors to ceramics and ceramic superconductors.[6,7] Co(II) and Gd(III) polyacrylates have been shown to possess magnetic ordering at low temperatures and spin–glass behavior on annealing.[8] The development of these materials requires a precise knowledge of their thermal behavior. There are a number of studies in the literature involving the thermal characterization of such complexes. Allan et al.[9] and more recently Sebastian et al.[10] have reported thermal studies on poly(acrylic acid) (PAA) complexes with various transition-metal ions.

In a previous publication,[11] we described the structural and thermal properties of chromium–polyacrylate complexes prepared from Cr(III) solutions aged for different times. The complexes prepared from olated chromium solutions were thermally less stable. In this article, we report an analysis of the dynamic thermogravimetry (TG) data to derive the kinetic parameters and the mechanism for the decomposition of chromium–polyacrylate complexes. The advantages of evaluating the reaction kinetics by dynamic methods are that they demand less time than isothermal methods and that a number of methods of data evaluation are available.

Nonisothermal methods have been extensively used for the study of the kinetics and mechanisms of condensed phase reactions.[12] In general, most methods of kinetic analysis of thermoanalytical data begin with the well-known Arrhenius equation [eq. (1)] and a rate expression [eq. (2)]:

$$k = A \exp(-E/RT) \tag{1}$$

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

where k is a specific rate constant, A is the pre-exponential factor (min^{-1}), E is the activation energy (kJ/mol), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature. $f(\alpha)$ is a so-called kinetic function that depends on the reaction mechanism, and α represents the fractional conversion (increasing from 0 to 1) in the solid reactant during the course of the reaction. If $f(\alpha) = (1 - \alpha)^n$ (where n is the reaction order) and, with a constant temperature increase, $dT/dt = \beta$ [where β is the heating rate (°C/min)], the integration of eq. (2) leads to

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$$g(\alpha) = \int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (3)$$

where $g(\alpha)$ is the integral function of the conversion and T_0 is the initial temperature. For the special case of $n = 1$

$$\int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = -\ln(1-\alpha) \quad (4)$$

For n not equal to zero or unity

$$\int_0^\alpha \left[\frac{1}{(1-\alpha)^n}\right] d\alpha = -\frac{1-(1-\alpha)^{1-n}}{1-n} \quad (5)$$

We have used the following techniques for solving the integral of eq. (3).

Coats–Redfern method[13]

Using an asymptotic approximation for the resolution of eq. (3), we can obtain the following equation:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \left(\frac{E}{RT}\right) \quad (6)$$

We supposed that $\ln(1 - \frac{2RT}{E}) \to 0$ for the Doyle approximation[14] while obtaining the natural logarithmic form:

$$\ln g(\alpha) \cong \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT}$$

E can be obtained from the slope of a plot of $\ln[g(\alpha)/T^2]$ versus $1000/T$.

Madhusudanan–Krishnan–Ninan method[15]

The Madhusudanan–Krishnan–Ninan method is similar to the Coats–Redfern and MacCallum–Tanner methods:

$$\ln\left[\frac{g(\alpha)}{T^{1.9206}}\right] = \ln\left(\frac{AE}{\beta R}\right) + 3.7678 - 1.9206\ln E$$
$$- 0.12040\left(\frac{E}{T}\right) \quad (7)$$

A plot of $\ln[g(\alpha)/T^{1.8843}]$ versus θ will give a straight line, and E and A can be calculated from it.

MacCallum–Tanner method[16]

The MacCallum–Tanner method provides an approximation integrated from the rate of degradation as a

function of temperature. The rate of degradation can thus be expressed by

$$\log g(\alpha) = \log\frac{AE}{\beta R} - 0.4828E^{0.4351} - \left(\frac{0.449 + 0.217E}{10^{-3}T}\right) \quad (8)$$

A plot of $\log g(\alpha)$ versus $1/T$ can give E from the slope and A from the intersection of the y axis.

van Krevelen method[17]

The van Krevelen integration method is expressed as follows:

$$n \neq 1 \quad \ln g(\alpha) = \ln\left[\frac{A(0.368/T_m)^x}{\beta(x+1)}\right] + (x+1)\ln T \quad (9)$$

where $x = E/RT_m$. T_m is the temperature at the maximum rate of weight loss [i.e., the differential thermogravimetry (DTG) peak temperature]. Therefore, E can be obtained from the slope of a plot of $\ln g(\alpha)$ versus $\ln T$.

Horowitz–Metzger method[18]

The Horowitz–Metzger method introduced a characteristic temperature, T_m, and a parameter, Θ, such that $\Theta = T - T_m$. If n is 1, T_m is defined as the temperature at which $(1 - \alpha)_m = 1/e = 0.368$, and the final expression is

$$\ln\ln g(\alpha) = \frac{E\theta}{RT_m^2}$$

If n is unknown, T_m is defined for the maximum heating rate.

When Θ is 0, $(1 - \alpha) = (1 - \alpha)_m$, $(1 - \alpha)_m = n^{1/1-n}$, and

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \ln\frac{ART_m^2}{\beta E} - \frac{E}{RT_m} + \frac{E\theta}{RT_m^2} \quad (10)$$

A plot of $\ln g(\alpha)$ versus Θ can yield E.

Criado–Malek–Ortega method[19]

If the value of E is known, the kinetic model of the process can be determined by this method. Criado et al.[19] defined the following function:

$$z(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)}{\beta}\pi(x)T \quad (11)$$

where $x = E/RT$, $z(\alpha)$ is a function of reaction degree, and $\pi(x)$ is an approximation of the temperature inte-

TABLE I
Algebraic Expressions for the Most Frequently Used Mechanisms of Solid-State Processes

No.	Mechanism	Symbol	Integral form [$g(\alpha)$]
1	N and G ($n = 1$)	A_1	$-\ln(1 - \alpha)$
2	N and G ($n = 2$)	A_2	$[-\ln(1 - \alpha)]^{1/2}$
3	N and G ($n = 3$),	A_3	$[-\ln(1 - \alpha)]^{1/3}$
4	N and G ($n = 4$),	A_4	$[-\ln(1 - \alpha)]^{1/4}$
5	Diffusion, 1D	D_1	α^2
6	Diffusion, 2D	D_2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
7	Diffusion, 3D	D_3	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
8	Diffusion, 3D	D_4	$[1 - (1 - \alpha)^{1/3}]^2$
9	Diffusion, 3D	D_5	$[(1 + \alpha)^{1/3} - 1]^2$
10	Diffusion, 3D	D_6	$\{[1/(1 - \alpha)]^{1/3} - 1\}^2$
11	Contracted geometry shape (contracting linear)	R_1	$1 - (1 - \alpha)^{1/2}$
12	Contracted geometry shape (cylindrical symmetry)	R_2	$1 - (1 - \alpha)^{1/3}$
13	Contracted geometry shape (spherical symmetry)	R_3	$1 - (1 - \alpha)^{1/3}$
14	Random nucleation with two nuclei on the individual	F_2	$1/[(1 - \alpha)]$
15		F_3	$1/[(1 - \alpha)^2]$

1D = one-dimensional; 2D = two-dimensional; 3D = three-dimensional; N and G = nucleation and growth.

gral that cannot be expressed in a simple analytical form. In this case, the fourth rational expression of Senum and Yang[20] has been used. Combining eqs. (2) and (11), we can obtain the following:

$$z(\alpha) = f(\alpha)F(\alpha) \qquad (12)$$

where $F(\alpha)$ is a function dependent on the real reaction mechanism.

Then, the master curves of different models listed in Table I can be obtained with this function. Comparing the plots of $z(\alpha)$ calculated by eq. (11) with experimental data with the master curves, we can determine the mechanism of a solid-state process.

EXPERIMENTAL

Four different products were prepared: a product prepared from a fresh Cr(III) solution (complex 1) and products prepared with Cr(III) solutions aged for 1 (complex 2), 3 (complex 3), or 5 weeks (complex 4). The reactions were started by the addition of a Cr(III) solution (15 mL, 2.5M) to a PAA solution (20 mL, 2.5M), with the medium pH kept around 8 through the dropping of concentrated ammonia. The reaction mixture was agitated for complete mixing during the reaction course. The gelatinous precipitates that formed (complexes 1–4) were removed by filtration and dried at room temperature for 24 h. The complexes were then washed with distilled water and ethanol and dried again. The preparation and analyses of the complexes were described previously.[11] TG analysis, DTG, and differential thermal analysis data were recorded with a Shimadzu DTG-60H thermal analyzer (Shimadzu, Kyoto, Japan) with a sample weight of approximately 3 mg, a dynamic nitrogen atmosphere (15 mL/min), and heating to 900°C at 20°C/min in alumina crucibles. The kinetic parameters were calculated from the linear plots of the left-hand side of the kinetic equations [eqs. (6)–(8)] against $1/T$. For the van Krevelen equation [eq. (9)], the left-hand side was plotted against ln T. The values of E and A were calculated from the slope and intercept of the straight lines, respectively.

RESULTS AND DISCUSSION

The complexes studied in this work were prepared from fresh and aged Cr(III) solutions. A description of the complexes is given in Table II.

The TG curve of PAA showed three weight-loss stages in the temperature range of 25–550°C. The first stage was due to the removal of adsorbed water molecules at 58°C. The second stage referred to the degradation of carboxyl groups at 316°C, and the third stage was the rupture of the polymer chain at 414–433°C. The TG curves of the metal complexes showed two stages. The first stage corresponded to the dehydration process and the decomposition of uncomplexed carboxylate groups. The second stage occurred at 591–813 K for complex 1, at 621–825 K for complex 2, at 582–798 K for complex 3, and at 590–804 K for complex 4. In all cases, the second stage was the major decomposition step and was used for the kinetic analysis of the TG curves. The decomposition onset and offset temperatures for PAA, its Cr com-

TABLE II
Chromium Contents and Crystallinities of the Complexes[a]

Sample	Aging time	Cr (%)	Crystallinity (%)
PAA	—	—	6.4
1	Fresh	7.3	7.7
2	1 week	8.5	6.7
3	3 weeks	9.7	Not recorded
4	5 weeks	15.5	6.5

[a] Data from ref. 11.

TABLE III
TG Data for the Thermal Degradation of PAA and Its Chromium Complexes

Complex	Initial decomposition temperature (K)	Final decomposition temperature (K)	Peak temperature in DTG (K)	Mass loss (%)
PAA	628	806	713	53.40
1	591	813	690	65.56
2	621	825	693	60.70
3	582	798	678	58.11
4	590	804	670	54.54

plexes, and the related mass losses are given in Table III.

Thermal data obtained at a single heating rate (20°C/min) were evaluated with the Coats–Redfern, Madhusudanan–Krishnan–Ninan, Horowitz–Metzger, MacCallum–Tanner, and van Krevelen methods and with the Criado–Malek–Ortega method for kinetic analysis. The values of n, E, and A, the mechanisms, and the linearization curves of the thermal degradation of PAA and the polymer–metal complexes were determined.

According to the Coats–Redfern method, the plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ gave straight lines with slopes equal to $-E/R$ (Fig. 1). The decomposition activation energies obtained by this approach at $0.05 < \alpha < 0.90$ were 187.78, 122.54, 116.66, 140.09, and 137.59 kJ/mol for PAA, 1, 2, 3, and 4, respectively.

The second method for the calculation of E was developed by Madhusudanan et al.[15] From the slopes of the straight lines in plots of $\ln[g(\alpha)/T^{1.9206}]$ versus $1/T$, the E values were determined to be 188.27, 123.12, 123.23, 140.63, and 138.13 kJ/mol for PAA, 1, 2, 3, and 4, respectively.

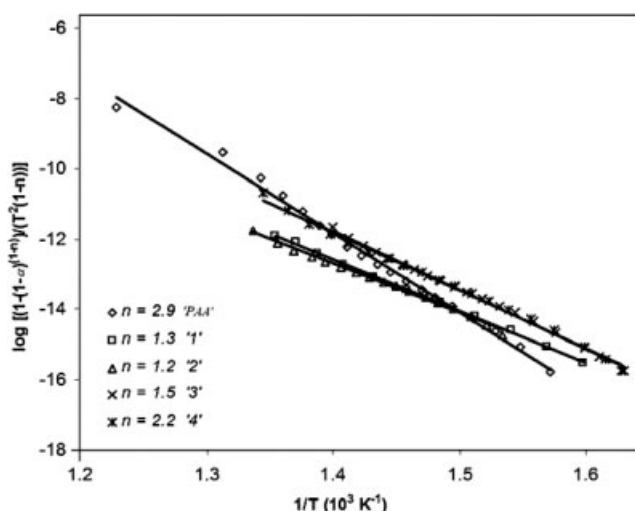The MacCallum–Tanner method also provided an approximated form of the rate of degradation as a function of temperature. Figure 2 presents a plot of log $g(\alpha)$ against $1/T$ obtained with this approach. E of PAA was found to be 185.96 kJ/mol and the values of the complexes were 121.75, 126.46, 143.43, and 141.08 kJ/mol for 1, 2, 3, and 4, respectively. An increase in E was noted in parallel to the aging period.

Figure 3 shows the values of E determined by the van Krevelen method. The values were found to be 214.15, 136.59, 134.02, 158.01, and 150.79 kJ/mol for PAA, 1, 2, 3, and 4, respectively.

Finally, as shown in Figure 4, in the case of the Horowitz–Metzger method, the values of E were calculated from the slopes of ln $g(\alpha)$ versus Θ plots to be 245.36, 156.43, 145.33, 176.94, and 168.32 kJ/mol for PAA, 1, 2, 3, and 4, respectively.

Table IV summarizes the values of n, A, α, the correlation coefficient (r), and E obtained by the five different methods examined in this study. For all the methods applied, the determination of A and n was possible from the expression of $g(\alpha)$ in eq. (3) and $n \neq 1$:

Figure 1 Coats–Redfern plots of PAA and Cr–PAA complexes.
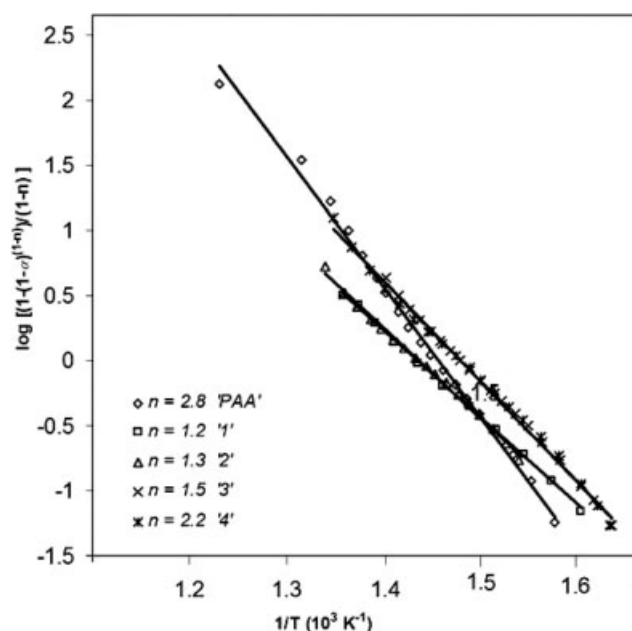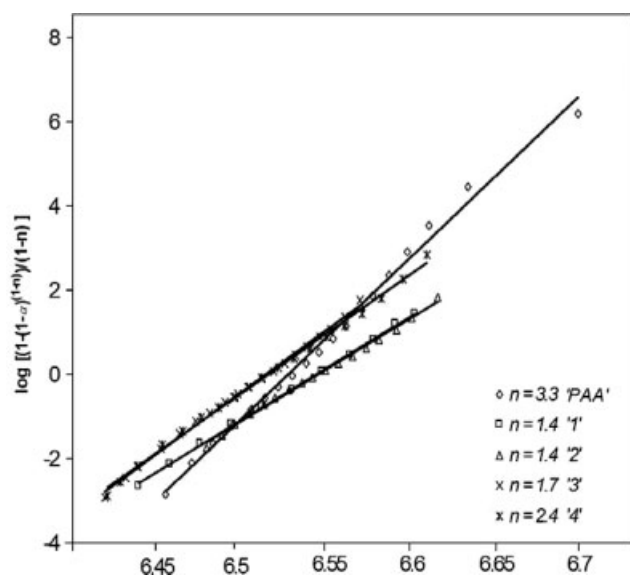

Figure 2 MacCallum–Tanner plots of PAA and polymer–metal complexes.

Figure 3 van Krevelen plots of PAA and polymer–metal complexes.

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

The E values obtained with the Coats–Redfern, Horowitz–Metzger, and MacCallum–Tanner methods were in good agreement with one another, and those obtained with the van Krevelen and Madhusudanan–Krishnan–Ninan methods were found to be 10–20 kJ/mol larger. However, they were similar to the values given in the literature for PAA and other metal–polymer complexes.[10] The average E value for the thermal decomposition of PAA in a nitrogen atmosphere, at a heating rate of 20°C/min, was about 187 kJ/mol according to the Coats–Redfern, Madhusudanan–Krishnan–Ninan, and MacCallum–Tanner methods. The apparent E values of the complexes under the same conditions were found to be smaller than that of the polymer itself. The stability of the uncomplexed PAA can be attributed to the presence of intermolecular hydrogen bonds between the carboxyl groups of the polymer chains, which are broken through complexation with Cr(III) ions. The E values of the complexes showed variations with respect to the aging time of the Cr(III) solutions used in the preparations. The complexes prepared from Cr(III) solutions aged for longer times had higher thermal decomposition activation energies. It appears that the interaction of multivalent, polynuclear Cr(III) species in the olated Cr(III) solutions with the polymer leads to the formation of stable ring structures[11] and hence kinetically stable activated complex structures. On the other hand, the interaction of various types of polynuclear species with the polymer backbone results in relatively unstable coordination geometries. Therefore,

the complexes prepared from olated Cr(III) solutions were thermodynamically less stable and had lower decomposition temperatures (Table III).

As shown in Table IV, the value of r for the linearization curves of PAA and the polymer–metal complexes was approximately 1.00, and the values of n obtained with the different methods for each sample were very similar. n increased for the complexes prepared from aged Cr(III) solutions in agreement with the increasing nuclearity of the Cr(III) species; however, it is difficult to rationalize an average value of n for the thermal degradation of the polymer–metal complexes.

We employed reference theoretical master curves to determine the reaction mechanism for the studied systems. According to Criado et al.,[19] a master plot is a characteristic curve independent of the condition of the measurement. Master curve plots of $z(\alpha)$ versus α for different mechanisms are illustrated in Figure 5.

The experimental data of $z(\alpha)$ for PAA agree very well with the D_6 master curve, whereas the experimental data of $z(\alpha)$ for the polymer–metal complexes agree with the master curve, which corresponds to D_3 and D_4 deceleration mechanisms. The fact that the decompositions of both PAA and Cr–PAA complexes are D_n types shows that chromium aging has no significant influence on the degradation mechanism.

CONCLUSIONS

A study on the thermal degradation of chromium–polyacrylate complexes was carried out with several kinetic methods. The degradation kinetics were investigated through the evaluation of the dynamic TG
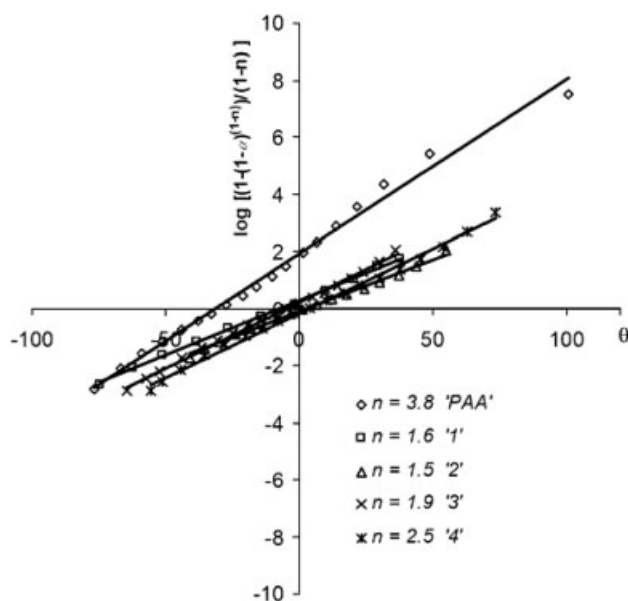
Figure 4 Horowitz–Metzger plots of PAA and polymer–metal complexes.

TABLE IV
Kinetic Parameters of the Thermal Degradation of PAA and Its Metal Complexes

| Method	Complex	n	E (kJ/mol)	A (min^{-1})	α	r
Coats–Redfern	PAA	2.9	187.78	8.9×10^{13}	0.05–0.95	0.99719
	1	1.3	122.54	4.6×10^{8}	0.06–0.91	0.99959
	2	1.2	116.66	1.4×10^{8}	0.15–0.95	0.99719
	3	1.5	140.09	2.3×10^{10}	0.05–0.90	0.99874
	4	2.2	137.59	1.4×10^{10}	0.05–0.90	0.99789
Madhusudanan– Krishnan–Ninan	PAA	2.9	188.27	2.6×10^{14}	0.05–0.95	0.99719
	1	1.3	123.12	1.4×10^{9}	0.06–0.91	0.99959
	2	1.3	123.23	1.3×10^{9}	0.15–0.95	0.99744
	3	1.5	140.63	6.1×10^{10}	0.05–0.90	0.99879
	4	2.2	138.13	4.3×10^{10}	0.05–0.90	0.99789
MacCallum–Tanner	PAA	2.8	185.96	1.4×10^{17}	0.05–0.95	0.99754
	1	1.2	121.75	8.2×10^{11}	0.06–0.91	0.99969
	2	1.3	126.46	1.9×10^{12}	0.15–0.95	0.99784
	3	1.5	143.43	9.2×10^{13}	0.05–0.90	0.99894
	4	2.2	141.08	5.8×10^{13}	0.05–0.90	0.99819
van Krevelen	PAA	3.3	214.15	1.3×10^{15}	0.05–0.95	0.99679
	1	1.4	136.59	2.0×10^{9}	0.06–0.91	0.99959
	2	1.4	134.02	1.2×10^{9}	0.15–0.95	0.99759
	3	1.7	158.01	1.6×10^{11}	0.05–0.90	0.99874
	4	2.4	150.79	4.2×10^{10}	0.05–0.90	0.99804
Horowitz–Metzger	PAA	3.8	245.36	2.3×10^{19}	0.05–0.95	0.99574
	1	1.6	156.43	4.7×10^{11}	0.06–0.91	0.99944
	2	1.5	145.33	5.9×10^{10}	0.15–0.95	0.99734
	3	1.9	176.94	4.9×10^{13}	0.05–0.90	0.99854
	4	2.5	168.32	1.0×10^{13}	0.05–0.90	0.99794
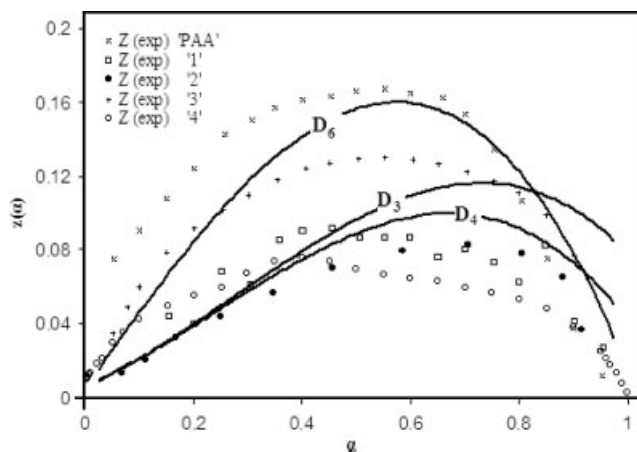
Figure 5 Master curves of $z(\alpha)$ and experimental data.

data obtained at a single heating rate. The thermal degradation mechanism for PAA and its chromium complexes is a decelerated D_n type, which indicates a solid-state process based on n-dimensional diffusion. Chromium aging has no significant effect on the mechanism; however, it increases the decomposition energies. The complexes prepared from aged Cr(III) solutions were kinetically more stable but thermodynamically less stable.

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