

STUDY ON THERMAL DECOMPOSITION KINETICS OF URUSHIOL METAL CHELATE POLYMERS*

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ABSTRACT

The thermal decomposition kinetics of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers has been studied by non-isothermal thermogravimetry. The results suggest that the thermal decomposition kinetics of three chelate polymers are all of first order. Their average activation energy values of the thermal decomposition calculated by Ozawa-(I) method are 110, 79, 136.98 and 163.64 kJ mol⁻¹ respectively, which increase linearly with the metal valence of the metal chelate polymers

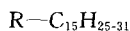
INTRODUCTION

The preparation and characterization of some urushiol-metal chelate polymers have been studied by the authors^[1-3]. The results suggest that urushiol metal chelate polymers have many good properties such as magnetism; good resistance to strong acids, strong alkalis and many kinds of salts, organic solvents; stable at high temperature and wear resistance; showing that the use of urushiol-metal chelate polymers have a promising prospect. In this paper, we studied the thermal decomposition kinetics of urushiol-Cu(Ⅱ), urushiol-Nd(Ⅲ), urushiol-Ti(Ⅳ) chelate polymers, whose molecular structure formulas and some properties are shown as follows.

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	Urushiol-Cu chelate polymers	Urushiol-Nd chelate polymers	Urushiol-Ti chelate polymers
Schematic structure formulas of compound			
Properties	Resistance to high temperature	Magnetism, resistance to high temperature	Resistance to acids, alkalis and high temperature



EXPERIMENTAL

The samples of urushiol-copper, urushiol-neodymium, urushiol-titanium chelate polymers were supplied by Institute of Polymer Science of Fujian Normal University. Thermogravimetric analysis was conducted using a Shimadzu DT-40 Thermal Analyzer under oxygen at a flow rate of 40 ml/min. The sample weight used was 3–5 mg. The heating rate was programmed as 3, 5 or 7 °C/min. The TG curves were recorded using a Shimadzu C-R6A data processing unit. Figs. 1, 2 and 3 show the TG curves of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers respectively (the heating rate: β_1 3 °C/min; β_2 5 °C/min; β_3 7 °C/min).

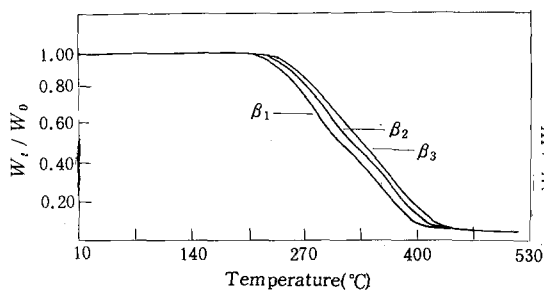


Fig. 1 TG curves of urushiol-Cu chelate polymers
(Heating rate: β_1 3 °C/min;
 β_2 5 °C/min; β_3 7 °C/min)

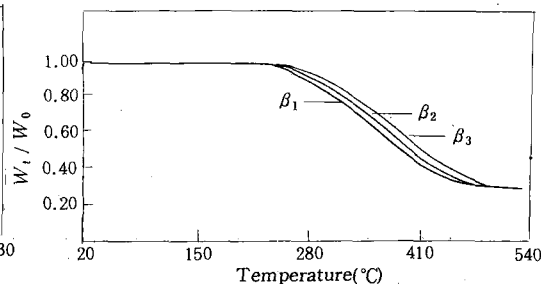


Fig. 2 TG curves of urushiol-Nd chelate polymers
(Heating rate: β_1 3 °C/min;
 β_2 5 °C/min; β_3 7 °C/min)

RESULTS AND DISCUSSION

In the kinetic analysis of the thermal decomposition of polymers, the reaction rate can be described as

$$dC/dt = kf(C) \quad (1)$$

where C is the fraction conversion.

$$C = (W_0 - W_t)/(W_0 - W_\infty) \times 100\% \quad (2)$$

here, W_0 —initial weight of the sample;

W_∞ —final weight of the sample;

W_t —sample weight at the time t .

k is the reaction rate constant.

$$k = A \exp(-E/RT) \quad (3)$$

here, E , A , R and T are the activation energy, the pre-exponential factor, the gas constant and the absolute temperature respectively; $f(C)$ is a function depending on the reaction mechanism. For simple reaction, $f(C)$ can be defined by eqn. (4)

$$f(C) = (1 - C)^n \quad (4)$$

where n is the reaction order.

From eqns. (1), (3) and (4)

$$dC/dt = A \exp(-E/RT)(1 - C)^n \quad (5)$$

If the temperature rise is linear, $\beta = dT/dt$, then

$$dC/dT = A/\beta \exp(-E/RT)(1 - C)^n \quad (6)$$

From eqn. (6), many methods can be given to calculate the kinetic parameters.

From eqn. (6)

$$\int_0^C \frac{dC}{(1 - C)^n} = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT \quad (7)$$

When $n=1$, the left-hand side of eqn. (7) can be given by

$$\int_0^C \frac{dC}{1 - C} = \ln\left(\frac{1}{1 - C}\right) \quad (8)$$

For non-isothermal thermogravimetric experiment, a thermal decomposition reaction will be generally completed at the temperature where the reaction rate is the greatest, therefore, $\exp(-E/RT)$ can take the form as follows.

$$\exp(-E/RT) = \exp(-T_m/T)^{E/RT} \simeq \left(\frac{T}{T_m} \exp(-1)\right)^{E/RT} \quad (9)$$

in which T_m is the temperature at which the reaction rate is the maximum.

Substituting eqns. (8), (9) into eqn. (7), taking natural logarithm and rearranging

$$\ln \ln \left(\frac{1}{1-C} \right) = (E/RT_m + 1) \ln T + \text{Const.} \quad (10)$$

After invoking a number of approximations, we can obtain the following approximate expression.

$$\ln \ln \left(\frac{1}{1-C} \right) = -\frac{E}{R} \times \frac{1}{T} + \text{Const.} \quad (11)$$

Fig. 4, Fig. 5 and Fig. 6 are plots of $\ln \ln [1/(1-C)]$ vs. $1/T$ for urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers respectively (the heating rate: β_1 , 3°C/min; β_3 , 7°C/min). From the figures, we can find that the curves of $\ln \ln [1/(1-C)]$ vs. $1/T$ for urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers are all linear, and the straight lines of different heating rate are parallel to each other. These results suggest that the thermal decomposition kinetics of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers are all of first order^[4].

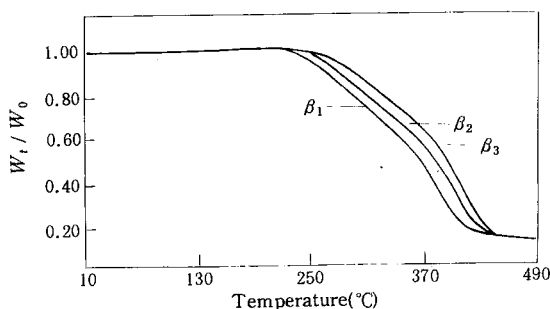


Fig. 3 TG curves of urushiol-Ti chelate polymers
Heating rate: β_1 3°C/min;
 β_2 5°C/min; β_3 7°C/min

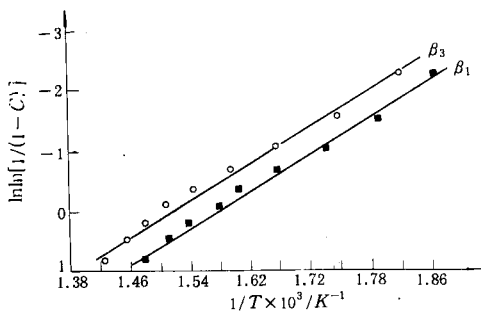


Fig. 4 Plots of $\ln \ln [1/(1-C)]$ vs. $1/T$ for urushiol-Cu chelate polymers. Heating rate: β_1 3°C/min; β_3 7°C/min

There are many methods to calculate the activation energy of the thermal decomposition of polymers. Here, we use the Ozawa-(I) method to calculate the activation energy.

From eqn. (6)

$$F(C) = \int_0^C \frac{dC}{(1-C)^n} = \frac{AE}{\beta R} p(x) \quad (12)$$

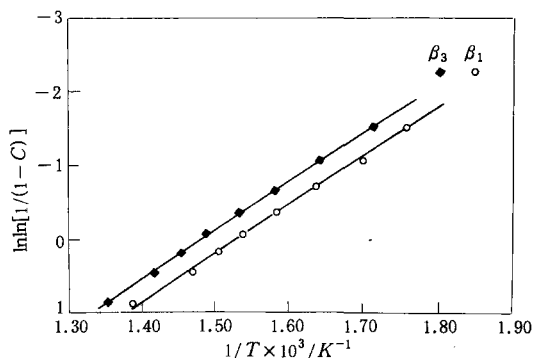


Fig. 5 Plots of $\ln\ln[1/(1-C)]$ vs. $1/T$ for urushiol-Nd chelate polymers. Heating rate: β_1 3 C/min; β_3 7 C/min

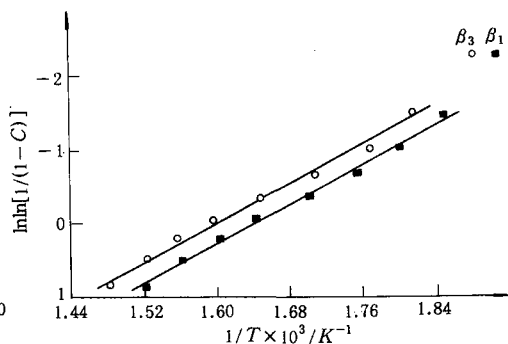


Fig. 6 Plots of $\ln\ln(1/(1-C))$ vs. $1/T$ for urushiol-Ti chelate polymers. Heating rate: β_1 3 C/min; β_3 7 C/min

Where $p(x)$ is the function introduced by Doyle⁽⁵⁾, and $x = E/RT$. If $20 < x < 60$, $p(x)$ can be expressed as

$$\log p(x) = -2.315 - 0.4567x \quad (13)$$

Taking the logarithm of eqn. (12), and substituting eqn. (13) into the right-hand side of eqn. (12) gives

$$\log F(C) = \log AE/R\beta - 2.315 - 0.4567E/RT \quad (14)$$

$$\log \beta = -2.315 + \log\left(\frac{AE}{RF(C)}\right) - 0.4567E/RT \quad (15)$$

Equation (15) indicates that $\log \beta$ vs. $1/T$ plots for a given value of C give a straight line, the slope of which gives the activation energy E ^[6].

Fig. 7, Fig. 8 and Fig. 9 are the plots of $\log \beta$ vs. $1/T$ for different C of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers respectively (C : 0.1–0.9, at 0.1 intervals). The parallel straight lines are obtained over almost the entire range of C . From the slopes of these straight lines, we can calculate the activation energy E for different C . The E values for each value of C of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers are listed in Table 1, Table 2 and Table 3, respectively.

The average E values of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers are 110.79 kJmol⁻¹, 136.98 kJmol⁻¹ and 163.64 kJmol⁻¹ respectively (C : 0.2–0.8). The plot of the average E values of urushiol-metal chelate polymers with different valence vs. their metal valences gives a straight line, which suggests that the average activation energy of the thermal decomposition of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate

$\frac{1}{T} \times 10^3$ $\log \beta$ $\beta / K_{\min}$		C	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
3	0.477		1.860	1.788	1.722	1.657	1.606	1.569	1.538	1.512	1.480
5	0.699		1.832	1.751	1.680	1.615	1.564	1.527	1.499	1.478	1.452
7	0.845		1.815	1.737	1.658	1.593	1.545	1.509	1.480	1.457	1.428
$E/kJmol^{-1}$			133.34	120.16	112.84	109.96	106.78	101.42	98.28	126.19	144.18
average $E/kJmol^{-1}$ ($C: 0.2-0.8$)			110.79								

$\frac{\frac{1}{T} \times 10^3}{\log \beta} / K^{-1} C$ $\beta / K_{\min}$		0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
3	0.477	1.847	1.758	1.696	1.635	1.584	1.537	1.504	1.466	1.387
5	0.699	1.826	1.741	1.668	1.608	1.559	1.516	1.475	1.442	1.368
7	0.845	1.803	1.715	1.645	1.584	1.534	1.489	1.455	1.418	1.351
E/kJmol ⁻¹		150.83	144.64	131.71	130.04	134.85	139.41	139.58	138.78	182.04
average E/kJmol ⁻¹ (C:0.2—0.8)		136.98								

$\frac{1}{T} \times 10^3 / K^{-1}$ $\beta / K \min$ $\log \beta$		0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
3	0.477	1.904	1.846	1.801	1.756	1.702	1.645	1.604	1.562	1.522
5	0.699	1.886	1.828	1.781	1.725	1.666	1.617	1.574	1.533	1.492
7	0.845	1.878	1.815	1.769	1.710	1.651	1.596	1.558	1.521	1.483
E/kJmol ⁻¹		163.09	163.84	145.64	136.90	131.04	142.00	211.17	214.81	252.42
average E/kJmol ⁻¹ (C: 0.2—0.8)		163.64								

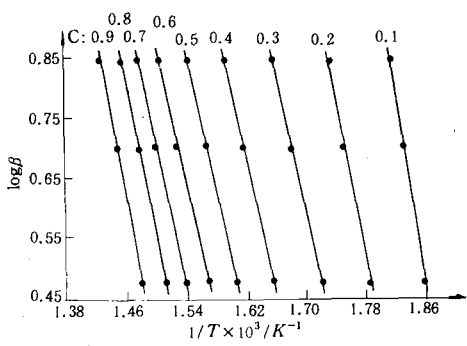


Fig. 7 Plots of $\log \beta$ vs. $1/T$ for urushiol-Cu chelate polymers

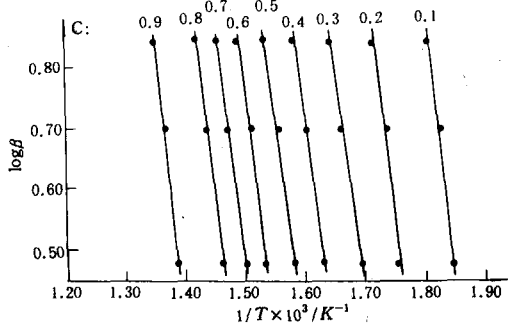


Fig. 8 Plots of $\log \beta$ vs. $1/T$ for urushiol-Nd chelate polymers

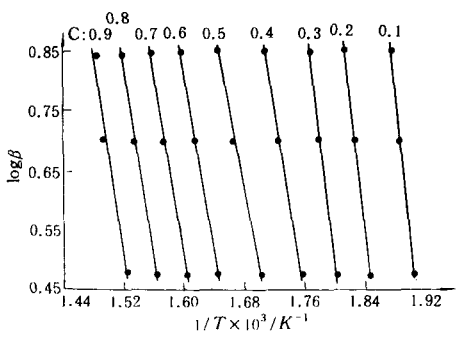


Fig. 9 Plots of $\log \beta$ vs. $1/T$ for urushiol-Ti chelate polymers

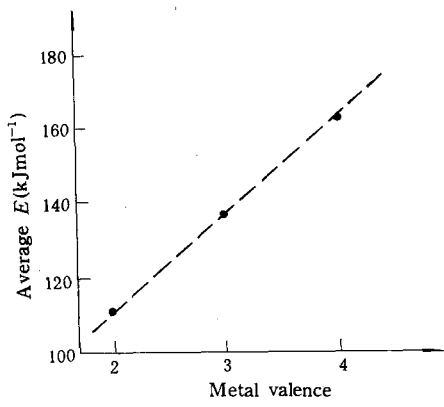


Fig. 10 Plot of average E vs. metal valence for urushiol-metal chelate polymers

CONCLUSION

The thermal decomposition kinetics of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers have been investigated. From the plots of $\ln \ln [1/(1-C)]$ vs. $1/T$ for urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers, the conclusion can be given that the thermal decomposition of urushiol-Cu, urushiol-Nd and urushiol-Ti chelate polymers follow first-order kinetics. The average E values of the thermal decomposition calculated by the Ozawa-(I) method are $110.79 \text{ kJmol}^{-1}$, $136.98 \text{ kJmol}^{-1}$ and $163.64 \text{ kJmol}^{-1}$ respectively, which increase linearly with their metal valences of the chelated metal.

Keywords:

Urushiol metal chelate polymers; Thermal decomposition kinetics

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