

Studies on Thermal Stability and Nonisothermal Thermal Decomposition Kinetics of Vinyl Chloride–Vinyl Acetate Copolymer Prepared via Microsuspension Polymerization

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ABSTRACT: The thermal stability and nonisothermal thermal decomposition kinetics of the vinyl chloride–vinyl acetate copolymer synthesized via microsuspension polymerization (MS–VC/VAc) were studied by dynamic TG. The results showed that MS–VC/VAc gives off hydrogen chloride and acetic acid (HAc) at the same time when it was heated. VAc content produces little effect on the thermal stability and the kinetic parameters. The activation energy for giving off HCl and HAc is in the range of 120–160 kJ/mol and the Arrhenius frequency factor 3.27×10^9 – $9.72 \times 10^{12} \text{ s}^{-1}$. For different heating rates, the kinetic model function of the thermal decomposition obeys the Avrami–Erofeev model equation, that is, $[-\ln(1 - a)]^{1/m}$ for $g(a)$, where $m = 0.65$ – 0.85 . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1057–1062, 2000

Key words: dynamic TG; kinetic model function; thermal stability; vinyl chloride–vinyl acetate copolymer; thermal decomposition

INTRODUCTION

Poly(vinyl chloride) is one of the most important vinyl polymers, whereas the vinyl chloride–vinyl acetate (VC–VAc) copolymer is one of the most important copolymers of vinyl chloride. It has been widely applied in industries and daily life due to its easy production and superior qualities.^{1,2} Thus, its thermal stability and thermal decomposition kinetics may be significant to its production and application.

In this article, the thermal decomposition of five samples of microsuspension polymerization MS–VC/VAc with various contents of VAc was studied by dynamic TG both under nitrogen and air atmo-

spheres at different heating rates. The activation energy and Arrhenius frequency factors were calculated using the Coats–Redfern equation³ by inputting different reaction orders n . The model function of the reaction kinetics was determined using Coats–Redfern and Madhusudanan, Krishman, and Ninan equations⁴ (MKN equation).

EXPERIMENTAL

Materials

The five samples of MS–VC/VAc with different contents of vinyl acetate shown in Table I used in this work were prepared by microsuspension polymerization at Hubei Institute of Chemistry. Their structures were characterized by IR. The content of VAc was determined by IR and acid–base titration.

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Table I TG Data of Five Samples of MS-VC/VAc with Different Contents of VAc

Sample	Content of VAc (%)	Mass Loss of HCl and HAc at the Same Time		Peak Temperature in DTG Curve (°C)
		Theor. (%)	Exp. (%)	
I	4	58.85	59.79	301.21
II	9	59.42	59.20	296.55
III	13	59.88	59.27	299.77
IV	16	60.22	59.69	296.53
V	20	60.67	60.62	294.21

Instrument

The thermogravimetric (TG) measurements were carried out on a TGS-2 thermol-balance (Perkin-Elmer Co., USA).

Sample Treatment and Experimental Conditions

The samples were dried for 24 h at 80°C to remove the adsorbed water. The conditions of TG operation were as follows: sample mass, about 10 mg; atmosphere: air or static nitrogen; and heating rates: 5, 10, 15, 20, 25, and 40°C/min.

RESULTS AND DISCUSSION

Thermal Decomposition Process of MS-VC/VAc

Typical TG and DTG curves for the MS-VC/VAc copolymer are presented in Figure 1. The TG

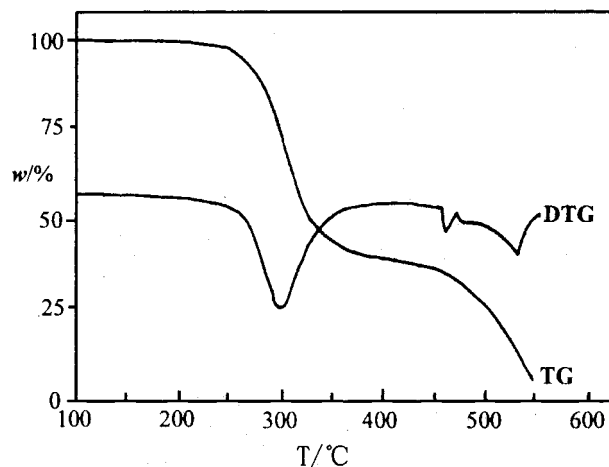
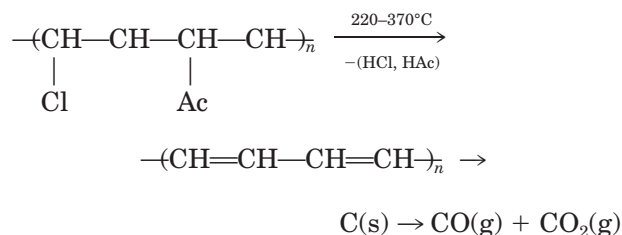


Figure 1 TG and DTG curves of samples I-IV in static air at a heating rate of 10°C/min.

characteristics of the samples shown are listed in Table I. The thermal decomposition process of MS-VC/VAc in air may be presented as



Nine model functions were used for evaluation of the kinetic parameters. They are given in Table II. According to the obtained TG curves, we can

Table II Nine Kinetic Functions Used for the Present Analysis

Mode	Differential Form $f(\alpha)$	Integral Form $g(\alpha)$
D1	$1/(2\alpha)$	α^2
D2	$-1/\ln(1-\alpha)$	$\alpha + (1-\alpha)\ln(1-\alpha)$
D3	$1.5(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	$1.5/[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$
F1 (A1)	$1-\alpha$	$-\ln(1-\alpha)$
A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

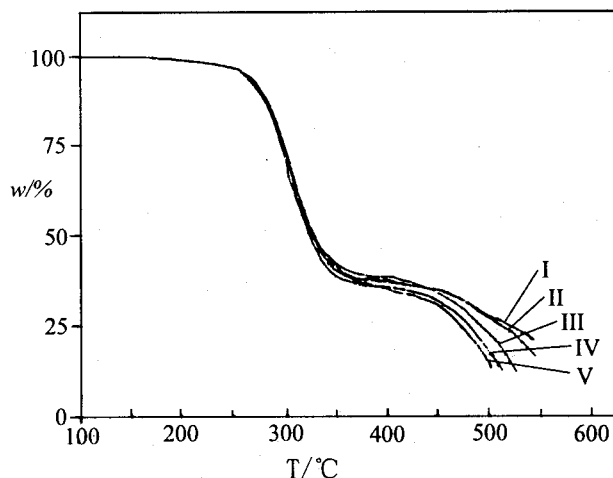


Figure 2 TG curves of the samples I–V in static air at a heating rate of 10°C/min.

calculate the transformation rate with the following formula:

$$\text{Transformation rate } \alpha = \frac{W_0 - W}{W_0 - W_\infty}$$

where W_0 is the original weight; W_∞ , the final weight; and W , the weight of the sample at $T^\circ\text{C}$.

TG curves of the five samples are given in Figure 2. The five TG curves are almost overlapped. From the data of Table I, we can see that HCl and acetic acid (HAc) are evolved simulta-

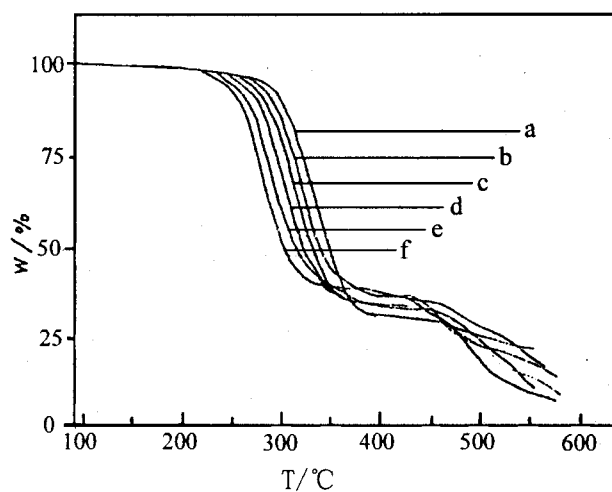


Figure 3 TG curves of sample III in static air for different heating rates: (a) 40°C/min; (b) 25°C/min; (c) 20°C/min; (d) 15°C/min; (e) 10°C/min; (f) 5°C/min.

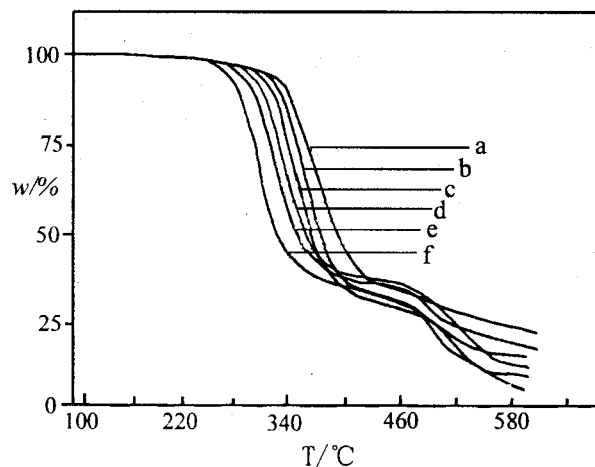


Figure 4 TG curves of sample III in static nitrogen at different heating rates: (a) 40°C/min; (b) 25°C/min; (c) 20°C/min; (d) 15°C/min; (e) 10°C/min; (f) 5°C/min.

neously. It can be thus assumed that the bond energies C—Cl and C—Ac are approximately equivalent and the content of VAc shows only a weak effect on the thermal stability of MS-VC/VAc.

Thermal Decomposition Kinetics of MS-VC/VAc

Kinetic Parameters

The TG curves of sample III in air and nitrogen are shown in Figures 3 and 4, respectively, at different heating rates. The corresponding values of E_a , A , and n , obtained by the Coats–Redfern method,³ are listed in Tables III–V.

Tables III and IV show that the decomposition reaction order decreases from 2.00 to 1.50 with increase of the heating rate under both air and nitrogen. At the same time, the correlation coefficient R improves with an increasing heating

Table III Kinetic Parameters of Sample III at Different Heating Rates in Air

Heating Rate (°C/min)	n	R	E_a (kJ/mol)	$\text{Ln}(A)$ ($A : \text{s}^{-1}$)
5	1.99	0.9965	155.7	28.5
10	1.91	0.9978	148.5	26.6
15	1.76	0.9990	156.8	27.8
20	1.59	0.9994	155.0	27.4
25	1.66	0.9997	156.5	27.5
40	1.50	0.9996	150.1	25.7

Table IV Kinetic Parameters of Sample III In Nitrogen

Heating Rate (°C/min)	<i>n</i>	<i>R</i>	E_a (kJ/mol)	Ln(<i>A</i>) (<i>A</i> : s ⁻¹)
5	1.99	0.9986	151.6	27.3
10	1.90	0.9993	148.1	25.9
15	1.68	0.9975	135.6	23.1
20	1.72	0.9990	137.0	23.2
25	1.45	0.9992	134.5	22.5
40	1.60	0.9996	133.6	22.1

rate. Maybe the reaction induction period was longer at a lower heating rate, but the data were taken in the entire reaction range at equal time intervals.

Table III shows that the values of E_a and *A* for different heating rates are approximately equivalent in air. Table IV shows that the values of E_a and *A* for different heating rates in nitrogen vary regularly and the values of E_a and *A* decrease at first and then approach constant values with increasing of the heating rate. These results are similar to those of Chou and Soong.⁵

The kinetic parameters of the five samples at 10°C/min are listed in Table V. They show that the values of *n* increase at first and then decrease with increase of the VAc content. The highest values were obtained for the sample containing 13% VAc.

Kinetic Mechanism Function

By substituting the nine model functions shown in Table I into both the equations of Coats–

Table V Kinetic Parameters of Samples I–V at 10°C/Min in Air

Sample	<i>n</i>	<i>R</i>	E_a (kJ/mol)	Ln(<i>A</i>) (<i>A</i> : s ⁻¹)
I	1.43	0.9965	132.2	22.6
II	1.49	0.9958	126.6	21.5
III	1.91	0.9978	148.5	26.6
IV	1.73	0.9974	139.8	24.7
V	1.70	0.9989	128.1	22.2

Redfern and MKN,⁴ the kinetic parameters of different mechanisms (see Table VI) were calculated. An attempt to obtain the proper function by comparing the kinetic parameters with the different ways proved to be quite difficult. Table VI shows that either different values of the kinetic parameters but with the best correlation coefficients (F1) or close values of kinetic parameters but poor correlation coefficients are obtained: D1, D2, or D4. It was found, however, that the kinetic parameters of the Avrami–Erofeev equation are close to those obtained from the Coats–Redfern equation and the correlation coefficient improves with decrease of *m* (*m* = 3, 2, 1).

The Avrami–Erofeev equation $g(\alpha) = [-\ln(1 - \alpha)]^{1/m}$ is an assumed formula and a best value of *m* was determined for the MS–VC/VAc decomposition reaction. The results (Table VII) show that this idea is feasible. The results are listed in Tables VIII and IX.

The data of Tables VIII and IX show that the values of *m* increase with an increasing heating

Table VI Kinetic Parameters of the Thermal Decomposition of Sample III at 20°C/min in Nitrogen

<i>g</i> (α)	Coats–Redfern Equation			MKN Equation		
	<i>R</i>	E_a (kJ/mol)	Ln(<i>A</i>) (<i>A</i> : s ⁻¹)	<i>R</i>	E_a (kJ/mol)	Ln(<i>A</i>) (<i>A</i> : s ⁻¹)
D1	0.9520	148.4	23.7	0.9522	148.5	23.8
D2	0.9657	165.6	26.8	0.9657	165.8	36.9
D3	0.9805	188.9	30.1	0.9805	188.9	30.5
D4	0.9712	173.1	27.2	0.9713	173.2	27.1
F1	0.9896	102.4	15.5	0.9896	102.6	15.7
A2	0.9868	46.2	3.7	0.9871	46.5	3.9
A3	0.9745	18.0	-2.3	0.9835	27.8	-0.2
R2	0.9707	83.7	10.7	0.9710	83.9	10.8
R3	0.9780	89.4	11.5	0.9710	89.6	11.7

Table VII Determined Value m of Sample III Model Function Am at 20°C/min in Nitrogen

Value of m	Coats–Redfern Equation			MKN Equation		
	R	E_a (kJ/mol)	$\ln(A)$ ($A : s^{-1}$)	R	E_a (kJ/mol)	$\ln(A)$ ($A : s^{-1}$)
0.85	0.9899	122.1	19.6	0.9879	122.6	19.7
0.80	0.9899	130.3	21.3	0.9900	130.6	21.4
0.75	0.9901	139.7	23.2	0.9901	139.9	23.3
0.70	0.9902	150.4	25.4	0.9902	150.6	25.4
0.65	0.9903	162.7	27.8	0.9903	162.9	27.9

rate and vary in the range of 0.65–0.85. The correlation coefficient becomes better with an increasing heating rate and maybe the reason is the supposed condition of the induction period assumed in the section Kinetic Parameters.

Thus, we can formulate the kinetic equation of thermal decomposition of MS–VC/VAc:

$$[-\ln(1 - \alpha)]^{1/m} = A \exp(-E_a/RT)t$$

m : 0.65–0.85, E_a : 120–160 kJ/mol, $\ln(A)$: 22–30, A : s^{-1} .

Thermal Stability

The effect of the content of VAc on the thermal stability of MS–VC/VAc was studied. From Table

V, it can be seen that the values of E_a and A of sample III are higher than are those of the other samples.

According to the following equation,⁶

$$\log(t) = \log(E_a/\phi R) - 2.315 + E_a/2.303RT' - 0.4567 \times E_a/RT$$

where T' is the constant temperature: 298.15 K. t is the time at T' when the sample lost the same mass as that at temperature T in the TG curve. The decomposition time (298.15 K) at different mass losses for different samples are listed in Table X, which shows that the thermal stability of all the samples are good, whereas that of sample III is probably the best.

Table VIII Model Function and Kinetic Parameters of Sample III at Different Heating Rates in Air

Heating Rate (°C/min)	Model Function	R	E_a (kJ/mol)	$\ln(A)$ ($A : s^{-1}$)
5	$A_{0.65}^a$	0.9791	159.3	28.4
	$A_{0.65}^b$	0.9792	159.5	28.5
10	$A_{0.70}^a$	0.9845	147.0	25.5
	$A_{0.70}^b$	0.9846	147.2	25.6
15	$A_{0.75}^a$	0.9866	153.1	26.4
	$A_{0.75}^b$	0.9867	153.3	26.5
20	$A_{0.80}^a$	0.9927	156.0	27.1
	$A_{0.80}^b$	0.9927	156.2	27.2
25	$A_{0.80}^a$	0.9942	160.3	27.8
	$A_{0.80}^b$	0.9943	160.5	27.8
40	$A_{0.80}^a$	0.9944	155.4	26.4
	$A_{0.80}^b$	0.9944	155.7	26.4

^a Coats–Redfern equation.

^b MKN equation.

Table IX Model Function and Kinetic Parameters of Sample III at Different Heating Rates in Nitrogen

Heating Rate (°C/min)	Model Function	R	E_a (kJ/mol)	$\ln(A)$ ($A : s^{-1}$)
5	$A_{0.70}^a$	0.9846	152.3	26.6
	$A_{0.70}^b$	0.9847	152.5	26.7
10	$A_{0.70}^a$	0.9855	153.1	26.2
	$A_{0.70}^b$	0.9856	153.3	26.3
15	$A_{0.75}^a$	0.9883	135.0	22.4
	$A_{0.75}^b$	0.9883	135.3	22.5
20	$A_{0.75}^a$	0.9901	139.7	23.2
	$A_{0.75}^b$	0.9901	139.9	23.3
25	$A_{0.85}^a$	0.9948	132.0	21.6
	$A_{0.85}^b$	0.9949	132.2	21.7
40	$A_{0.80}^a$	0.9923	132.1	21.3
	$A_{0.80}^b$	0.9924	132.4	21.4

^a Coats–Redfern equation.

^b MKN equation.

Table X Times of Thermal Decomposition of Five Different Samples at 298.15 K in Air

Sample	Rest Mass (%)	Time (min)	Rest Mass (%)	Time (min)	Rest Mass (%)	Time (min)
I	90.22	4.81×10^{10}	70.95	8.32×10^{10}	50.54	1.27×10^{11}
II	90.40	2.65×10^{10}	70.96	4.58×10^{10}	50.00	7.13×10^{10}
III	89.40	2.05×10^{11}	71.03	3.56×10^{11}	48.73	6.92×10^{11}
IV	89.99	8.84×10^{10}	71.60	1.51×10^{11}	52.09	2.47×10^{11}
V	89.10	2.78×10^{10}	73.18	4.50×10^{10}	51.34	7.65×10^{10}

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