On the Thermal Degradation of Poly(styrene sulfone)s. V. Thermogravimetric Kinetic Simulation of Polyacrylamide Pyrolysis

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ABSTRACT: The kinetics involved in the thermal degradation of polyacrylamide under nitrogen atmosphere were studied by using consecutive reactions of a kinetic model to dynamic thermogravimetric data. The model proposed correlates the thermograms obtained at thermogravimetric and differential thermogravimetric data with the same set of kinetic parameters. The first stage of polyacrylamide decomposition, where the deamonation of the polyacrylamide and the dehydration of acrylamide units and the formation of a proportion of unvolatile imides and nitrile and aliphatic organic compounds can be fitted satisfactorily when in a model based on a single reaction. The second stage, corresponding to the breakdown of the imides formed and the polymer backbone, also can be correctly represented by a model based on a single reaction. In this article, a discussion about the applicability of the model is presented and the results obtained are compared to those obtained by Flynns's and Friedman's analytical methods, respectively. The maximum decomposition temperature, shape index for dynamic condition and lifetime, and degree of decomposition for isothermal condition of thermal behavior of polyacrylamide are predicted via mathematical simulation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1540–1548, 2002

Key words: polyacrylamide; thermogravimetric; thermal degradation; simulation; activation energy; pyrolysis

INTRODUCTION

Polyacrylamide is a widely used biomaterial and is one of the most important wastewater treatment polymers. It is well known that it is used as a flocculant, thickener, cross-linker, reducer of hydraulic resistance in liquids, and oil liquefier.[1–5] The major market for polyacrylamide in Taiwan is as a flocculant for wastewater treatment plants. However, the thermal decomposition of polyacrylamide is important in the posttreated burning in the disposal of solid slurry, which makes a flocculant between the several compositions of wastewater. Although there are several publications that have been devoted to studies of thermal degradation of various polymer systems, polyacrylamide has received little attention.[6–10]

The previous studies allow us to define different thermal stages of the thermal degradation of polyacrylamide.[11] Thermal degradation of polyacrylamide is a two-stage process. The first stage mainly involves the designing of a deamination process of polyacrylamide and formation of imides, similar to that observed on other intermolecular or intramolecular deamonation in the pyrolysis of other amides.[12,13] This polymer material is the precursor to the formation of a polyaromatic carbonaceous structure as a residue that undergoes pyrolysis to break down into polymer backbone.

Numerous investigations of the thermal degradation of various polymers has shown the value of the thermogravimetric analysis technique. The kinetics of the thermal decomposition of solids in general and of polymeric materials in particular have been widely studied by the dynamic and isothermal thermogravimetric techniques.[14,15] Kinetic data obtained from thermogravimetric analysis may be used as the standard of judgment for the choice of a polymer. Very useful information about kinetic constants, activation energy, reaction order, number of different processes taking place, and so forth can be obtained from the analysis of the thermogravimetric data.[16] Only a few researchers have studied the kinetic decomposition of polyacrylamide with the thermogravimetric technique in dynamic conditions. In all the cases, various established but approximate methods were applied to solve the differential kinetic equation.

Methods of kinetic data analysis have been classified into integral,[17] differential,[18] and special[19] methods by many authors. These methods have usually been applied to the study of the decomposition of polymeric materials from thermogravimetric data. Most of them involve some degree of approximation and simplification. In general, they calculate a set of

kinetic constants for each heating rate and sometimes set the reaction order to unity. The diversity of the calculation methods does not allow us to give preference to any one of them. Moreover, it has been found that, for the same kinetic model, these methods do not always reproduce the values of the kinetic parameters when the same data are used for computation; for example, the activation energy for a diglycidyl ether of bisphenol-A polymer curved with polyamine has been quoted in the literature in the 43–138 kJ/mole range.[20]

For many years, when compilation methods were not available, these methods provided reasonably good results. Nevertheless, there are some recent papers that show that different methods of calculation of the kinetic parameters may lead to different results. Moreover, the established methods assume that the degradation process takes place via a single reaction. Polymer degradation is a complex phenomenon, and this assumption is therefore questionable. The determination of kinetic parameters from the data of dynamic thermogravimetry is one of the most difficult kinetic problems.

In this work, a kinetic model suggested by Marcilla et al.[22] is applied to dynamic thermogravimetric data for polyacrylamide decomposition. The consecutive results of the kinetic model fit the two stages of the polyacrylamide decomposition to two single reactions in the series and simultaneously correlate the two stages observed and the data obtained at different heating rates. The results obtained with this technique are compared with the results obtained by the most widely used traditional methods, namely, the Flynn-Wall and Friedman analytical methods. Moreover, in this study, the decomposition time, lifetime, and degree of decomposition for isothermal conditions of thermal behavior of polyacrylamide were being predicted via mathematical simulation.

EXPERIMENTAL

The reactive substance used in this study was a white powder among 80–100 mesh of a standard polyacrylamide, which was prepared from the monomer by polymerization with potassium persulphate and isopropanol aqueous solution under a nitrogen atmosphere.[11,23] The polymer was precipitated by further addition of isopropanol. The precipitate was then washed with the same solvent three times, and dried in a vacuum oven to a constant weight at 60°C. The average molecular weight of the polymer was determined by Ubblehode viscosity using an infrared photosensor analysis system in a sodium nitrate solution at 30°C, and was 6.4×10^4. All reagents were of the EP grade. For the determination of the rate of thermal degradation of polyacrylamide, the polyacrylamide was heated to a given temperature using a Perkin-Elmer thermogravimetric analysis series 7 (USA). Initial temperature was 100°C, and final temperature 550°C. Heating rates of 5°, 10°, and 20°C/min under 60 mL/min N_2 and a sample weight of 6 mg were tested. A continuous record of the change in both the temperature and the weight of the sample cell was taken, as well as one of the differential change in weight. The computation of kinetic parameters for the thermal degradation program was carried out from thermogravimetric data using a software programs, and running on a TATUNG Co. Taiwan compatible PC (Taiwan).

RESULTS AND DISCUSSION

Experimental data of thermal degradation of polyacrylamide

In thermogravimetric measurements, the degree of decomposition can be calculated as follows:

$$X = (W_0 - W)/(W_0 - W_f) \tag{1}$$

where X is degree of decomposition and W, W_0, and W_f are the actual, initial, and final weights of the sample, respectively. Figure 1 shows the experimental results of thermal degradation of polyacrylamide obtained at a different heating rate (5°C/min). The primary derivatives of TG curves show two significant changes in their slopes, which may be assigned to two successive stages of the decomposition of the thermal degradation of polyacrylamide. A weight loss of around 20% in the temperature range 370°–375°C can be observed. This weight loss basically corresponds to the evolution of NH_3.
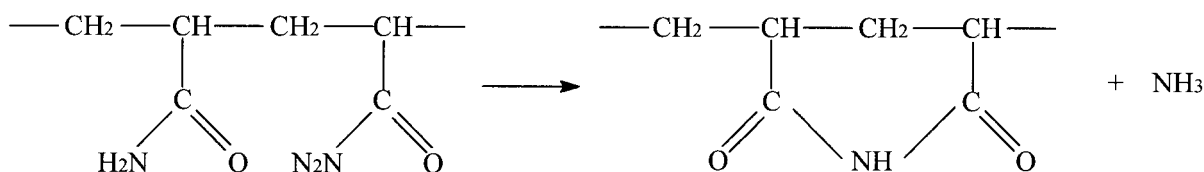
The total weight loss in this stage is higher than the stoichiometric quantity of ammonia in the polyacrylamide and may correspond to the formation of some aromatic hydrocarbons, nitrile, aliphatic, and imides.[6,24] A second weight loss can be observed above 375°C that corresponds to the pyrolysis of the
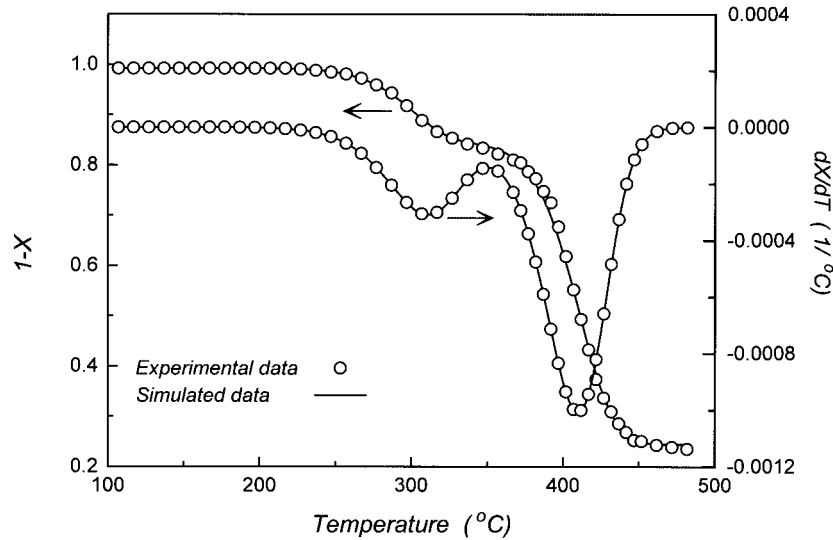
Figure 1 Thermogravimetry and differential thermogravimetric curves of polyacrylamide thermal degradation at a heating rate of 5°C/min.

imides formed during the first stage. After this, a black residue is obtained.[8]

Application of the Friedman and Flynn-Wall methods to the experimental data

The Friedman method[25] has been applied to the first and the second decomposition stages of polyacrylamide. This is a widely used method and is based on the following general kinetic equation:

$$dX/dt = k \cdot f(X) \tag{2}$$

where dX/dt is the decomposition rate and k is the decomposition rate constant, which can be expressed by the Arrhenius equation:

$$k = A \cdot \exp(-Ea/RT) \tag{3}$$

where A is the preexponential factor (1/s), E_a is the activation energy (J/mole), R is the gas constant (8.314 J/g-mol × K), and T is Kelvin temperature (K). Substitution of eq. (3) into eq. (2) yields

$$dX/dt = A \cdot f(X)\exp(-Ea/RT) \tag{4}$$

Thus, taking logarithms of this differential equation, the following expression can be obtained:

$$\ln(dX/dt) = \ln[A \cdot f(X)] - Ea/RT \tag{5}$$

This method requires several thermograms to obtain heating rates. By plotting $\ln(dX/dt)$ against $1/T$ at constant values of X obtained from each thermogram, a heating rate, a set of straight lines can be obtained. The slope of each line is $-E_a/R$, and the intercept is

$\ln(A \times f(X))$. If the thermal decomposition of polyacrylamide followed a single reaction order, that is, $f(X) = (1 - X)^n$, with n as the empirical order of decomposition, the value of $\ln(A \times f(X))$ against the value of $\ln(1 - X)$ should provide a straight line with slope n and intercept $\ln A$ in the following:

$$\ln[A \cdot f(X)] = \ln(A) + n \ln(1 - X) \tag{6}$$

In this way, a single set of kinetic parameters can be obtained from data at different heating rates.

Figure 2 corresponds with the plot of the intercept $\ln(A \times f(X))$ against $\ln(1 - X)$ for the experimental results for the first stage (95%–80%) and the second stage (80%–25%) of polyacrylamide thermal decomposition. It was found that eq. (6) could not fit the two-
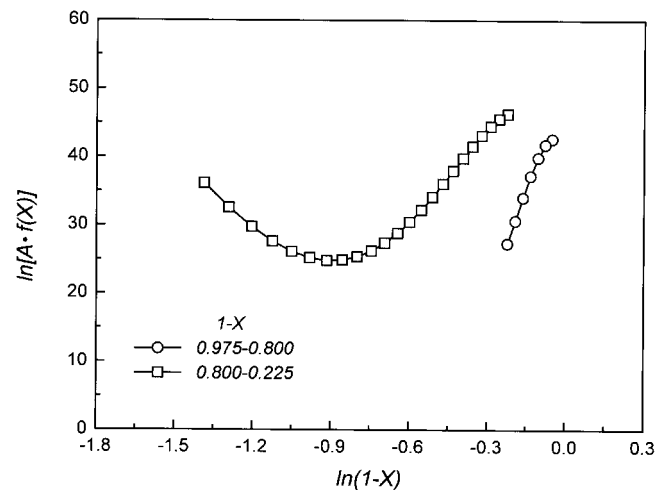
Figure 2 Friedman calculation of the reaction order and the pre-exponential factor from experimental data.

TABLE I
Activation Energies and Constants for the Equation $\ln[A \cdot f(X)] = b_3(1 - X)^3 + b_2(1 - X)^2 + b_1(1 - X)^1 + b_0$ for Thermal Degradation of Polyacrylamide by Flynn-Wall's and Friedman's Methods

		Flynn-Wall	Friedman				
Exp. no.	Degree of decomposition X	Activation energy, Ea (kJ/mole)	Activation energy, Ea (kJ/mole)	b_3	b_2	b_1	b_0
1-stage	0.05–0.20	142.7	144.4	−2960	7370	−5980	1610
2-stage	0.20–0.75	217.6	220.1	−569	1060	−581	124

stages thermal degradation of polyacrylamide under unity reaction order. To solve these phenomena, Yang[26] studied the thermal degradation of poly(acrylamide sulfone)s, which occurred the same thermal degradation behavior; a third-order polynomial of experimental relation between residue weight fraction and temperature for describing the thermal degradation of poly(acrylamide sulfone)s was suggested in his study. The values of the kinetic parameters obtained applying Yang's method to the thermal degradation of polyacrylamide of the experimental data are shown in Table I. The kinetic parameters obtained for the two stages depend on the X considered, which, technically, can be obtained. Moreover, the analytical range of polyacrylamide cannot be applicable to the overall thermal behavior of polyacrylamide, especially in the early stage and in the mixed region of the two stages of thermal degradation, proving either the complex reaction of the kinetic model or the failure of the analytical kinetic method failure in describing the overall experimental data. Moreover, in the integrated method, a method described by Flynn-Wall,[27] the activation energy of a polymer degradation process is obtained from the following equation:

$$Ea = -18.2 \times d \log(RH)/d(1/T) \qquad (7)$$

where Ea is activation energy (kJ/mole) and Rh is heating rate (°C/min). The results are shown in Table I. However, eq. (7) is an empirical one because it cannot obtain preexponential factors and thermal decomposition order. There is a slight difference between the Flynn-Wall's and Friedman's analytical methods with respect to activation energy.

Kinetic model for describing the thermal degradation of polyacrylamide

To analyze this thermal degradation behavior and elucidate the reason for the failure of above methods,

a kinetic model was proposed for describing the thermal degradation of polyacrylamide. Marcilla and Beltran,[22] who studied the poly(vinyl chloride) pyrolysis by thermogravimetric kinetic have suggested the kinetic model for describing the thermal decomposition of poly(vinyl chloride). In this study, a different procedure proposed by Marcilla et al.[22] was used to obtain the corresponding parameters; the results obtained with the experimental data and with the correlation obtained by Yang[11] in the earlier article have been compared.

The two stages of polyacrylamide decomposition can be associated with two consecutive reactions, which may be represented by the processes

$$\mathrm{PAA} \xrightarrow{k_1} a\,\mathrm{Gas} + b\,\mathrm{PA} \qquad (8)$$

$$b\,\mathrm{PA} \xrightarrow{k_2} c\,\mathrm{Gas'} + e\mathrm{P} \qquad (9)$$
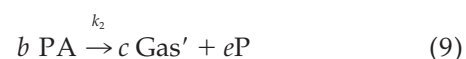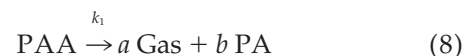
where Gas, Gas', PAA, PA, and P correspond to the gases of the initial and residue generated in the two stages; a, b, c, and e are the yield coefficients; and k_1 and k_2 are the kinetic constants. When the yield coefficients are constant and independent of the heating rate, the stoichiometric amounts are almost equivalent for each degree of decomposition;[28] that is, $a = b$ and $c = e$.

To determine the weight fractions of the component in such a mechanism, which depends on time (temperature), the rate equations are first written down for each component substance; it is necessary to obtain the solution of these simultaneous differential equations. The material balances for the foregoing of reactions the rate equations can be also written as

$$d(\mathrm{PAA})/dt = -k_1(\mathrm{PAA})^{n_1}; \qquad (10)$$

TABLE II
Kinetic Parameters Obtained with the Simulated Model for Thermal Degradation of Polyacrylamide

Exp. no.	Decomposition order, n	Pre-exponential factor, A (s^{-1})	Activation energy, Ea (kJ/mole)	Yield coefficient	Variation coefficient CV (%)	Linear coefficient, r
1-stage	1.28	2.2×10^9	131.1	0.76	0.0514	0.9995
2-stage	1.16	2.4×10^{12}	192.2	0.19		
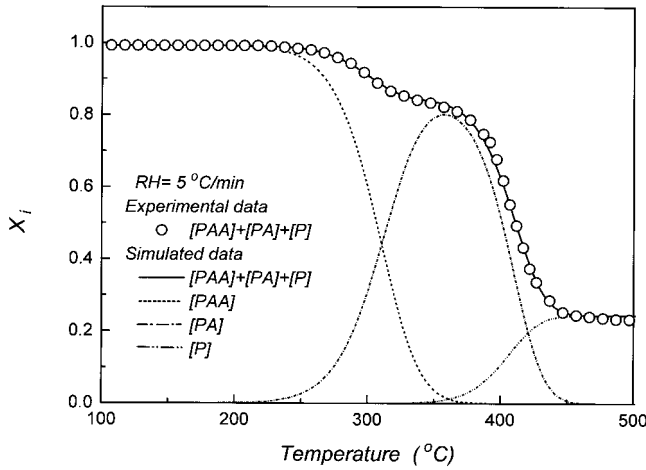
Figure 3 The weight fraction of PAA, PA, and P for consecutive reactions:

$$d(PA)/dt = b[k_1(PAA)^{n_1} - k_2(PA)^{n_2}]; \quad (11)$$

$$d(P)/dt = e[k_1(PA)^{n_2}], \quad (12)$$

where n_1 and n_2 are orders of decomposition. This system of equations can be written as an Arrhenius-type function of the temperature:

$$d(PAA)/dt = -A_1 \exp(-E_{a_1}/RT)(PAA)^{n_1}; \quad (13)$$

$$\begin{aligned} d(PA)/dt = b[A_1 \exp(-E_{a_1}/RT)(PAA)^{n_1} \\ - A_2 \exp(-E_{a_2}/RT)(PA)^{n_2}]; \quad (14) \end{aligned}$$

$$d(P)/dt = e[A_3 \exp(-E_{a_3}/RT)(PA)^{n_2}], \quad (15)$$

where A_1, A_2 and E_{a_1}, and E_{a_2} are the preexponential factors and the activation energies of the first and the second stage reactions, respectively. The systems of reactions used a fourth-order Runge Kutta algorithm method[29] to solve the differential rate equation in this study. The method can be outlined very briefly as follows:

$$dX/dt = A/RH \cdot \exp(-Ea/RT) \cdot (1 - X)^n \quad (16)$$

$$X' = f(X, T)$$

$$k_1 = \Delta T \cdot f(T_n, X_n)$$

$$k_2 = \Delta T \cdot f(T_n + \Delta T/2, X_n + k_1/2)$$

$$k_3 = \Delta T \cdot f(T_n + \Delta T/2, X_n + k_2/2)$$

$$k_4 = \Delta T \cdot f(T_n + \Delta T, X_n + k_3)$$

$$X_{(n+1)} = X_{(n)} + (k_1 + 2k_2 + 2k_3 + k_4)/6 \quad (17)$$

The Box optimization method[30] was used to calculate the kinetic parameters. The function to be minimized (τ) was

$$\tau(A_1, A_2, E_{a_1}, E_{a_2}, E_{a_3}, n_1, n_2, n_3) = \sum_{i=1}^{m} (X_{exp} - X_{calc})^2, \quad (18)$$

where m is the number of data point and the subscripts exp and calc mean experimental and calculated values using the model proposed.

The validity of the models was tested by the value of the variation coefficient (CV) and correlation coefficient (r), calculated as follows:
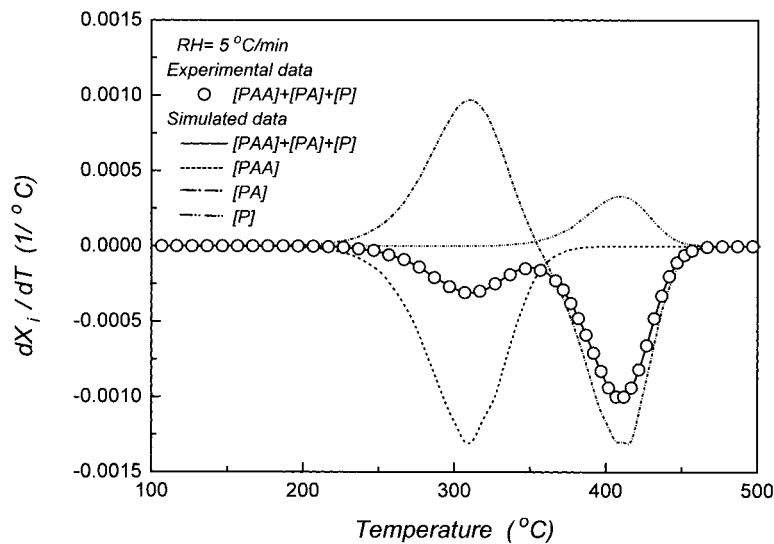
Figure 4 The differential weight fraction of PAA, PA, and P for consecutive reactions:
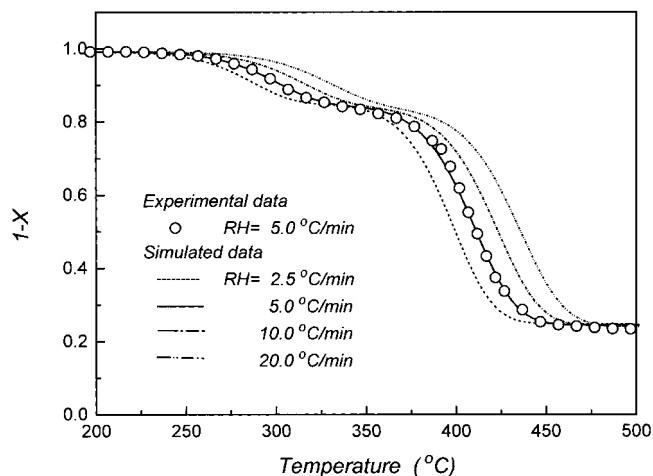
Figure 5 Reproduction of the polyacrylamide thermogravimetric curves from the simulated model at heating rate at 2.5°, 5°, 10°, and 20°C/min.

$$CV(\%) = [\tau/(D - P)]^{1/2}/X_{exp} \times 100\% \qquad (19)$$

$$r = Sx_{exp}x_{calc}/(Sx_{exp}x_{exp}Sx_{calc}x_{calc})^{1/2} \qquad (20)$$

where D and P are the number of data and parameters fitted, respectively, and X_{exp} is the average of the experimental values; S is variation.

In all these cases, the thermograms obtained at different heating rates were simultaneously correlated with the same set of kinetic parameters. The simulated data are obtained to fit all the experimental data, and no variation of these with the heating rate is required. The kinetic parameters obtained with the model are shown in Table II. Figure 3 shows the degree fraction of decomposition characteristics of the weight–fraction curves for the three components, PAA, PA, and P:

PAA decreases with the time (temperature), PA rises to maximum and then falls, and P rises continuously. Moreover, Figure 4 shows a comparison with experimental results. This model, based on consecutive reactions, provides an exacting representation of the experimental results. The same result is shown on the curve dX/dt versus T during the two stages, respectively, as shown in Figure 4. Results obtained by the mass spectroscopy of Leung et al.[6] revealed different parallel processes in the thermal decomposition of polyacrylamide. According to these authors, the thermal decomposition of polyacrylamide begins with the evolution of NH_3, and as soon as the imide sequences appear along the side chain, an involved process begins in which a small proportion of unsaturated aromatic compounds are formed simultaneously with NH_3 and H_2O. During the second stage of polyacrylamide decomposition, the evolution of alkyl aromatics together with a small quantity of CO_2, yielding a residual char.

Comparison with kinetic parameters obtained by other analytical methods

The kinetic parameters obtained for the first stage with the model were as follows: activation energy = 131.1 kJ/mole, pre-exponential factor = 2.2×10^9 s^{-1}, reaction order = 1.28. Kinetic parameters found in the literature for polyacrylamide decomposition using dynamic thermogravimetric data are in all cases fitted to a single process, and different values are obtained for each heating rate. Results obtained by Yang[10] for the first stage are 128.0 kJ/mole for E_a, at 5°, 10°, 20°, and 40°C/min, obtained by the Flynn-Wall method, and similar to what is presented here. However, the author reported that these parameters need at least three
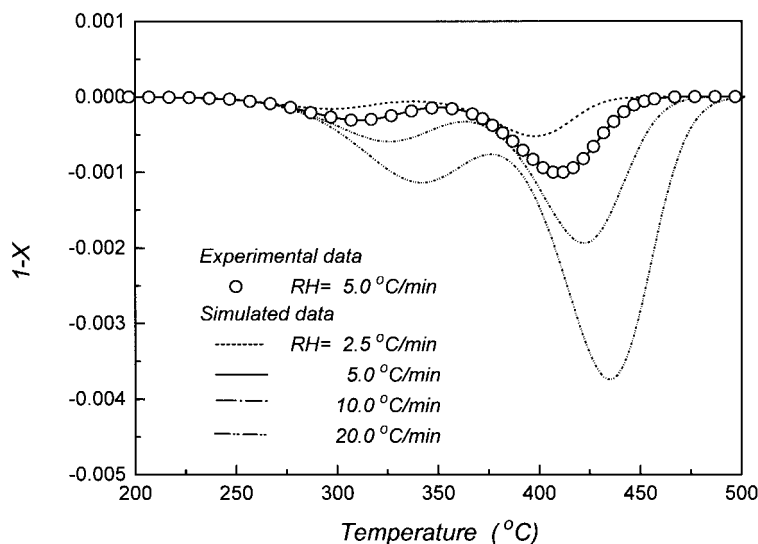
Figure 6 Reproduction of the polyacrylamide differential thermogravimetric curves from the simulated model at heating rate at 2.5°, 5°, 10°, and 20°C/min.

TABLE III
The Simulated Decomposition Data of Thermal Degradation Polyacrylamide

RH (°C/min)	T_m (°C) 1-stage	T_m (°C) 2-stage	T_1^* (°C)	T_2 (°C) 1-stage	T_2/T_1	T_1 (°C)	T_2 (°C) 2-stage	T_2/T_1	S-shape[†] 1-stage	S-shape 2-stage
2.5	277	382	277	317	1.14	382	417	1.10	0.90	0.71
5.0	292	392	292	332	1.14	392	432	1.10	0.96	0.71
10.0	307	407	302	345	1.14	407	447	1.10	1.07	0.71
20.0	322	417	317	362	1.14	417	457	1.10	1.27	0.71
Average					1.14			1.10	1.05	0.71

* T_1, T_2 are the temperature at the first and second inflection points of the curve of dX/dT versus the temperature for each thermal degradation stage.
† S-shape = $|(d^2X/dT^2)_1/(d^2X/dT^2)_2|$.

various heating rates. Moreover, the results obtained by Yang[11] at 10°C/min by applying a modification of the Friedman method were 137.2 kJ/mole, 1.82 min^{-1}, and 1.0 for E_a, k, and n, respectively. The author applied different kinetic methods to the first stage of polyacrylamide decomposition, obtaining only slight differences depending on the method used and on the experimental conditions. The results show a little dispersion. Differences can be attributed to the effect of experimental conditions, to the method of parameter estimation, to the kinetic model used, and to the characteristics of the polyacrylamide used in each study.

For the second stage, the values obtained were 192.2 kJ/mole for the activation energy, 2.4 × 10^{12} s^{-1} for the pre-exponential factor, and 1.16 for the reaction order. Only a few recent papers have studied the kinetic parameters of the second stage of polyacrylamide decomposition. Results obtained by Yang[11] for the second stage are 190.4 kJ/mole for E_a, at 5°, 10°, 20°, and 40°C/min, obtained by Flynn-Wall method, and similar to what is presented here. In this work, the Friedman method is applied to the experimental results modeled by two competitive reactions, both yielding char and gases, respectively. The kinetic parameters reported were 190.8 kJ/mole for the activation energy, 4.82 min^{-1} for the pre-exponential factor, and 1.0 for the reaction order. These values are close to those reported here.

Decomposition behavior of polyacrylamide via model simulation

TGA curves of different heating rates were used for simulating by using the activation energies 131.1 and 192.2 kJ/mole, exponential factors of 2.2 × 10^9 and 2.4 × 10^{12} s^{-1}, and 1.28 and 1.16 orders for of polyacrylamide, respectively. A series of simulated curves of TG and DTG curves at four different heating rates, 2.5°, 5°, 10°, and 20 °C/min, can be generated as shown in Figures 5 and 6. The maximum decomposition, T_m, can be obtained at the maximum decomposition rate in two stages. The data are listed in Table III. The maximum decomposition temperatures of the two-stages thermal degradation of polyacrylamide were 292° and 392°C, respectively.

To quantitatively describe the peak shape of differential thermogravimetric curve, a shape index was proposed by Kissinger.[31] Defined as the absolute value of the ratio of the slopes' tangents to the curve at the inflection points, the shape index can be expressed analytically as

$$S = |(d^2X/dT^2)_1/(d^2X/dT^2)_2| \tag{21}$$

where subscripts 1 and 2 refer to the value of these quantities at the inflection points; that is, where $d^3X/dT^3 = 0$ for each thermal degradation stages. Figure 7

TABLE IV
Predicted Lifetime of Thermal Degradation of Polyacrylamide

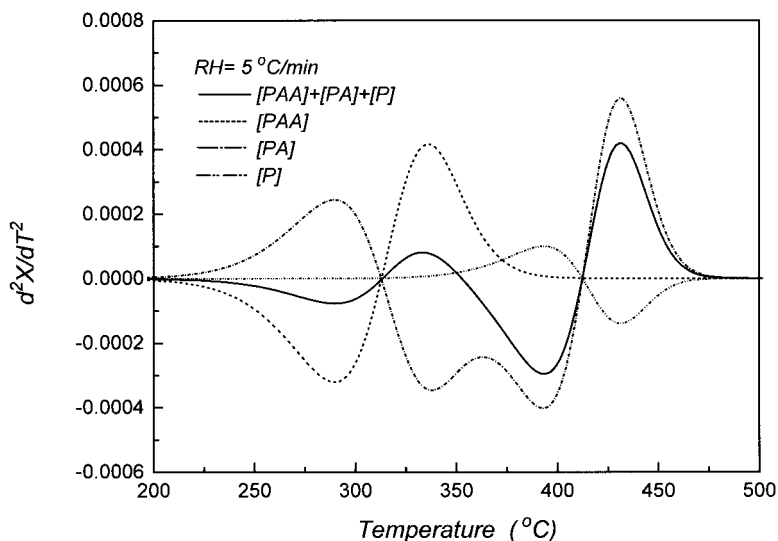| Temperature (°C)	Unit	X 5%	X 10%	X 15%	X 20%
100	year	5.92	14.3	28.0	58.3
120	month	8.76	21.2	41.3	85.5
140	month	1.33	3.21	6.26	12.4
160	day	7.25	17.2	33.6	70.0
180	day	1.49	3.60	7.0	14.6
200	hour	8.53	20.7	40.1	84.0
220	hour	2.28	5.53	10.8	22.4
240	min	41	99	193	403
260	min	13.5	32.5	64	136
280	min	4.8	11.6	22.7	48.2

Figure 7 d^2X/dT^2 curves of PAA, PA, and P for consecutive reactions versus temperature.

is generated using eqs. (16) and (17) and T_1 as well as T_2 (T_1 and T_2 are the temperature at the first and second inflection points of the curve of dX/dT vs. temperature for each thermal degradation stage, respectively) and can be obtained from the maximum points of the curve of d^2X/dT^2 curve. All the values of T_1 and T_2 are summarized in Table III. The values of T_2/T_1 were 1.14 and 1.10 were for the first stage and second stage of thermal degradation of polyacrylamide, respectively. The average values of 1.05 and 0.71 of the shape index were also calculated, showing the symmetric shape of the decomposition of polyacrylamide in the two thermal degradation stages, respectively.

The decomposition time in isothermal conditions for the thermal degradation of polyacrylamide, based on eqs. (15) and (16), of $1 - X$ versus degradation time, is shown in Figure 8 via simulation. As can be seen,
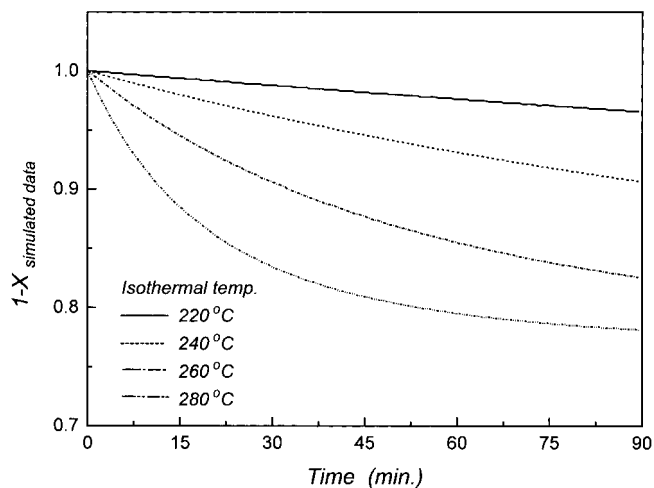
the decomposition at 280°C is much faster than that at 240°C. We can also see that 97.4% of the polyacrylamide remain after 20 min at 240°C compared to 87.5% left at 280°C.

The degree of decomposition at different degree of decomposition, using Eqs. (16) and (17), can also be predicted and are shown in Figure 9. The results show that the degree of thermal decomposition of polyacrylamide increases with increasing of the aging temperature and total time. Moreover, in order to calculate the estimated time of polyacrylamide to failure, a term called "lifetime", t_f, is defined when the degree of decomposition reactions, i.e., 1-X=0.95.[30] The predicted lifetime of polyacrylamide can be calculated using Eqs. (16) and (17) as well as the values of the activation energy and frequency factor listed in Table 4. It can be seen very clearly from Table 4 that stati-
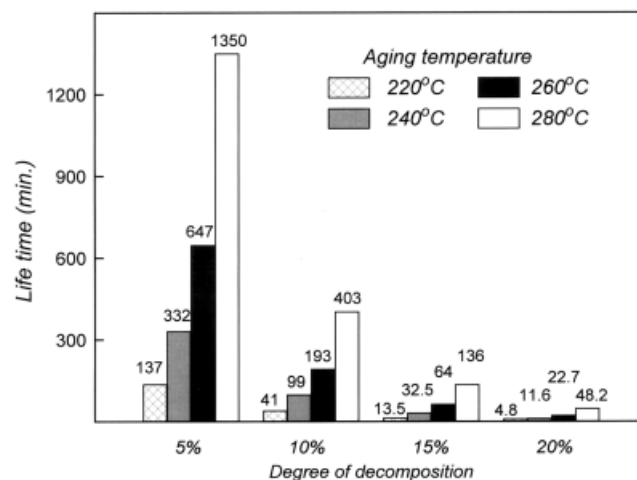

Figure 8   Isothermal curves of thermal degradation of polyacrylamide at different temperatures.

Figure 9   Lifetime versus temperature at different degrees of decomposition of polyacrylamide.

cally used polyacrylamide polymer at temperature 100°C will last for several years without failure.

CONCLUSION

The two stages involved in the thermal decomposition of polyacrylamide have been simultaneously correlated by means of a kinetic model. Data obtained at a heating rate have been satisfactorily correlated with kinetic parameters, proving that there is no need to allow these parameters to vary with the heating rate. The first peak observed, corresponding to the deammonation of the polyacrylamide together with the formation of different aromatic compounds. The second peak observed, corresponding to the break the backbone and imides formed. A kinetic model involving a single reaction step for this process provides an apparently good representation of experimental data.

The results obtained for Ea, k and n agreed reasonably with those obtained by integration of the kinetic equation but the data dispersion significantly affects the reaction order. The reaction order, the activation energy and the pre-exponential factor were evaluated from common thermogravimetric and differential thermogravimetric curves experimentally obtained. The reaction was found under this experimental condition to be of 1.28 order with activation energy of 131.1 kJ/mole and pre-exponential factor 2.2×10^{-9} s^{-1} in the first degradation stage and 1.16 order with activation energy of 192.2 kJ/mole and pre-exponential factor 2.4×10^{12} s^{-1} in the second stage, respectively. Moreover, the Flynn-Wall and Friedman methods were also applied to the experimental data by separating each stage. There were slight differences in activation energy depending on the analytical method. The use of method in this study involving the integration of the kinetic equation to analyze the experimental data and the simultaneously correlation of data at different heating rates, especially for complex reaction seem to be advisable.

The simulated curves can be drawn via mathematical treatment and a computer program. From the simulated method, T_m, T_1, T_2, T_2/T_1 and shape index can be calculated. Also, the predicted lifetime, T_f, based on thermal degradation, can be calculated at different temperature.

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