

Kinetics of Hydrolysis of Poly(α -olefin-co-maleic anhydride)

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Synopsis

The kinetics of hydrolysis of poly(α -olefin-co-maleic anhydride) dissolved in a paraffinic solvent was studied. This process was followed for the situation where the copolymer solution was in contact with an immiscible water layer. The hydrolysis, as monitored spectroscopically, was observed to follow pseudo-first-order kinetics with respect to the copolymer concentration. The rate was proportional to the water/paraffin interfacial surface area and inversely proportional to the volume of the copolymer solution for a given interfacial surface area. These results are consistent with the hypothesis that the hydrolysis occurs at the paraffin/water interface. An Arrhenius plot yielded a value of 11.1 kcal/mole for the activation energy.

INTRODUCTION

Recently we have been concerned with studying the solid-state properties¹ and polymerization kinetics² of alpha-olefin/maleic anhydride copolymers. The solid-state properties of these materials are of considerable interest because the side chains of these materials can be crystallizable.¹ Past investigations have been performed on materials in the anhydride form. Because hydrolysis would be expected to change the solution and solid-state properties of these copolymers it is necessary to have information concerning the rate of this process. For example, hydrolysis has been observed to result in a 15% increase in hydrodynamic volume for poly(1-decene-co-maleic anhydride) dissolved in tetrahydrofuran (THF).¹ In the past infrared (IR) spectroscopy has proven effective in monitoring the extent of hydrolysis in this system and we have again employed this technique.

EXPERIMENTAL

The material studied was polymerized as previously by C. J. Verbrugge (S. C. Johnson and Son, Inc.) and consists of maleic anhydride and alpha-olefins ranging in length from 18 to 28 carbons.¹ Since under the polymerization conditions maleic anhydride forms primarily an alternating copolymer with olefins, we will refer to the polymerizate as a copolymer.³ A 15% by weight solution of the copolymer was prepared in Isopar E. This solvent is a mixture of paraffinic isomers available from Exxon. All of the studies involved exposing the copolymer solution to an interface of high purity water.

Experiments were either static or dynamic in nature. The dynamic experiment consisted of vigorously mixing known amounts of the copolymer solution with high purity water. The static experiments were performed by carefully

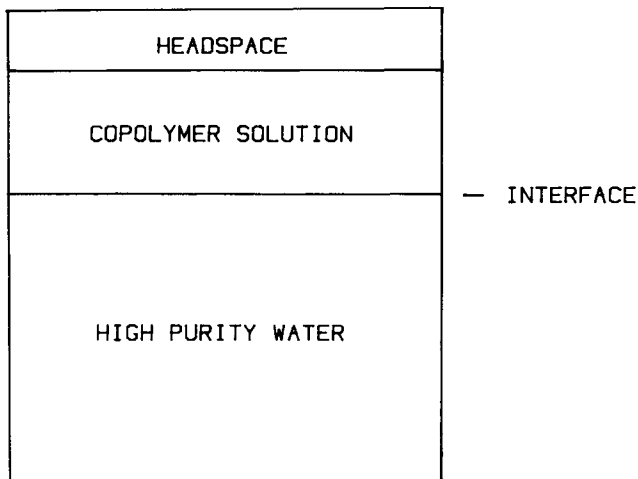


Fig. 1. Schematic representation of the experimental set up.

pouring the copolymer solution over water so that no mixing occurred. This resulted in a two-phase copolymer solution/water system as depicted in Figure 1. Because of the limited solubility of the copolymer in water, partitioning of this material between the two phases is not of concern.

Infrared spectra were taken on a Perkin Elmer 283 Spectrometer and the hydrolysis was followed by monitoring the absorbances at 1710 cm^{-1} (acid carbonyl) and 1780 cm^{-1} (anhydride carbonyl).^{4,5} Since the ratio of extinction coefficients for these bands is approximately one, percent hydrolysis was calculated from the absorbances as follows:¹

$$\% \text{ Acid} = \frac{A_{1710}}{A_{1710} + A_{1780}} \times 100\%$$

Samples were prepared for analysis by taking aliquots from the top of the copolymer solution followed by casting onto NaCl plates.

RESULTS AND DISCUSSION

Effect of Agitation on the Rate of Hydrolysis

This aspect of the study is concerned with the effect of agitation on the rate of hydrolysis of a mixture of 300 mL of copolymer solution and 700 mL H_2O . In one case, the copolymer solution was carefully poured over the H_2O and no mixing occurred (static experiment). In the agitated case the mixture was vigorously stirred throughout the reaction. A plot of percent hydrolysis versus time is depicted in Figure 2 for these two experimental conditions. The hydrolysis is observed to proceed considerably faster in the stirred case. As will be discussed subsequently, this is believed to occur because of the increased surface area of the copolymer solution/ H_2O interface which is induced via agitation.

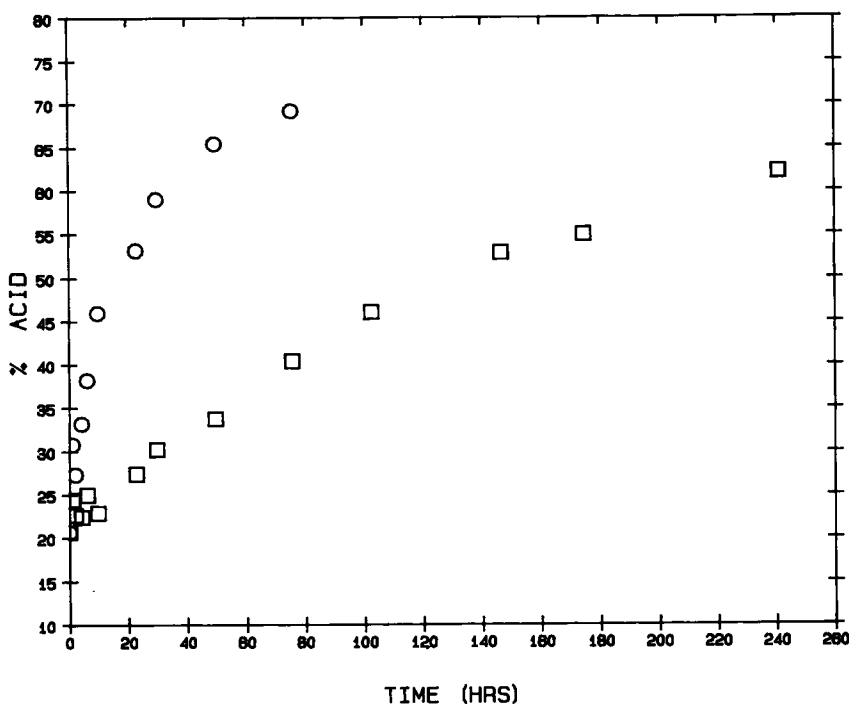


Fig. 2. Plot of percent acid versus time for a mixture of 300 mL of copolymer solution and 700 mL H_2O . Square = static experiment, Circle = continuously stirred.

Effect of Surface Area and Copolymer Solution Volume on the Rate of Hydrolysis

In order to determine the effect of surface area on the rate of hydrolysis a static experiment was designed in which the volumes of the phases were kept constant (300 mL copolymer solution/700 mL H_2O) and the surface area was varied by changing the dimensions of the hydrolysis vessel. The results, depicted in Figure 3, reveal that the rate of hydrolysis for a given volume of copolymer solution increases with increasing interfacial surface area. The effect of changing the volume of the copolymer solution was investigated using a vessel having a surface area of 120 cm^2 (Fig. 4). The results indicate that for a given surface area, the rate of hydrolysis increases with decreasing copolymer solution volume.

Reaction Kinetics

The results discussed above indicate that the hydrolysis occurs at the interface of the copolymer solution and H_2O . However, the mechanism of the process (i.e., diffusion or reaction controlled) has not been established. It is instructive to consider the implications of four possible models on the kinetics of hydrolysis. Complete derivations of the equations which follow are presented in the Appendix.

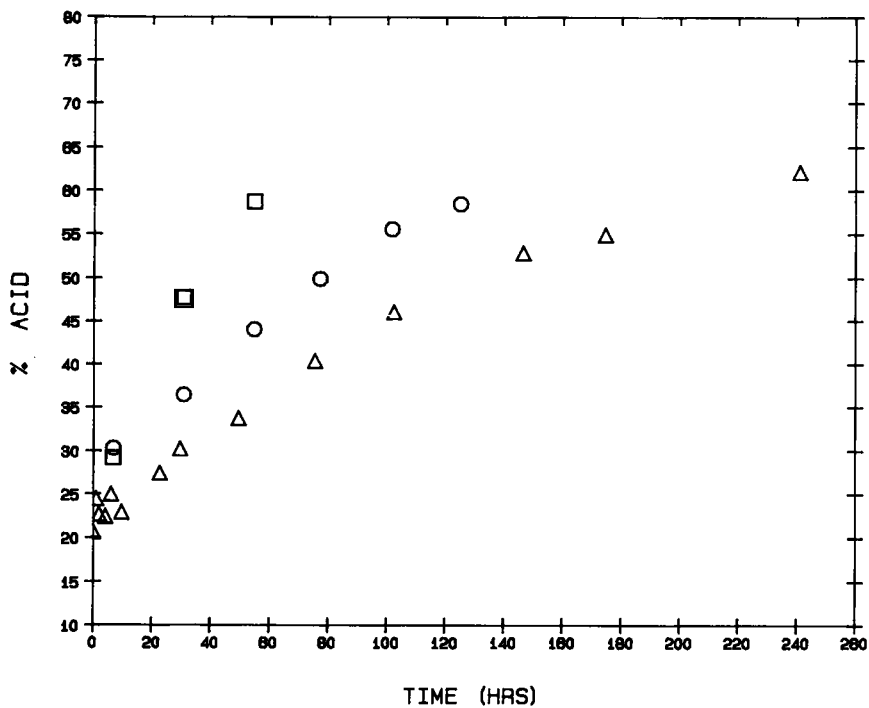


Fig. 3. Plot of percent acid versus time showing the influence of interfacial surface area on the hydrolysis rate. Triangle = 120 cm², circle = 192 cm², square = 608 cm².

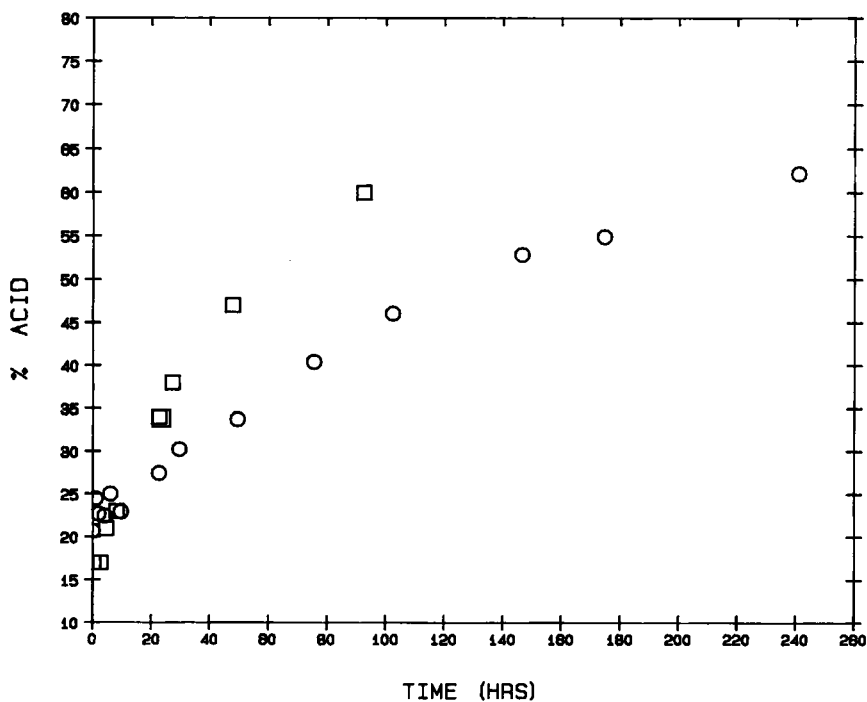


Fig. 4. Plot of percent acid versus time showing the influence of copolymer solution volume on the hydrolysis rate. Circle = 300 mL, square = 100 mL.

CASE I

Hypothesis. The diffusion of H_2O across the copolymer solution/water interface is controlling the rate of reaction.

Implication. This mechanism would yield the following zero-order rate equation:

$$[\text{MAH}]_t = [\text{MAH}]_0 + Ct \quad (1)$$

where

t = time

$[\text{MAH}]_t$ = MAH concentration at time t

$[\text{MAH}]_0$ = MAH concentration at start

$C = DA [\text{H}_2\text{O}]_w / VX$

and

D = diffusion coefficient of H_2O across copolymer solution/ H_2O interface

A = interfacial area

$[\text{H}_2\text{O}]_w$ = $[\text{H}_2\text{O}]$ in the bulk water

V = volume of polymer solution

X = thickness of interface

Conclusion. Since plots of % hydrolysis versus time are nonlinear, the rate of reaction is not controlled by diffusion of H_2O across the interface.

CASE II

Hypothesis. The H_2O saturates the copolymer solution and maintains a constant concentration due to rapid diffusion of H_2O across the interface. The rate of reaction is controlled by the rate of hydrolysis within the copolymer solution phase.

Implication. This mechanism would yield the following pseudo-first-order rate equation:

$$\ln \frac{[\text{MAH}]_t}{[\text{MAH}]_0} = k't \quad (2)$$

where

$$k' = k[\text{H}_2\text{O}]_i$$

and

k = reaction rate constant

$[\text{H}_2\text{O}]_i$ = $[\text{H}_2\text{O}]$ in copolymer solution

Conclusion. As will be discussed subsequently, the data do fit a first-order plot. However, we can eliminate this hypothesis because it does not predict a surface area effect.

CASE III

Hypothesis. Diffusion of the hydrolyzed copolymer from the interface to the surface of the copolymer solution layer (where the sampling takes place) is controlling the observed reaction rate.

Implication.

$$\frac{[\text{MAH}]_a - [\text{MAH}]_t}{[\text{MAH}]_a - [\text{MAH}]_0} = 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n + 1/2)\pi} \exp - \left((n + 1/2)^2 \pi^2 Dt/b^2 \right) \cos(n + 1/2)\pi v/b \quad (3)$$

where

$[\text{MAH}]_a = [\text{MAH}]$ at the interface

D = diffusion coefficient for the hydrolyzed polymer in the solvent

b = thickness of the copolymer solution layer

v = sampling distance as measured from the surface

Conclusion. Analysis of the data according to the above implication resulted in a poor fit. Equation (3) does not include convection, so we have applied it only to the static experiments. This equation is obtained by notational changes from the solution in Ref. 6, p. 356 for the transient conduction of heat into a slab of thickness $2b$ from both boundary surfaces.

CASE IV

Hypothesis. The reaction rate is limited by the reaction at the interface and diffusion of the polymer in the solvent occurs rapidly.

Implication. A pseudo-first-order rate equation is predicted as follows:

$$\ln \frac{[\text{MAH}]_t}{[\text{MAH}]_0} = \frac{kfA}{V} t \quad (4)$$

where

k = reaction rate constant

f = moles H_2O /interfacial area

A = interfacial area

V = volume of polymer solution

Conclusion. To prepare a first-order plot of the hydrolysis data it is necessary to modify Eq. (4) to correct for incomplete conversion to acid at time = ∞ :⁷

$$\ln \frac{[\text{MAH}]_t - [\text{MAH}]_{\infty}}{[\text{MAH}]_0 - [\text{MAH}]_{\infty}} = \frac{kfA}{V} t \quad (5)$$

where

$[\text{MAH}]_{\infty} = 30\%$

$[\text{MAH}]_t = \%$ anhydride at time t

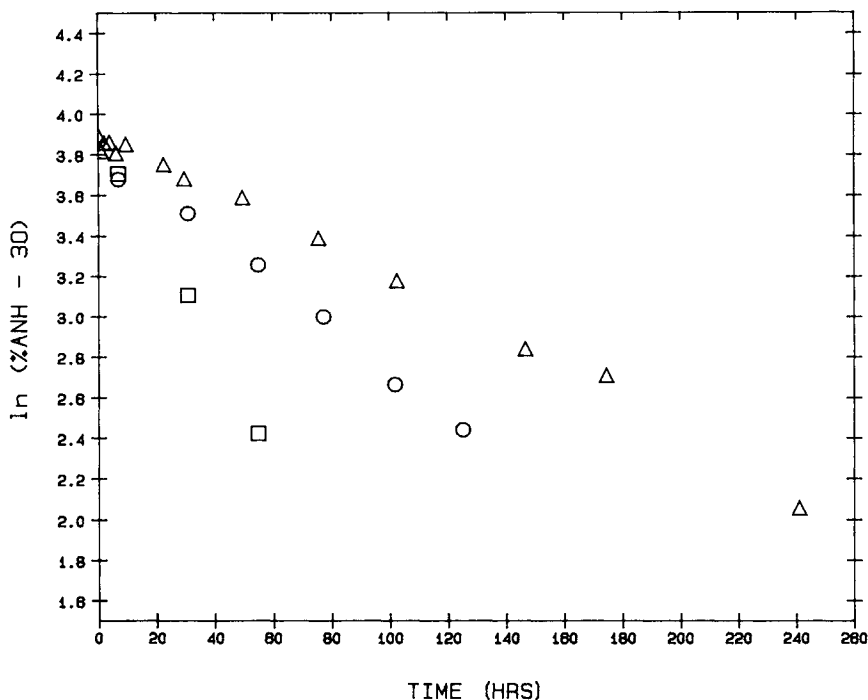


Fig. 5. First-order plot showing the influence of interfacial surface area on the hydrolysis rate. Triangle = 120 cm², circle = 192 cm², square = 608 cm².

First-order plots of the data depicted in Figures 3 and 4 are presented in Figures 5 and 6, respectively. The slopes resulting from the least-squares lines through the data in these figures are summarized in Table I. From Eq. (5) we realize that these values are equal to kfA/V . Multiplying these values by V/A for each particular experiment results in a value for kf (last column of Table I). The value of this effective rate constant appears relatively constant with the possible exception of the experiment with the largest interfacial area (experiment C). The discrepancy of the data from this experiment may be due to the fact that this value is based on only three data points. It is concluded that the observed rate of hydrolysis is dictated by the hydrolysis rate at the interface.

Temperature Dependence of the Rate Constant

The temperature dependence of the effective rate constant (kf) was determined employing the same experimental parameters as experiment D (Table I). Figure 7 depicts a plot of $\ln(kf)$ versus $1/T$ (Arrhenius plot). A least-squares fit resulted in an energy of activation (E_a) of 11.1 kcal/mole and a pre-exponential factor of 2.55×10^6 cm/h.

CONCLUSION

The hydrolysis of a solution of an alpha-olefin/maleic anhydride copolymer over water was determined to occur at the copolymer solution/water inter-

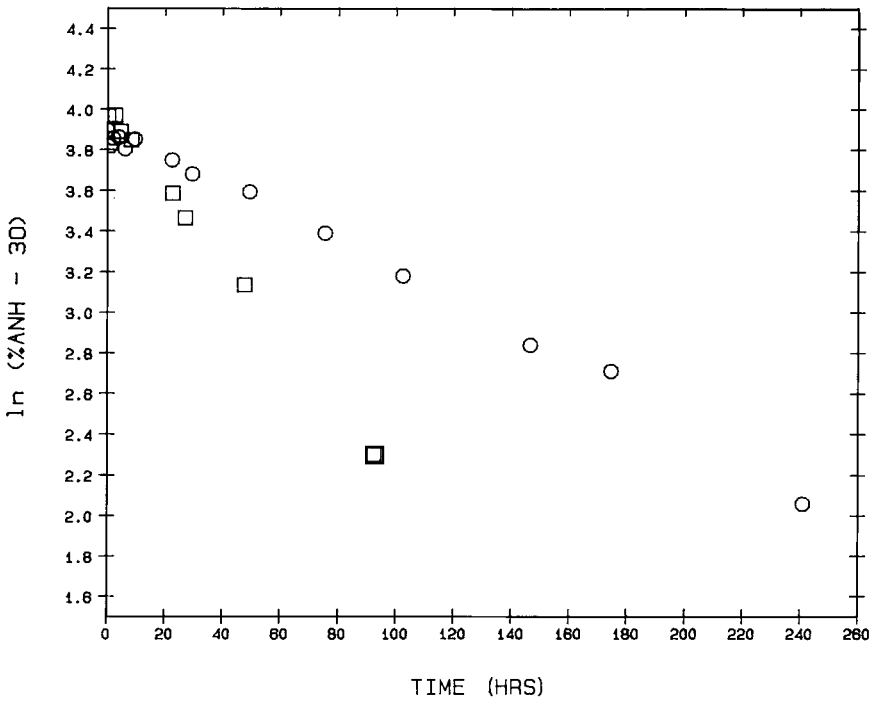


Fig. 6. First-order plot showing the influence of copolymer solution volume on the hydrolysis rate. Circle = 300 mL, square = 100 mL.

TABLE I

Experiment	Volume of copolymer solution (cm ³)	Interfacial area (cm ²)	Slope $k_f A/V$ (h ⁻¹)	k_f (cm/h)
A	300	120	.007	.018
B	300	192	.011	.017
C	300	608	.027	.013
D	100	120	.018	.015

face. The hydrolysis, as monitored spectroscopically, was found to follow pseudo-first-order kinetics with respect to the maleic anhydride concentration. The observed rate is proportional to the interfacial surface area and inversely proportional to the volume of the copolymer solution. An activation energy of 11.1 kcal/mole was calculated from a plot of the apparent rate constant versus $1/T$.

APPENDIX

Case I

For this case the rate-limiting step is the diffusion of H₂O across the copolymer solution/water interface. The net flux J (i.e., moles/cm² · sec) of

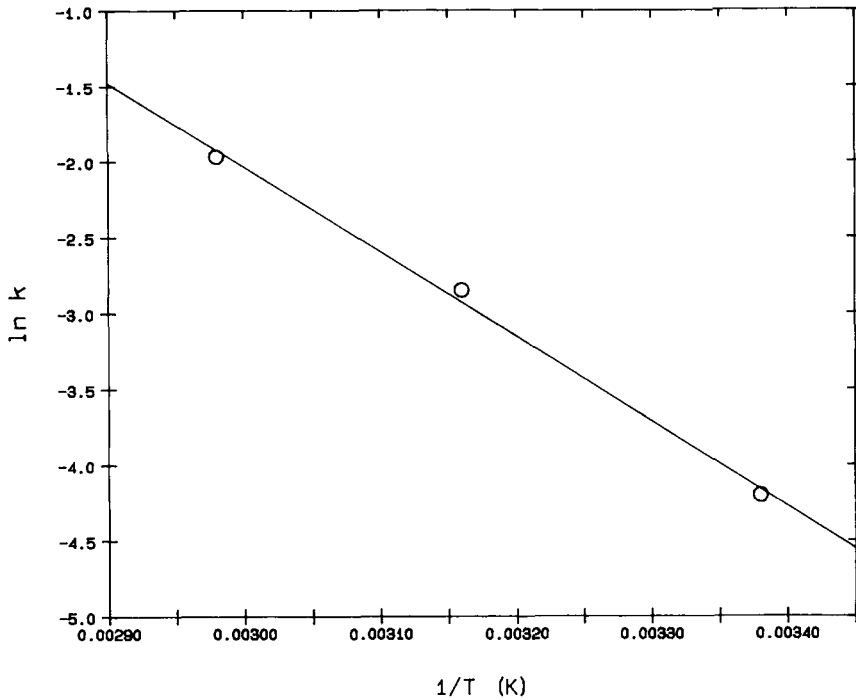


Fig. 7. Plot of $\ln(kf)$ versus $1/T$ (Arrhenius plot) for a static experiment.

H_2O across the interface is given by Fick's first law:

$$J = D \left(\frac{[H_2O]_w - [H_2O]_a}{X} \right)$$

where

D = diffusion coefficient of H_2O across copolymer solution/ H_2O interface

$[H_2O]_w$ = $[H_2O]$ in bulk water

$[H_2O]_a$ = $[H_2O]$ at copolymer solution side of interface

X = interfacial thickness

The change in maleic anhydride concentration with time is, therefore, given by the flux relative to the copolymer solution volume:

$$\frac{-d[MAH]}{dt} = \frac{DA}{V} \left(\frac{[H_2O]_w - [H_2O]_a}{X} \right)$$

where

A = interfacial area

V = volume of copolymer solution

Assuming $[H_2O]_a = 0$, integration yields:

$$[MAH]_t = [MAH]_0 - \frac{DA[H_2O]_w}{VX} t$$

Case II

This mechanism assumes a constant water concentration in the copolymer solution due to water saturation. A pseudo-first-order rate equation is appropriate:

$$\frac{-d[\text{MAH}]}{dt} = k[\text{H}_2\text{O}]_i[\text{MAH}]$$

where

k = reaction rate constant

$[\text{H}_2\text{O}]_i = [\text{H}_2\text{O}]$ in copolymer solution

Assuming $[\text{H}_2\text{O}]_i = \text{constant}$, integration yields:

$$\ln \frac{[\text{MAH}]_t}{[\text{MAH}]_0} = k[\text{H}_2\text{O}]_i t$$

Case IV

This case assumes that the limiting step is the hydrolysis which takes place at the copolymer solution/water interface. In the rate equation which follows the term fA/V represents the effective water concentration which is a constant.

$$\frac{-d[\text{MAH}]}{dt} = \frac{kfA}{V}[\text{MAH}]$$

where

f = moles H_2O /unit surface area

A = interfacial surface area

V = volume of copolymer solution

integrating yields:

$$\ln \frac{[\text{MAH}]_t}{[\text{MAH}]_0} = \frac{kfA}{V} t$$

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