

Alkaline Hydrolysis of Homopolymers and Copolymers of 2-Hydroxypropyl Methacrylate

JOSEPH DALY* and ROBERT W. LENZ†

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

SYNOPSIS

Homopolymers of 2-hydroxypropyl methacrylate (HPMA) and copolymers with acrylic acid (AA) were prepared in 1,4-dioxane. The reactivity ratios were determined to be $r_{AA} = 0.27 \pm 0.04$ and $r_{HPMA} = 2.2 \pm 0.2$. The alkaline hydrolysis by sodium hydroxide of the HPMA monomer and polymers showed that while the HPMA monomer hydrolyzed readily as expected for a low-molecular-weight carboxylic ester the HPMA homopolymer and water-soluble sodium acrylate (NaA) copolymers were extremely resistant to alkaline hydrolysis. The saponification reaction followed a second-order rate equation, being first order with respect to both HPMA and hydroxide ion concentration. The Arrhenius parameters, activation energy E and frequency factor A , for the alkaline hydrolysis of HPMA monomer in water were found to be $E = 10.3$ kcal/mol and $A = 1.5 \times 10^8$ L/mol min, and those for the NaA-HPMA copolymers in water were found to be $E = 24$ kcal/mol and $A = 4 \times 10^{12}$ L/mol min. The NaA-HPMA copolymers had a limiting extent of hydrolysis, ranging from 9–90% ester conversion. A sharp rate decrease at low conversion was noted during the HPMA homopolymer hydrolysis in 58/42 dimethyl sulfoxide/water, allowing the calculation of two distinct reaction rates. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Water-soluble copolymers of acrylic acid or its alkali salts with acrylic and methacrylic esters are widely used in various branches of industry as aqueous phase dispersants, flocculants, and heat exchanger scale reducers. These copolymers are often employed in alkaline environments, where their water solubility is enhanced as the polyacid converts to the polysalt form. For example, the subject polymers were synthesized for use as dispersants or fluidifiers in Portland cement.¹ As such, the saponification of the acrylic or methacrylic ester is an important consideration. Also, the hydrolysis reaction of these copolymers has been used as a controlled release mechanism for drugs, fertilizers, or water solubility. While this study focuses on hydrolysis in the solution state, other investigators researched the alkaline hydrolysis of polymers as beads in suspension.^{2–5}

It has been previously shown that polymeric methacrylic esters are highly resistant to alkaline hydrolysis, whereas the monomers, and acrylic ester monomers and polymers, are not.^{6,7} In general, the differences in rates observed between monomers and their polymers are due to steric differences and to the fact that reaction along a polymer chain involves introduction of a new functional group (e.g., conversion of an ester group to an acid group in hydrolysis) that may either retard or accelerate the reaction of neighboring groups. Also, conversion of functional groups along the polymer chain can change the microenvironment and chain coiling, thus complicating reaction kinetics. Several researchers have developed theories of macromolecular reactivity in the framework of models that consider the influence of reacted groups on nearby initial groups in the polymeric chain.^{8,9}

This article presents a study of the saponification of water-soluble copolymers of sodium acrylate (NaA) and 2-hydroxypropyl methacrylate (HPMA). These copolymers are water soluble only at pH values of approximately 8 and greater. The water-insoluble HPMA homopolymer was also

* Present address: Peace Corps, Nepal.

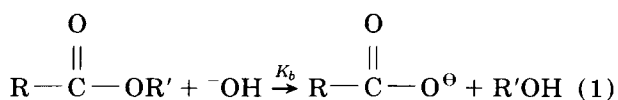
† To whom correspondence should be addressed.

studied in 58/42 dimethyl sulfoxide (DMSO)/water solution. The rate constants were determined at various temperatures to allow the construction of Arrhenius plots, from which the reaction activation energy (E) and frequency factor (A) were determined. These parameters allow one to predict the rate of saponification of NaA-HPMA copolymers at various temperatures and alkaline pH values.

THEORY OF SAPONIFICATION KINETICS

In the presence of alkali, the carbonyl carbon of the carboxylic acid ester (CAE) is attacked by hydroxyl ion, leading to the following bimolecular reaction and kinetic equation:

Reaction



Note that as strong base is consumed weak base is produced. The reaction obeys the second-order rate law:

Second-order rate equation

$$\frac{d[\text{CAE}]}{dt} = -K_b[\text{CAE}][^-\text{OH}] \quad (2)$$

where $[\text{CAE}]$ and $[^-\text{OH}]$ is the concentration of carboxylic acid ester and hydroxide ion at time t , respectively, and K_b is the second-order rate constant for the basic hydrolysis reaction. Solving for $K_b t$, one obtains:

Integrated equation

$$\frac{1}{[^-\text{OH}]_0 - [\text{CAE}]_0} \ln \frac{100[^-\text{OH}]_0 - p[\text{CAE}]_0}{[^-\text{OH}]_0(100 - 2p)} = K_b t \quad (3)$$

where p is defined as the percent hydrolysis and subscript 0 designates initial concentrations. For

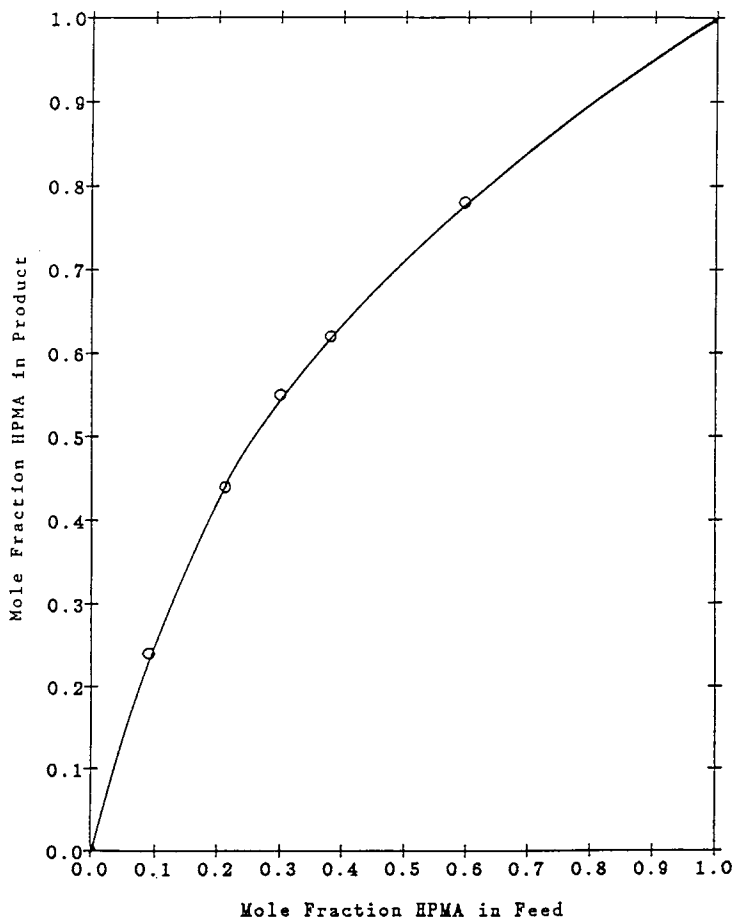


Figure 1 Copolymer composition as a function of monomer feed composition for the copolymerization of HPMA and AA.

notation purposes, the left side of eq. (3) will be labeled Y .

Thus, K_b was experimentally determined according to eq. (3) by measuring the percent hydrolysis, p , at various times, t . Construction of a graph of the left side of eq. (3) (Y) vs. time yields a straight line from which K_b is obtained as the slope.

Determination of the rate constant K_b at various temperatures (T) allowed the determination of activation energies (E) and frequency factors (A) for hydrolysis according to the Arrhenius equation:

$$K = Ae^{-E/RT} \quad (4)$$

where R is the universal gas constant (1.987 cal/gmol °C). Experimentally, the activation energy and frequency factor are determined according to eq. (5) by plotting $\ln K$ vs. $1/T$:

$$\ln K = \ln A - E/RT \quad (5)$$

The slope of the line yields E while A is obtained as the y -intercept.

If $[\text{OH}^-]_0 \gg [\text{CAE}]_0$, eq. (3) reduces to the following pseudo-first-order rate equation:

$$\frac{1}{[\text{OH}^-]_0} \ln(100/100 - p) = K_b t \quad (6)$$

EXPERIMENTAL

Synthesis of HPMA Homopolymer and AA Copolymers

Homopolymers of HPMA and copolymers with AA were prepared in 1,4-dioxane at 30 wt % monomers at 60°C and 0.60 mol % azobis(isobutyronitrile) (AIBN) under a nitrogen purge. The molecular weight was controlled by adding butanethiol as a chain transfer agent at up to 8 mol %.

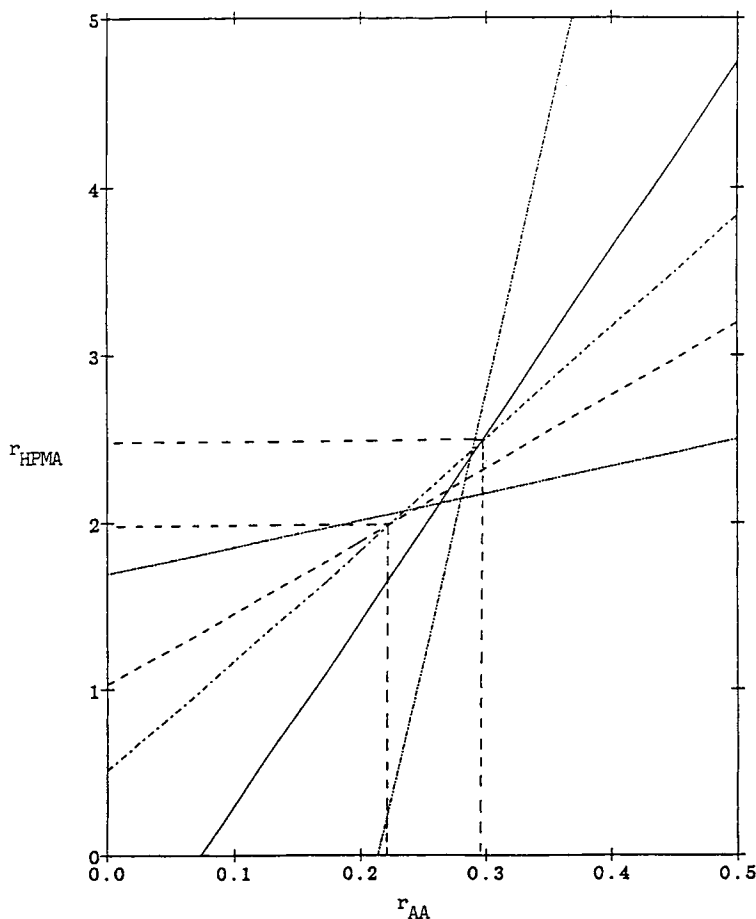


Figure 2 Mayo-Lewis plot of reactivity ratios for the copolymerization of HPMA and AA.

Stepwise, the designated amounts of HPMA and AA monomers, 1,4-dioxane, and butanethiol were charged to the reaction vessel and the reaction mixture was purged with nitrogen for 30 min. The designated amount of AIBN was then added and the reaction vessel lowered into a 60°C heating bath. The polymerizations were allowed to run to high conversion, except in the case of the reactivity ratio determinations.

The polymerization product was precipitated by dropwise addition to diethyl ether and reprecipitated by dissolution in methanol and reprecipitation in diethyl ether. This product was then dried *in vacuo* at 80°C for 12 h and crushed to yield a fine white powder.

Characterization of AA-HPMA Copolymers

The number and weight average molecular weights were determined by size exclusion chromatography (SEC) using tetrahydrofuran as the elution solvent

with five μ Styragel columns (Waters Associates, Milford, MA).

The ratio of HPMA-AA monomeric units in the copolymer was determined by gravimetric acid-base titration of the AA unit as follows. The poly(HPMA-co-AA) was dissolved in 50/50 methanol/water solution and titrated with aqueous sodium hydroxide. Titration end points were determined either conductometrically or with phenolphthalein as an indicator in a KCl salt solution. The neutral salt was added to give a sharp pH swing and a correspondingly sharp indicator end point by shielding the neighboring carboxylate groups on the polymer chain from each other and thus increasing the apparent acidity of the remaining AA units.

Titration analysis of the AA homopolymer showed that it contained a significant quantity of residual solvent. This would put the gravimetric determination of the ratio of monomeric units in the copolymer in error unless it was accounted for. PAA is notorious for this characteristic, being cited as

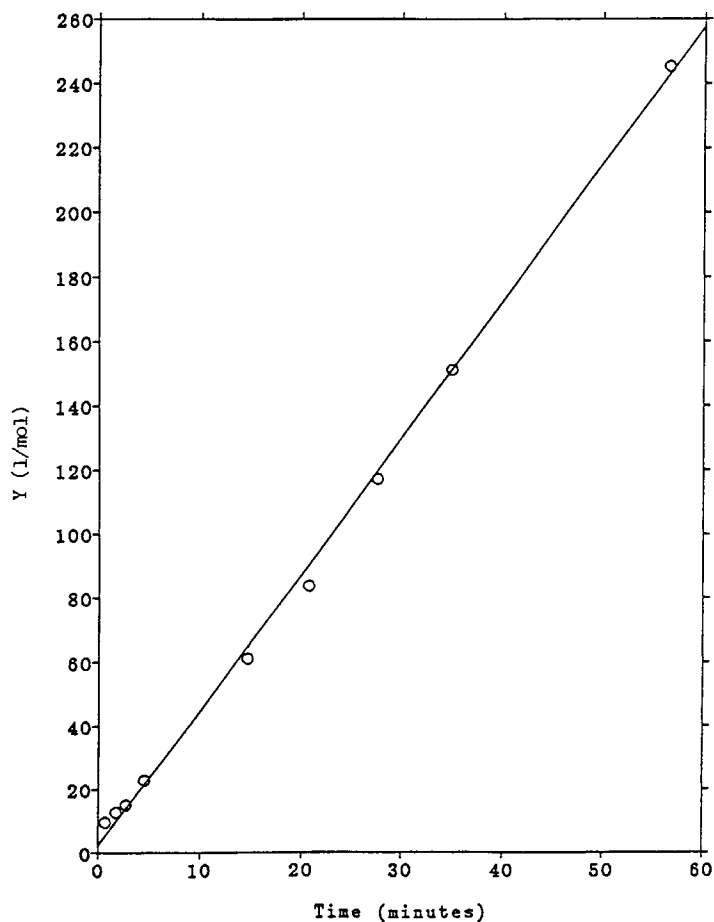


Figure 3 Plot of Eq. (3) for the rate of alkaline hydrolysis of HPMA monomer in water at 20.8°C.

retaining at least 10% solvent after prolonged vacuum drying at 60°C.^{10,11} The PAA product purified and dried as detailed above consistently showed an AA content of 87.0 ± 0.5 . Since the HPMA does not normally hold solvent, the copolymers were all estimated to contain 10% residual solvent.

Alkaline Hydrolysis Procedure

Kinetic experiments were performed in a 50-mL reaction flask equipped with a magnetic stirrer, which was jacketed by a flowing liquid (water or glycerol) having a controlled temperature to $\pm 0.1^\circ\text{C}$. The alkaline hydrolysis of the HPMA monomer and NaA-HPMA copolymer was conducted in distilled water. The copolymer feed was the poly(AA-co-HPMA), produced and purified as described above, and as it entered into the aqueous sodium hydroxide the AA units were neutralized to create the water-soluble poly(NaA-co-HPMA). Due to its insolubility,

HPMA homopolymer was hydrolyzed in 58/42 (v/v) DMSO/water solutions. Although the HPMA homopolymer had the disadvantage of not being water soluble, it offered the important advantages of a more accurate knowledge of the initial HPMA unit concentration and sharper indicator end points.

The percent hydrolysis was determined by acid-base titrations, which indicated the amount of hydroxide ions consumed.

The procedures used for the various hydrolysis studies are given below.

Alkaline Hydrolysis of HPMA Monomer

The appropriate amounts of distilled water and HPMA monomer were entered into the reaction flask such that the total solution volume would be 50 mL upon addition of aqueous sodium hydroxide and to give an HPMA monomer concentration of from 0.013–0.14 M and an NaOH concentration approximately double the monomer concentration.

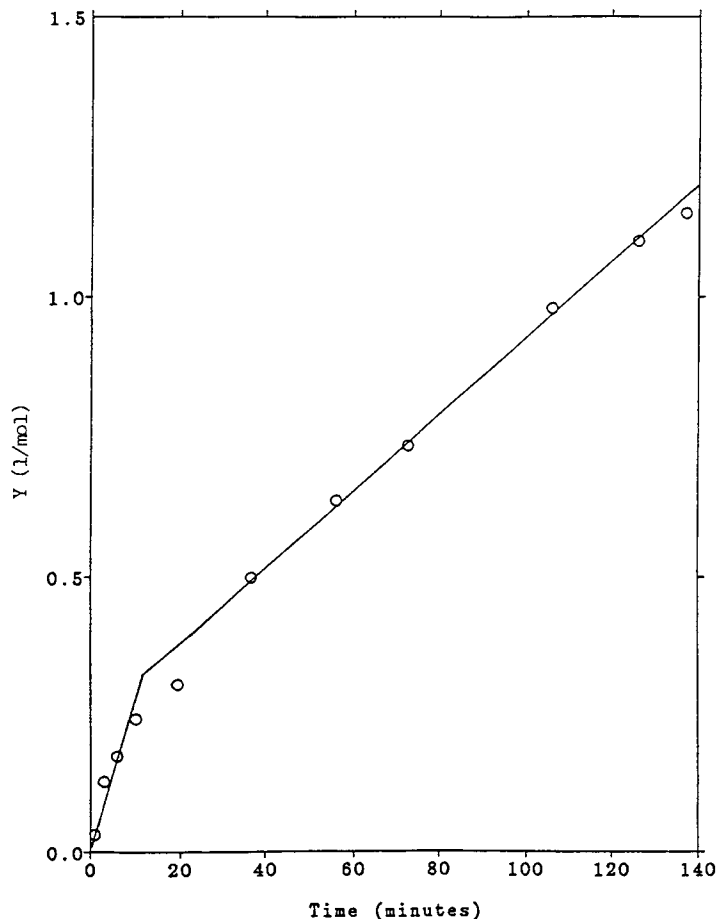


Figure 4 Plot of Eq. (3) for the alkaline hydrolysis of HPMA homopolymer in 55/45 DMSO/H₂O at 97.5°C.

The contents of the reactor were allowed to reach reaction temperature. At time zero, 1–5 mL 1*N* NaOH was added, resulting in a total solution volume of 50 mL. For reactions run below room temperature, the sodium hydroxide solution was chilled in an ice bath prior to addition.

At appropriate time intervals, 1-mL samples were extracted and quenched in 1–3 mL 0.36*N* HCl. The excess acid was then back-titrated with 0.02*N* NaOH, bromothymol blue being used as an indicator.

Alkaline Hydrolysis of HPMA Homopolymer

The HPMA homopolymer employed had a M_n of 4200 and M_w of 6600 as determined by SEC. It had been polymerized as described above using 6 mol % butanethiol.

Approximately 1.7 g poly(HPMA) was weighed accurately and dissolved in 13 mL DMSO. To this 5 mL distilled water was added and the solution vol-

ume adjusted to 20 mL with additional DMSO. Total DMSO required was from 13.9–14.0 mL. This solution was entered into the reaction flask and allowed to reach the reaction temperature. At time zero, 5 mL 5*N* NaOH was added. This gave a solution volume of 25 mL, with initial hydroxide and HPMA unit concentrations of approximately 1*N* and 0.47 *M*, respectively.

At appropriate time intervals, 0.5-mL samples were extracted and quenched in a solution consisting of 5 mL 0.5*N* KCl and 5 mL methanol and titrated to a bromothymol blue end point with 0.024*N* HCl.

Alkaline Hydrolysis of NaA-HPMA Copolymers

A quantity of poly(AA-co-HPMA), of known wt % AA, was weighed accurately to give 3–7 mM HPMA units, assuming 10 wt % of the copolymer was solvent for reasons as described above. This poly(AA-co-HPMA) was neutralized to poly(NaA-co-HPMA) with 1 or 5*N* NaOH with distilled water

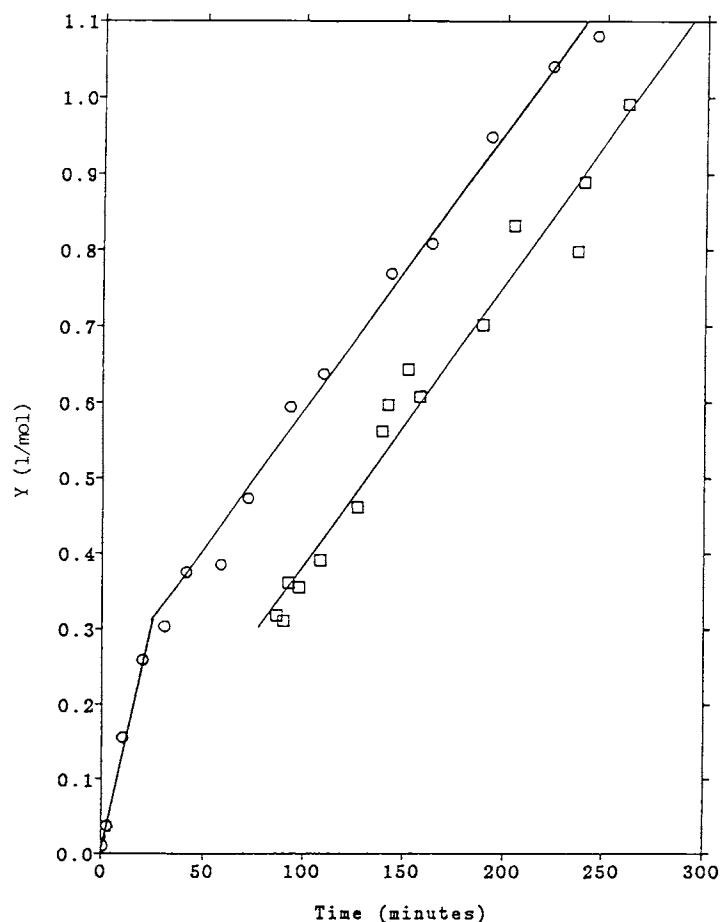


Figure 5 Plot of Eq. (3) for the rate of alkaline hydrolysis of HPMA homopolymer in 55/45 DMSO/water at 88.5°C; ○ and □ plots are for two separate reactions.

dilution and icebath cooling. As the copolymer was neutralized, it became water soluble. The volume of the solution was adjusted such that the total solution volume would be 25 mL upon addition of excess sodium hydroxide.

This neutral, aqueous solution of poly(NaA-co-HPMA) was entered into the reaction flask and allowed to reach reaction temperature. At time zero, 1 or 5N NaOH was added to bring the total solution volume to 25 mL, with an HPMA monomeric concentration in the range of 0.12–0.28 M and $[\text{OH}^-]$ approximately two times $[\text{HPMA}]$.

At appropriate time intervals, 1-mL samples were extracted and titrated with HCl to either a thymol blue end point or a conductimetric end point. Samples using the indicator were quenched in 10 mL 0.5N KCl and titrated with 0.02 or 0.04N HCl. Samples titrated conductimetrically were quenched in 25 mL 50/50 MeOH/H₂O and titrated with 1N HCl.

RESULTS

Reactivity Ratios

The reactivity ratios for the AA–HPMA pair were determined from the feed ratio of monomers and the resultant low conversion copolymer composition as determined by gravimetric acid-base titration analysis of the AA unit.

Figure 1 illustrates the composition of the copolymer formed as a function of the feed composition. From these relative compositions, the reactivity ratios were calculated by the Finemann–Ross,¹² Kelen–Tudos,¹³ and Mayo–Lewis¹⁴ methods. The three methods led to the same result. The Mayo–Lewis plot is shown in Figure 2 and serves to indicate the precision of the reactivity ratios, which here are determined to be $r_{\text{AA}} = 0.27 \pm 0.04$ and $r_{\text{HPMA}} = 2.2 \pm 0.2$.

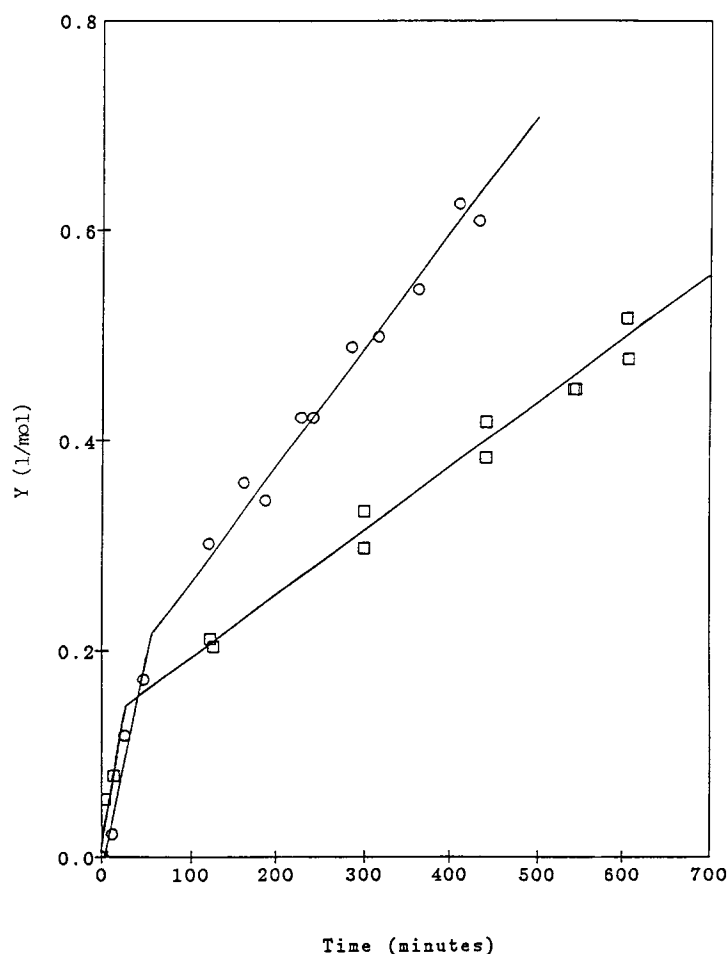


Figure 6 Plot of Eq. (3) for the rate of alkaline hydrolysis of HPMA homopolymer in 55/45 DMSO/water: (O) at 75.2°C; (□) at 66.5°C.

Alkaline Hydrolysis Rates

Plots of the left side of eq. (3), Y , versus time for the basic hydrolysis of (1) HPMA monomer in water, (2) HPMA homopolymer in 58/42 (v/v) DMSO/H₂O, and (3) NaA-HPMA copolymers in water are presented in Figures 3, 4-6, and 7 and 8, respectively. Only exemplary figures are shown for the HPMA monomer and NaA-HPMA copolymer in water, whereas all figures of the HPMA homopolymer in 58/42 (v/v) DMSO/H₂O are shown to demonstrate the abrupt reaction rate change.

From Figures 4-6 of the HPMA homopolymer hydrolysis, it is evident that the hydrolysis reaction experiences an abrupt rate decrease at approximately 16% conversion. The reaction is therefore characterized by two individual steps for which two individual rate constants can be determined, K_{b1} for the first step and K_{b2} for the second step.

As Figures 7 and 8 of the copolymer hydrolysis show, the experimental variation was high. This was

mainly due to the indistinct end points observed when titrating the NaA-HPMA copolymers. Only three of the six plots showed a rate decrease similar to that observed for the HPMA homopolymer hydrolysis curves, and so only one rate constant has been calculated.

Second-order rate constants (K_b) obtained from the slopes of the figures are summarized in Table I.

Arrhenius plots were constructed from the values in Table I according to eq. (5). This is demonstrated in Figure 9 for the HPMA homopolymer hydrolysis, with separate lines constructed for the first (K_{b1}) and second (K_{b2}) steps. The activation energies E and the frequency factors A as determined by this method are given in Table II.

A limiting extent of alkaline hydrolysis was observed for the NaA-HPMA copolymers, as shown in Table III. Other researchers studied in detail the limiting degree of ester hydrolysis for methyl methacrylate polymers and found that the limit was dependent not only upon the overall chemical com-

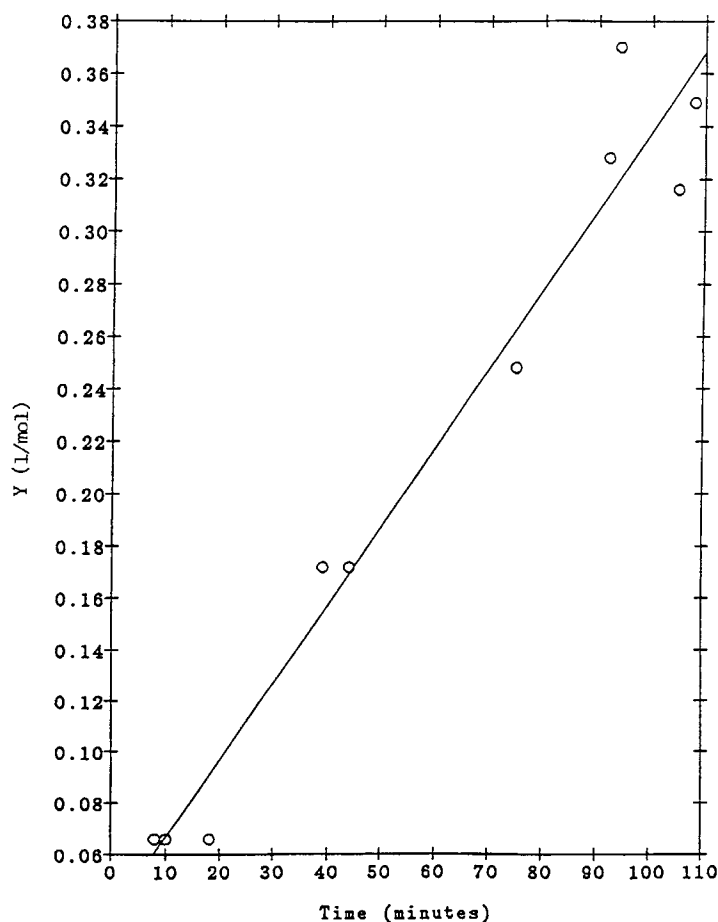


Figure 7 Plot of Eq. (3) for the rate of alkaline hydrolysis of 52/48 AA/HPMA copolymer in water at 81.0°C.

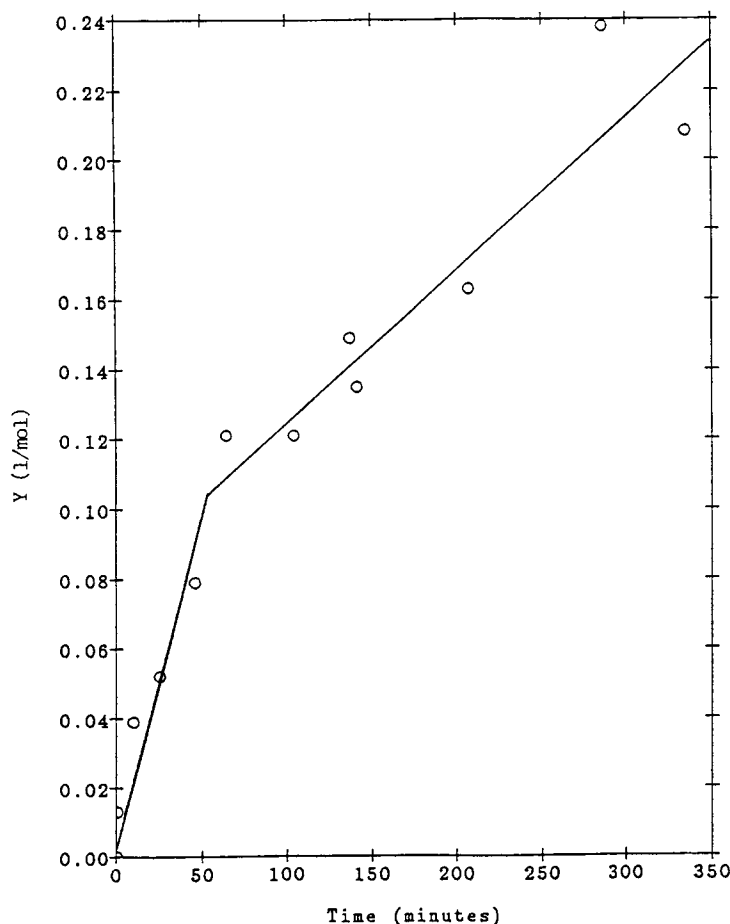


Figure 8 Plot of Eq. (3) for the alkaline hydrolysis of 52/48 AA/HPMA copolymer in water at 60.0°C.

position but also upon the stereochemical structure of the polymer chain.^{6,7}

DISCUSSION

The results of the alkaline hydrolysis of HPMA monomer in water were well behaved and indicated that the kinetic eqs. (2) and (3) did indeed describe the hydrolysis reaction. The determined Arrhenius parameters of $E = 10.3$ kcal/mol and $\log A = 8.18$ are in the normal range for alkaline hydrolysis of low-molecular-weight carboxylic esters. For comparison, the parameters for the similar monomer ethyl acrylate were determined by Pekarinen¹⁵ to be $E = 11.95$ kcal/mol and $\log A = 7.64$.

The results for the HPMA homopolymer in 58/42 (v/v) DMSO/H₂O and the NaA-HPMA copolymer in water showed that the HPMA polymers are highly resistant to alkaline hydrolysis, in contrast to the behavior of the monomer. To demonstrate the magnitude of the difference in hydrolysis rates that the Arrhenius parameters in Table II predict, the calculated times for 5% hydrolysis conversion

for the HPMA monomer and NaA-HPMA copolymers in water at various temperatures and pH values are presented in Table IV. For these calculations at the constant pH values, the pseudo-first-order rate equation was used [eq. (6)], which is valid when $[\text{OH}^-] \gg [\text{HPMA}]^0$.

These predicted times for 5% ester hydrolysis illustrate the HPMA polymers' extreme resistance to alkaline hydrolysis. Only under severe conditions does the hydrolysis rate become appreciable.

Smets and De Loecker¹⁶ investigated the alkaline hydrolysis of copolymers of methyl methacrylate and methacrylic acid. The rate of hydrolysis at various temperatures showed that the activation energy E was quite high and dependent upon the initial copolymer composition. For copolymers with initial methyl methacrylate contents of 83 and 66%, the activation energies in 1N NaOH were found to be 24.5 and 22.2 kcal/mol, respectively. These values correspond well with the activation energy of 24 kcal/mol found here for the NaA-HPMA copolymers.

Table I Reaction Rate Constants for the Alkaline Hydrolysis of HPMA Monomers and Polymers

HPMA Monomer in Water		
Temperature (°C)	$K_b \times 10^3$ (L/mol min)	
20.8	4200	
20.8	3020	
20.8	2750	
12.0	1830	
5.9	1360	
5.9	1300	
0.0	844	
0.0	801	

HPMA Homopolymer in 58/42 (v/v) DMSO/H ₂ O		
Temperature (°C)	$K_{b1} \times 10^3$ (First Step) (L/mol min)	$K_{b2} \times 10^3$ (Second Step) (L/mol min)
97.5	29.4	7.1
88.5	—	3.8
88.5	14.5	3.9
75.2	4.2	1.1
66.5	4.3	0.61

NaA-HPMA Copolymer in Water		
Temperature (°C)	$K_b \times 10^3$ (L/mol min)	Feed NaA/HPMA (mol/mol)
60.0	0.37	52/48
70.7	0.77	62/38
79.5	2.4	56/44
81.0	3.1	52/48
88.1	4.7	56/44
88.7	5.8	62/38

The results in Table II show that the activation energy for the hydrolysis of HPMA homopolymer is 21 kcal/mol whereas that for the copolymer is 24 kcal/mol. This difference is most likely due to the change in solvent from the DMSO/H₂O solutions to water. Alkaline hydrolysis rates typically undergo large accelerations upon addition of a dipolar aprotic solvent such as DMSO, apparently due to increased solvation of the transition state, which lowers the activation energy.¹⁷

A step decrease in the reaction rate, such as observed here for the HPMA homopolymer in 58/42 (v/v) DMSO/H₂O, has also been observed by Moens and Smets during the alkaline hydrolysis of polyacrylamide in water, the rate change occurring at about 40% hydrolysis.¹⁸ Polymethacrylamide, on the other hand, shows a gradually decreasing rate "constant" with increasing hydrolysis conversion, as opposed to the abrupt change, as demonstrated by Kawabe and Yanagita.^{19,20} They studied the alkaline hydrolysis of poly(methyl methacrylate) in 29/71 acetone/water and proposed that the reaction proceeds in four steps, as reasoned from the occurrence of four environments of varying reactivity as the neighboring groups are hydrolyzed. In such a way, the kinetic behavior is compared with the titration behavior of poly(acrylic acid).

The disappearance of the abrupt rate change on going from the HPMA homopolymer to the copolymer may be due to the change in the solvent system from DMSO/H₂O to 100% water. Such solvent effects have previously been demonstrated by Vanzo,²¹ where the neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) showed an abrupt rate decrease when hydrolyzed in 90/10 (v/v) DMSO/H₂O, but no rate decrease was observed in 50/50 solutions or in 100% water.

Several other researchers investigated the effects of solvents on alkaline hydrolysis rates.²² Pasch et al.²³ concluded that the alkaline hydrolysis of methyl methacrylate-ethyl acrylate copolymers in pure DMSO leads to products having molecular weights

Table II Arrhenius Parameters *E* and *A* for the Alkaline Hydrolysis of HPMA

Sample	Solvent	<i>E</i> (kcal/mol)	<i>A</i> (L/mol min)	log <i>A</i>
HPMA monomer	100% H ₂ O	10.3	1.5×10^8	8.18
HPMA homopolymer	55/45 DMSO H ₂ O			
First Step		17	4×10^{14}	14.6
Second Step		21	1.6×10^{16}	16.2
NaA-HPMA copolymers	100% H ₂ O	24	4×10^{12}	12.6

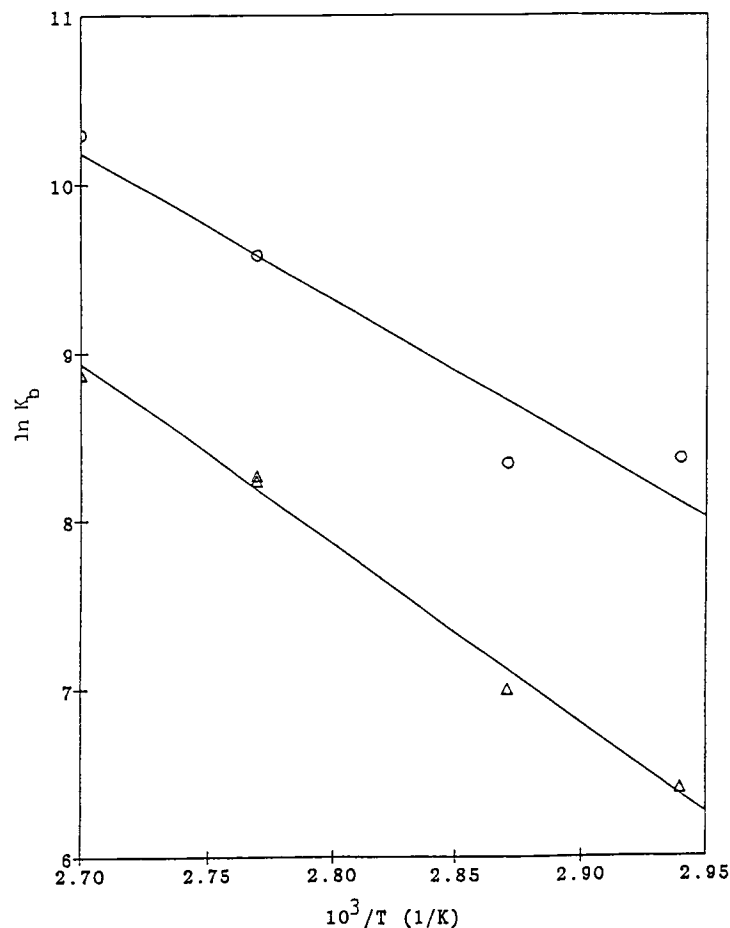


Figure 9 Arrhenius plot for the alkaline hydrolysis of HPMA homopolymer: (O) for the first step (K_{b1}); (Δ) for the second step (K_{b2}).

significantly lower than those of the original copolymers. Mixtures of ethanol and DMSO did not lead to such molecular weight regression. Sandner and Bischof²⁴ studied the rate of alkaline hydrolysis of poly(methyl methacrylate) and copolymers with ethyl acrylate in aqueous mixtures of ethanol, iso-

propanol, DMSO, and 1,4-dioxane. The rate was found to increase with increasing dielectric constant of the solvents and decreasing capability of solvation of OH^- ions. Thus, rates were faster in propanol

Table III Limiting Extent of Conversion for the Alkaline Hydrolysis of NaA-HPMA Copolymers

Feed NaA/HPMA (mol/mol)	M_n	Limiting % Hydrolysis	Temperature (°C)
52/48	2,100	18	81
52/48	2,100	11	60
52/48	2,100	9	46
56/44	11,000	90	88
56/44	11,000	48	79
62/38	1,600	30	96
62/38	1,600	33	89
62/38	1,600	33	71

Table IV Time Calculated for 5% Hydrolysis Conversion for HPMA Monomer and HPMA Copolymers at Various Temperatures and pH Values

pH	Temperature (°C)	Polymer Time	Monomer Time
14	90	14 min	0.3 ms
	60	290 min	1.0 ms
11	90	10 days	0.3 s
	60	201 days	1.0 s
	30	20 years	5.0 s
9	90	2.8 years	0.5 min
	60	55 years	1.9 min
	30	centuries	8.0 min

than in ethanol and were strongly reduced at higher water contents.

Kopic et al.²⁵ hydrolyzed styrene-acrylonitrile copolymers of various compositions by a tenfold excess of potassium hydroxide in dioxane solutions, as well as in ethanol and aqueous suspensions. The reaction rates decreased notably in the order dioxane > ethanol > water. The structure of the copolymer was seen to have a dominant influence on the hydrolysis rate. Work by other investigators indicated how structural changes in polymers affect hydrolysis reactivity.²⁶⁻²⁹ The effect of the type of alkali has also been studied.^{30,31} Komissarov and Baranboim³² found that vibration increased the alkaline reaction rate of polyacrylonitrile.

These references serve to indicate that the hydrolysis rates of methacrylate polymers are dependent upon many variables, such as solvent, ionic strength, and possibly vibration. The changing molecular structure along the polymer chain, or even breakdown of the polymer to lower-molecular-weight segments, can further complicate the reaction kinetics.

CONCLUSIONS

The hydrolysis of HPMA as either the monomer or along a polymer chain follows second-order reaction kinetics, being first order with respect to both hydroxide and HPMA concentration. The rate of hydrolysis of the HPMA monomer is fast, with complete hydrolysis occurring within moments of being in moderately alkaline solutions of pH above 9 at normal ambient temperatures. While following the same reaction kinetics, the rate of hydrolysis of the HPMA polymer is orders of magnitude slower and can be considered stable toward alkaline hydrolysis as it will hydrolyze at an appreciable rate only if the reaction conditions are severe. The use of DMSO as a cosolvent with water can increase the rate of hydrolysis of the polymer.

REFERENCES

- J. M. Gaidis and J. M. Daly, U.S. Pat. 4,968,734 (1990).
- J. Seidl, A. Matejicek, E. Krejcar, and J. Horky, *J. Appl. Polym. Sci.*, **30**(4), 1741 (1985).
- A. Matejicek, J. Seidl, E. Krejcar, and J. Matyas, *Angew. Makromol. Chem.*, **121**, 171 (1984).
- A. Matejicek, J. Seidl, E. Krejcar, and J. Matyas, *Angew. Makromol. Chem.*, **120**, 105 (1984).
- W. Heidmann and H. Koester, *Makromol. Chem.*, **181**(12), 2507 (1980).
- F. C. Baines and J. C. Bevington, *J. Polym. Sci.: Part A-1*, **6**, 2433 (1968).
- J. C. Bevington, R. Brinson, and B. J. Hunt, *Makromol. Chem.*, **134**, 327 (1970).
- N. A. Plate and M. V. Lomonosov, in *Proceedings, NATO, Advanced Study Inst. Reactions on Polymers*, J. A. Moore, Ed., D. Reidel Pub. Co., Boston, MA, July 1973, pp. 169-187.
- J. Jakes, *Collect. Czech. Chem. Comm.*, **45**(4), 1197 (1980).
- S. Crisp, B. G. Lewis, and A. D. Wilson, *J. Dent. Res.*, **54**, 1238 (1975).
- G. H. Peterson, *J. Polym. Sci.*, **28**, 458 (1958).
- M. Finemann and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
- T. Kelen and F. Tudos, *J. Macromol. Sci.-Chem.*, **A9**(1) (1975).
- F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
- Pekariinen, *Ann. Acad. Sci., Fennicae*, **AII**(62) (1954).
- G. Smets and W. De Loecker, *J. Polym. Sci.*, **41**, 375 (1959).
- P. Haberfield, J. Friedman, and M. F. Pinkston, *J. Am. Chem. Soc.*, **94**, 71 (1972).
- J. Moens and G. Smets, *J. Polym. Sci.*, **23**, 931 (1957).
- H. Kawabe and M. Yanagita, *Bull. Chem. Soc. Jpn.*, **42**(11), 3109 (1969).
- H. Kawabe and M. Yanagita, *Bull. Chem. Soc. Jpn.*, **44**(2), 310 (1971).
- B. E. Vanzo, *Synthesis, Characterization, and Hydrolysis Behavior of Poly(Alkyl Styrenesulfonates)*, Ph.D. Dissertation, Polymer Science and Engineering, University of Massachusetts, 1984.
- S. Okano and H. Sobue, *Seikei Daigaku Kogakubu Kogaku Hokoku*, **17**, 1319 (1974).
- H. Pasch, H. Schulze, and G. Schulz, *Makromol. Chem.*, **188**, 1047 (1987).
- B. Sandner and C. Bischof, *Angew. Makromol. Chem.*, **115**, 207 (1983).
- M. Kopic, F. Flajsman, and Z. Janovic, *J. Macromol. Sci.-Chem.*, **A24**(1), 17 (1987).
- P. Bajaj, R. B. Chavan, and B. Manjeet, *J. Macromol. Sci.-Chem.*, **A22**(9), 1219 (1985).
- E. N. Zil'berman and A. A. Starkov, *Tr. Khim. Khim. Teknol.*, **2**, 74 (1974).
- M. F. Mamedov, B. R. Serebryakov, A. A. Bunyat-Zade, and T. B. Dadashev, *Vysokomol. Soedin., Ser. A*, **14**(1), 107 (1972).
- Y. Sakaguchi, K. Tamaki, and K. Kitajima, *Kobunshi Kagaku*, **27**(307), 845 (1970).
- Y. Sakaguchi, T. Hamada, K. Tamaki, and J. Nishino, *Kobunshi Kagaku*, **30**(1), 18 (1973).
- S. A. Zainutdinov, A. K. Makhkamov, and K. S. Akhmedov, *Dokl. Akad. Nauk Uzb. SSR*, **27**(5), 29 (1970).
- S. A. Komissarov and N. K. Baramboim, *Vysokomol. Soedin., Ser. B*, **11**(11), 805 (1969).

Received September 6, 1991

Accepted December 9, 1991