# Thermal Degradation of Poly(ethylene oxide) and Polyacrylamide with Ascorbic Acid

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**ABSTRACT:** The degradation of poly(ethylene oxide) and polyacrylamide in aqueous solution was studied with ascorbic acid. Gel permeation chromatograph was used to monitor molecular weight dynamics with time. A model based on continuous distribution kinetics showed that the experimental data matched well with theory. The results showed that the degradation of polymers is significantly enhanced in the presence of ascorbic acid. The degradation rate initially increased with ascorbic acid concentration but was independent of it at higher concentrations. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3067–3072, 2006

**Key words:** poly(ethylene oxide); polyacrylamide; degradation; recycling; water soluble polymers; temperature; activation energy

## INTRODUCTION

Water soluble polymers form a major class of industrially important polymers. Of these, poly(ethylene oxide) and polyacrylamide have diverse applications in various branches of industry.[1,2] Growing environmental concern for the safe disposal has resulted in greater drive to find newer methods for polymer degradation. Pyrolysis is the most common method employed for polymer degradation but degradation in solution is more advantageous.[3,4] The reactions caused by free radicals in solutions are very rapid and therefore many initiators capable of producing free radicals are commonly used in polymerization reactions. These initiators can also be used for the oxidative degradation of polymers in solution.[5,6] Ascorbic acid (AA) is a well-known natural antioxidant, commonly referred to as vitamin C. It is used as a food additive and for the prevention of common cold and even certain types of cancer. Structurally it is a sugar acid, which is unstable in air and oxidizes to give dehydroascorbic acid with the formation of a radical intermediate.[7] Polymerization with redox systems containing ascorbic acid has been effective in synthesizing polymers with considerable average molecular weight and rate of polymerization and conversion. The aqueous polymerization of acrylamide was investigated in the presence of air[8] with potassium permanganate in the ascorbic acid system in acidic pH. The initial rate of polymerization increased with AA concentration up to $6 \times 10^{-3}$ mol/L, but subsequent increase in AA concentration decreases the rate and conversion. A similar study of polymerization of acrylamide was conducted with an ascorbic acid–peroxydisulfate system.[9] The rate was found to be constant in the range of AA concentration between $8 \times 10^{-4}$ and $22 \times 10^{-4}$ mol/L and varied as inverse half power at higher concentrations. The overall activation energy was found to be 12.2 kcal/mol. The aqueous polymerization of acrylonitrile with the same initiating system showed that the rate decreased with ascorbic acid concentration beyond $3 \times 10^{-3}$ mol/L. The rate also remained unchanged up to 40°C and thereafter decreased with increase in temperature.[10] Methylmethacrylate and methylacrylamide were polymerized with the same redox system of ascorbic acid–peroxydisulfate.[11,12] Acrylic acid and sodium acrylate were polymerized by ascorbic acid–hydrogen peroxide system with activation energies of 18 and 15 kcal/mol, respectively.[13] Copolymerization was also found to be effective by using only ascorbic acid as the initiator. Kuramoto et al.[14] studied the copolymerization of styrene and fumaronitrile with AA in dioxane in the presence of methanol. The reaction proceeded to form a 1:1 alternating copolymer with the polymerization occurring due to the formation of free radicals from ascorbic acid. In all the above studies, oxygen seemed to be a promoter rather than an inhibitor of polymerization, though the converse is usually true of polymerization reactions. In fact, higher rates of polymerization were obtained in the presence of oxygen

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than in its absence. The effect of ultrasound and ionizing γ-rays in the degradation of ascorbic acid was enhanced in the presence of oxygen.[15]

To the best of our knowledge, only one study has investigated the use of ascorbic acid for the degradation of polymers. The investigation on pectin solutions, produced from orange peel, showed significant viscosity decrease on the addition of ascorbic acid[16] with free radicals being assumed the cause of initiation of the degradation. In the present study, the degradation of poly(ethylene oxide) and polyacrylamide solutions in the presence of ascorbic acid has been investigated. A model based on continuous distribution kinetics was developed to determine the rate coefficients. The effect of temperature and the concentration of ascorbic acid on the degradation were also investigated.

## EXPERIMENTAL

### Materials

Poly(ethylene oxide) was obtained from Sigma Aldrich. Polyacrylamide was synthesized from aqueous solution of acrylamide using potassium persulfate as initiator (0.03%). The reaction was carried out at 50°C by continuously flushing nitrogen into the reaction vessel. The polymer was precipitated with methanol and filtered and dried in vacuum at 60°C till constant weight was obtained. Ascorbic acid (S.D. Fine chemicals, India) was of 99% purity.

### Solution degradation experiments

The polymer solution was prepared by dissolving the polymer in double-distilled deionized water. The concentration of ascorbic acid varied from 0.2 to 4 g/L depending on the polymer. About 15 mL of the polymer solution was taken in culture tubes with screw caps. The temperature (40–70°C) was maintained by a thermostated water bath controlled by a PID controller and the variation in temperature was ±1°C. The tubes were placed in the water bath till they reached the desired temperature and then ascorbic acid was added to the polymer solution. Oxygen is purged into the system for 15 min to ensure that the system is saturated with oxygen. No degradation was observed at all temperatures with and without ascorbic acid if no oxygen was purged into the system. In the presence of oxygen, only samples containing ascorbic acid degraded to lower molecular weight. Control experiments were also conducted at each temperature to verify that no degradation of the polymer occurred without ascorbic acid.

### GPC analysis

The molecular weight distribution was monitored by gel permeation chromatography (GPC). The GPC con-
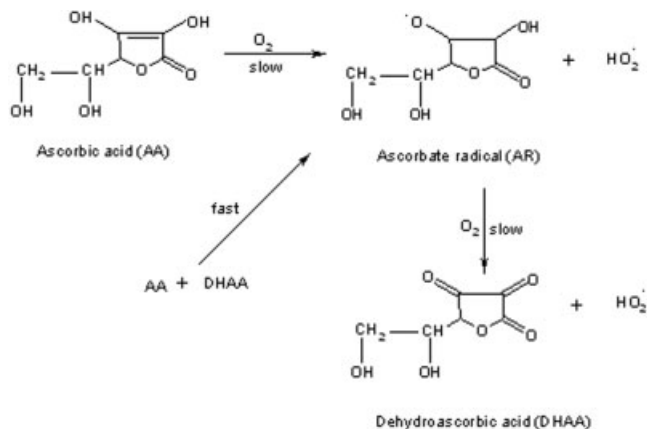


**Scheme 1**

sisted of Ultrahydrogel linear SEC column (Waters, Milford, MA) measuring $7.8 \times 300$ mm$^2$ maintained at 30°C. Double-distilled deionized water was used as eluent at a flow rate of 0.5 mL/min. The refractive index was monitored continuously with a differential refractometer (Waters). About 800 $\mu$L of sample was injected into the system to obtain a chromatogram and converted to molecular weight by using narrow-distribution polyethylene oxide calibration standards. The initial number–average molecular weight, $M_{n0}$, for PEO and PAM were 850,000 and 321,000, respectively.

## RESULTS AND DISCUSSION

### Theoretical model

The emphasis of this section is to develop a theoretical model that is consistent with the reactions that occur when ascorbic acid reacts with polymer. Because no reaction occurs in the absence of ascorbic acid, the model should predict this also. The ascorbic acid dissociates into two radicals, which reacts with the polymer through hydrogen abstraction.

As shown in Scheme 1, the cleavage of ascorbic acid, $C$, results in the formation of the ascorbate radical, $C^*$, and HO$_2$ radical. This can be written as

$$C \xrightarrow{k_p} C^* + HO_2^* \qquad (1)$$

where $k_p$ represents the rate coefficient for dissociation. The rate of ascorbic acid disappearance by dissociation is thus given by

$$\frac{dc_P}{dt} = -k_p c_p \qquad (2)$$

where $c_p$ denotes the molar concentration of ascorbic acid. The hydrogen abstraction from polymer chain,
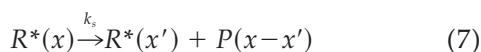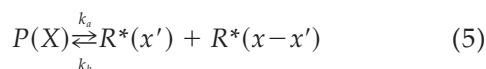
$P(x)$, occurs through the ascorbate radicals reversibly with rate coefficients of $k_d$ and $k_{\mathrm{dr}}$. This reaction is represented as

$$C^* + P(x) \underset{k_{dr}}{\overset{k_d}{\rightleftarrows}} CH + R^*(x) \qquad (3)$$
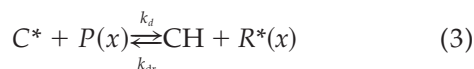
On the basis of eq. (3), the population balance for the consumption of ascorbate radicals can be written as

$$dc(t)/dt = k_p c_p(t) - c(t) \int_0^\infty k_d(x')p(x',t)dx'$$

$$- c(t) \int_0^\infty k_{\mathrm{dr}}(x')r(x',t)dx' \qquad (4)$$

The degradation of the polymer can be represented by the following steps[17] where $P(x)$ and $R^*(x)$ represents the polymer and the polymer radical of molecular weight $x$, respectively.

$$P(X) \underset{k_b}{\overset{k_a}{\rightleftarrows}} R^*(x') + R^*(x-x') \qquad (5)$$

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftarrows}} R^*(x') \qquad (6)$$

$$R^*(x) \overset{k_s}{\rightarrow} R^*(x') + P(x-x') \qquad (7)$$

Equation (5) represents the initiation and termination reactions that occur during polymer degradation with rate coefficients of $k_a$ and $k_b$, respectively. The hydrogen abstraction from the polymer chain is reversible with rate coefficients of $k_h$ and $k_H$ and is represented by eq. (6). The depropagation step occurs by the irreversible $\beta$-scission of the polymer chain with rate coefficient $k_s$ and is shown in eq. (7). The initiation and termination steps are much less frequent compared to the depropagation steps and can be neglected. Thus the population balance equations for polymer and the polymer radical is given by[17]

$$\partial p(x,t)/\partial t = -k_d(x)c(t)p(x,t)+k_{\mathrm{dr}}(x)c(t)r(x,t)$$

$$-k_h(x)p(x,t)+k_H r(x,t)+\int_x^\infty k_s(x')r(x',t)\Omega(x,x')dx' \qquad (8)$$

$$\partial r(x,t)/\partial t=k_d(x)c(t)p(x,t))-k_{\mathrm{dr}}(x)c(t)r(x,t)+k_h(x)p(x,t)$$

$$-k_H r(x,t)-k_s(x)r(x,t)+\int_x^\infty k_s(x')r(x',t)\Omega(x,x')dx' \qquad (9)$$

For random chain scission, the stoichiometric kernel, $\Omega(x,x')$, is given by $1/x'$.[17] The rate coefficients are assumed to be linearly dependent on molecular weight; thus, $k_d(x) = k_d x$. Applying the moment operation on eqs. (8) and (9) yields,[17]

$$\frac{dp^{(j)}}{dt} = -k_d c(t)p^{(j+1)} + k_{\mathrm{dr}}c(t)r^{(j+1)}$$

$$- k_h p^{(j+1)} + k_H r^{(j+1)} + \frac{k_s}{j+1}r^{(j+1)} \qquad (10)$$

$$\frac{dr^{(j)}}{dt} = k_d c(t)p^{(j+1)} - k_{\mathrm{dr}}c(t)r^{(j+1)}$$

$$+ k_h p^{(j+1)} - k_H r^{(j+1)} - k_s\frac{j}{j+1}r^{(j+1)} \qquad (11)$$

The quasi-steady state approximation, which assumes that the change in the radical concentration is zero, can be applied to eq. (11) and the radical concentration is

$$r^{(j+1)} = (j + 1)p^{(j+1)}\frac{k_d c(t) + k_h}{jk_s + (j + 1)(k_{\mathrm{dr}}c(t) + k_H)} \qquad (12)$$

The solution of the differential eq. (4) (by assuming $k_{\mathrm{dr}}$ is less compared to $k_d$) gives

$$c(t) = \frac{c_{p0}k_P\, e^{-k_P t}(-1 + e^{(k_p - k_d p_0^{(1)})t})}{k_p - k_d p_0^{(1)}} \qquad (13)$$

Equation (13) thus represents the variation of the concentration of the ascorbate radical with time where $c_{p0}$ and $p_0^{(1)}$ represent the initial mass concentration of ascorbic acid and polymer, respectively. Substituting the expression for $c(t)$ from eq. (13) in eq. (10) and assuming $k_d p_0^{(1)}$ is much smaller than $k_p$ and when $j = 0$, the zeroth moment representing the molar concentration of polymer, $p^{(0)}$, is

$$\frac{dp^{(0)}}{dt} = \frac{k_{\mathrm{oxd}}c(t)p_0^{(1)}}{1 + (k_{\mathrm{dr}}/k_H)C(t)} \qquad (14)$$

where $k_{\mathrm{oxd}} = k_s k_d/k_H$. On solving eq. (14),

$$\frac{M_{n0}}{M_n} - 1 = \frac{M_{n0}k_1}{k_p}\left[ k_p t + \ln\left\{\frac{c_{p0} + (k_2 p_0^{(1)}/k_p)}{c_{p0} + (k_2 p_0^{(1)} e^{k_p t}/k_p)}\right\}\right] \qquad (15)$$

where $M_n$ is the number–average molecular weight and is given as, $M_n = p^{(1)}/p^{(0)}$, $k_1 = k_s k_d/k_{\mathrm{dr}}$, and $k_2 = k_d k_H/k_{\mathrm{dr}}$. Equation (15) thus represents the variation of the number–average molecular weight with time. Because all parameters are known, the rate coefficients $k_1$ and $k_2$ can be obtained by nonlinear regression of experimental data. The rate co-
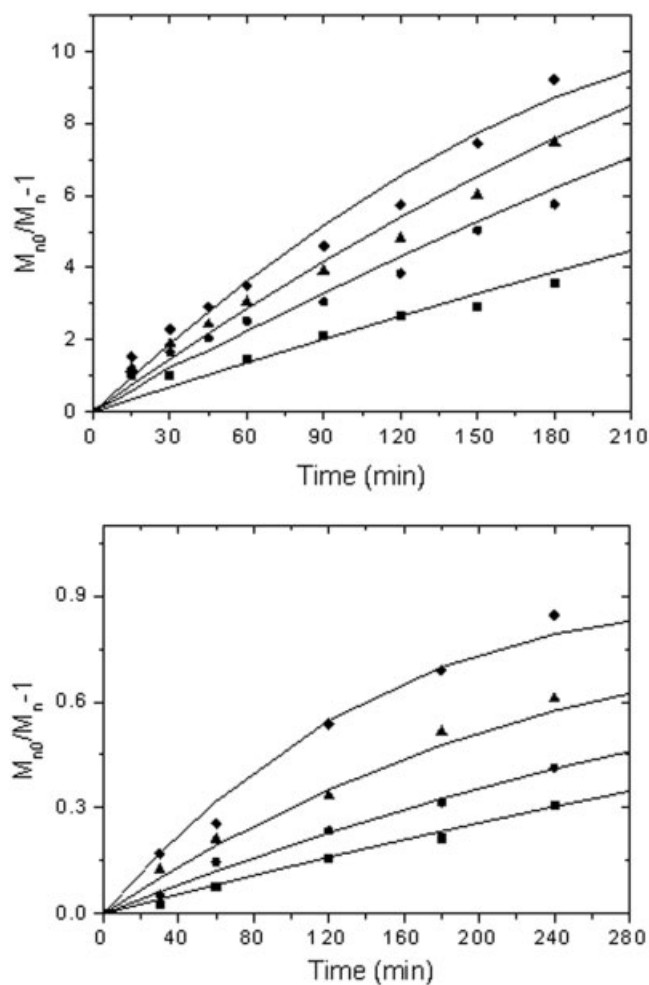
**Figure 1** Variation of $[(M_{n0}/M_n) - 1]$ with time at different temperatures at a fixed polymer concentration of 2 g/L. The concentration of ascorbic acid used for the degradation of PEO and PAM was 0.5 and 1 g/L, respectively. The points are from experiment and the solid lines are from theory by nonlinear regression of experimental data. (a) PEO and (b) PAM. (■), 30°C; (●), 40°C; (▲), 50°C; and (♦), 60°C.

efficient, $k_p$, for ascorbic acid degradation at different temperatures was taken from literature.[18] When ascorbic acid concentration is zero, the expression reduces to

$$\frac{M_{n0}}{M_n} - 1 = 0 \qquad (16)$$

This indicates that no degradation can be observed in the absence of ascorbic acid, and is consistent with experimental data.

### Degradation with ascorbic acid

The degradation of PEO and PAM was conducted at five different temperatures and at different concentrations of ascorbic acid and polymer. The initial pH of

PEO and PAM solutions was 6.4 and 7.2, respectively. On adding ascorbic acid to the solutions, pH dropped to 3.5 for both the polymer solutions. After reaction and subsequent degradation, the pH of the final solutions remained at 3.5. To verify whether the degradation occurred due to acidic pH, the experiments were also conducted at pH of 3 in the absence of ascorbic acid. No decrease in the molecular weight of the polymer samples was observed. This shows that ascorbic acid is primarily responsible for the polymer chain scission. Ascorbic acid in aqueous solution undergoes a two-step oxidation–reduction process in the presence of oxygen. The decomposition is a pH-dependent process and in acidic pH, the following mechanism is valid. A one-electron oxidation of ascorbic acid produces semidehydroascorbic acid radical that disproportionates into dehydroascorbic acid and ascorbic acid.[10]

The degradation of PEO and PAM by ascorbic acid at different temperatures is shown in Figure 1(a,b), for PEO and PAM, respectively. The degradation rate coefficients $k_1$ and $k_2$ are obtained by nonlinear regression of experimental data with eq. (16) and are given in Table I for both PEO and PAM. The Arrhenius dependence of degradation rate is shown in Figure 2(a,b). The activation energies, $E_1$ and $E_2$, obtained from the temperature dependence of rate coefficients, $k_1$ and $k_2$, for PEO are 4.5 and 4.4 kcal/mol, respectively. Similarly for PAM, the values of $E_1$ and $E_2$ are 9.2 and 8.5 kcal/mol, respectively.

The effect of ascorbic acid concentration on the degradation of PEO and PAM was also studied. The variation of $(M_{n0}/M_n) - 1$ with time at different concentrations of AA for PEO and PAM at 50°C is given in Figures 3(a) and 3(b), respectively. The degradation rate increases with an increase in AA concentration initially and the rate saturates at higher concentrations of AA. As the concentration of ascorbic acid is large, the variation of $(M_{n0}/M_n) - 1$ is equal to $k_{oxd}k_H M_{n0} t/k_{dr}$, i.e., independent of ascorbic acid concentration. The

**TABLE I**
**Rate Coefficients for the Degradation of PEO and PAM in Presence of Ascorbic Acid (AA)**

| Temperature (°C) | $k_1$ $(10^{-8})$ (mol/g/min) | $k_2$ $(10^{-6})$ (mol/g/min) |
|---|---|---|
| *PEO 2 g/L, AA 0.5 g/L* | | |
| 30 | 5.0 | 4.0 |
| 40 | 7.0 | 5.0 |
| 50 | 8.0 | 6.0 |
| 60 | 10.0 | 8.0 |
| *PAM 2 g/L, AA 1.0 g/L* | | |
| 30 | 1.3 | 1.0 |
| 40 | 2.0 | 2.0 |
| 50 | 3.0 | 3.0 |
| 60 | 4.7 | 4.0 |

rate coefficient values are the same, as obtained earlier. PEO degraded at a lesser concentration of ascorbic acid (0.2–0.7 g/L) whereas PAM required a higher concentration (1–4 g/L).

The variation of degradation rate with the polymer concentration (2–10 g/L) was also studied at 50°C and at 0.5 and 1 g/L concentration of ascorbic acid for PEO and PAM, respectively. The degradation profiles were consistent with that obtained by substituting the polymer concentration in eq. (16). This indicates that the model is suitable for a wide range of polymer and ascorbic acid concentration.

## CONCLUSIONS

The degradation of PEO and PAM by ascorbic acid was found to be very efficient. Higher molecular weight polymer degraded rapidly even at 30°C. Moreover, significant rate of degradation of the polymers was obtained even with low concentrations of ascorbic
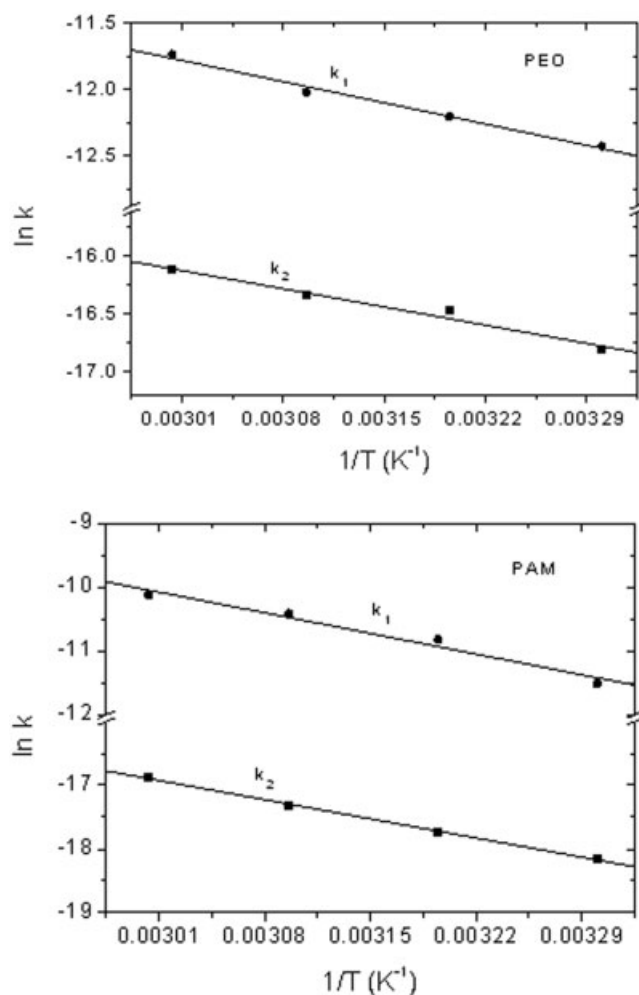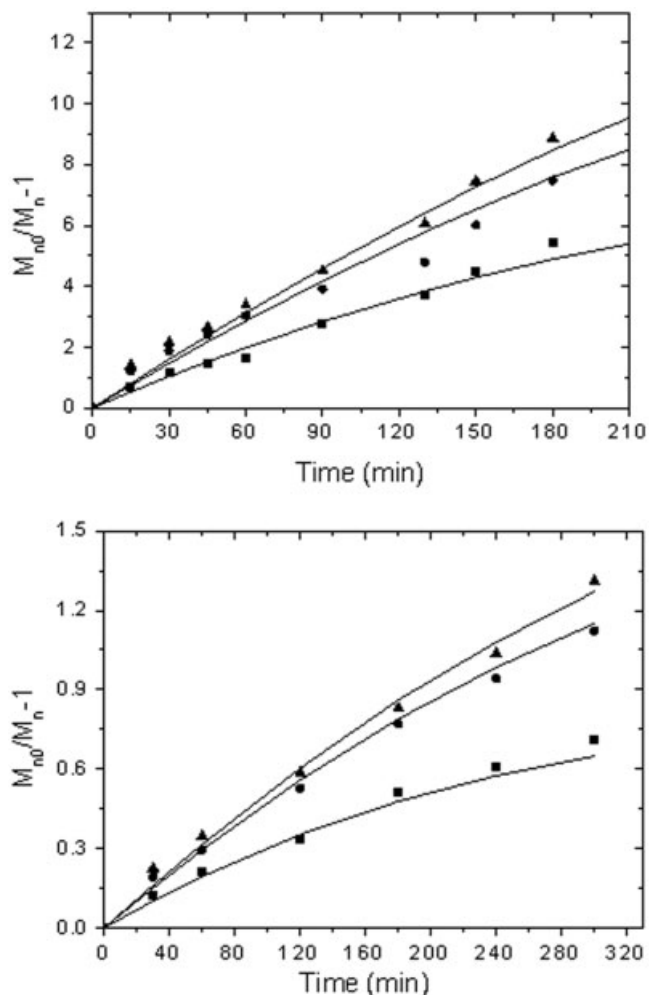


**Figure 3**  Variation of $[(M_{n0}/M_n) - 1]$ with time at different concentrations of ascorbic acid at a fixed temperature of 50°C and polymer concentration of 2 g/L. The points are from experiment and the solid lines are from theory by nonlinear regression of experimental data. (a) PEO and (b) PAM. (■), 0.2 g/L; (●), 0.5 g/L; and (▲), 0.7 g/L for PEO. (■), 1 g/L; (●), 3 g/L; and (▲), 4 g/L for PAM.

acid. Thus, ascorbic acid serves as an inexpensive, efficient, and nontoxic chemical for the degradation of PEO and PAM. From a commercial viewpoint, these properties make it an attractive reagent for use in polymer degradation.

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**Figure 2**  Variation of the overall rate coefficient with temperature. (a) PEO and (b) PAM. (■), $k_1$ and (●), $k_2$.

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