# Kinetic Models for the Autocatalytic Deprotection of Copolymers Based on 4-Hydroxystyrene and Styrene*

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## SYNOPSIS

Poly(tert-butylcarbonyloxystyrene) by itself or as a component in a copolymer decomposes at elevated temperatures (about 130–150°C) to give the free phenolic group, isobutylene, and carbon dioxide. It has been found that the isothermal conversion of the ester (the protected phenol) to the free phenol proceeds slowly at first but accelerates with time so that the rate of reaction increases until more than half the reaction is over. Thus, the pattern of conversion with time is typical of an autocatalytic process. Although the classical model of autocatalysis which we reported earlier gave a qualitative representation of the process, two modifications to the model result in a much better approximation to the actual experimental data. These two experimentally rational modifications take into account the very real decrease in the volume of the reacting system as conversion (deprotection) proceeds and the possibility that the catalyzed (fast) reaction is second order in free phenol. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In the absence of any added acid catalyst, the decomposition of poly(tert-butylcarbonyloxystyrene), abbreviated here as PBOCST, exhibits the classical features of an autocatalyzed reaction,[1] i.e., the isothermal conversion of the ester to the free phenol form proceeds slowly at first but accelerates with time so that the rate of reaction increases until more than half the reaction is over. When a strong acid is added, even in small quantity, the rate is governed by the added material and does not show such extremely nonlinear behavior.[2–4]

The deprotection reaction is of interest because the polymer is useful as a resist material for electron-beam patterning in microlithography. Exposure of a thin film of PBOCST to a modest dose (10 $\mu$C/cm$^2$) of 20 kV electrons is enough to deprotect a small fraction of the phenolic groups (Fig. 1). Subsequent heating causes both the exposed and unexposed polymers to undergo deprotection, but the unexposed portion lags behind the exposed portion. Thus, by stopping the thermal deprotection at the proper time, there is enough difference in alkali solubility between the two areas to permit the liquid development of a useful image.[1]

Autoacceleration of chemical reactions is not uncommon. The well-known Trommsdorff effect in polymerization is due mainly to the increase in viscosity of the system. Adiabatic reactions also can show an increase in rate because of the increase in temperature which offsets the decreasing concentration of reactants. In the deprotection system, the reaction is essentially isothermal with no obvious change in mobility of radicals with conversion. Thus, it seems reasonable to propose that the initial conversion of some ester groups to free phenol generates a catalyst for further deprotection. In other words, it is a classical autocatalytic reaction.

## MODELS FOR AUTOCATALYSIS

### Theoretical Models and Experimental Data

The typical experimental data for deprotection can be compared with various theoretical models as
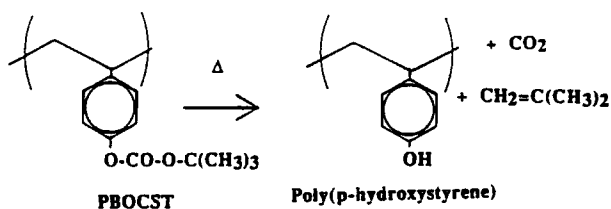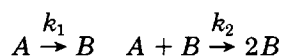
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**Figure 1**   Deprotection reaction of PBOCST and co-polymers.

shown in Figure 2. The equations corresponding to the four possible models are derived later in the Derivations section. First, consider the classical case of two reactions with no change in volume in the reacting system. Assume that the two reactions are

$$A \xrightarrow{k_1} B \quad A + B \xrightarrow{k_2} 2B$$

where the protected (ester) groups correspond to $A$ and the free phenol groups correspond to $B$. The classical model for autocatalysis is represented by

$$\{1/(1 + R)\}\{\ln\{(fR + 1)/(1 - f)\} = kt \quad (1)$$

where $f$ is the degree of conversion; $t$, the time; $R$, the ratio $A_0 k_2 / k_1$; and $A_0$, the initial molar concentration of $t$-BOC groups.

There are two experimentally rational modifications which can be made to the classical model of autocatalysis. The first is the very real decrease in volume of the reacting system as conversion proceeds. We can modify the previous model[5] by assuming that the volume at some time $t$ is changed to $V$ from its initial value of $V_0$ according to the relationship
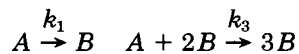
$$V/V_0 = 1 + \beta f \quad (2)$$

With $x = (1 - f)$, this case is represented by

$$\frac{-(1 + \beta)}{(1 + R + \beta)} \ln\left[\frac{1 + R + \beta - (\beta + R)x}{x}\right]$$

$$+ \frac{\beta}{(\beta + R)} \ln[1 + R + \beta - (\beta + R)x] = -k_1 t \quad (3)$$

The second modification assumes that the catalyzed (fast) reaction is of a third order.

We assume[6] that the two reactions are such that

$$A \xrightarrow{k_1} B \quad A + 2B \xrightarrow{k_3} 3B$$

As a result, conversion now is given by

$$-k_1 t = \left[\frac{1}{2(1 + R')}\right]\ln\left[\frac{(1 - f)^2}{(1 + R'f^2)}\right]$$

$$+ \left(\frac{\sqrt{R'}}{1 + R'}\right)\tan^{-1}(-f\sqrt{R'}) \quad (4)$$

where $R' = k_3 A_0^2 / k_1$.

Finally, as seen in Figure 2, a combination of the two modifications (with $\beta = -0.50$) gives a very good approximation to the experimental data according to the equation

$$\left\{\frac{1}{2(1 + 4R')}\right\}\ln(1 - f)^2 + \left\{\frac{4\sqrt{R'}}{(1 + 4R')}\right\}$$

$$\times \left[\tan^{-1}\left\{\frac{(1 - 2R'f)}{2\sqrt{R'}}\right\} - \tan^{-1}\left\{\frac{1}{2\sqrt{R'}}\right\}\right]$$

$$= -k_1 t \quad (5)$$

In each case for Figure 2, constants were fitted to the data using an optimization program (Excel™).

When data on various compositions or temperatures are compared on the same coordinates, a convenient shortcut method is to plot the fractional conversion of ester to phenol groups, $f$, vs. a reduced time, $q$, which is real time, $t$, normalized by the half-life, $t_{1/2}$, which is the time when $f = 0.5$, i.e.:
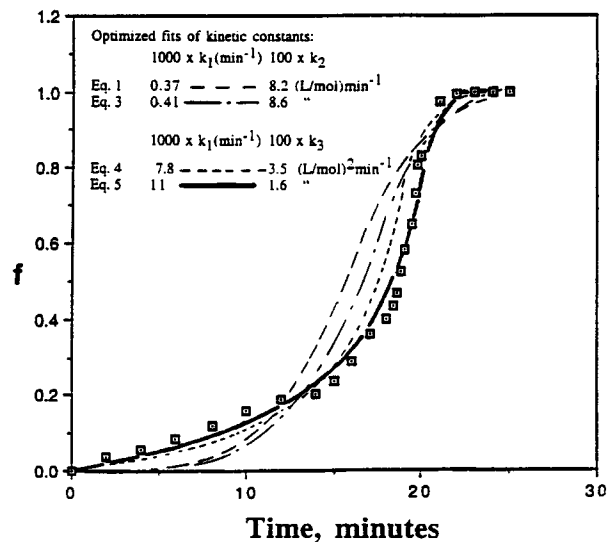
$$q = t/t_{1/2} \quad (6)$$



**Figure 2**   Comparison of deprotection kinetics for homopolymer. Points are experimental data at 150°C. Lines correspond to the four models [eqs. (1) and (3)–(5)].
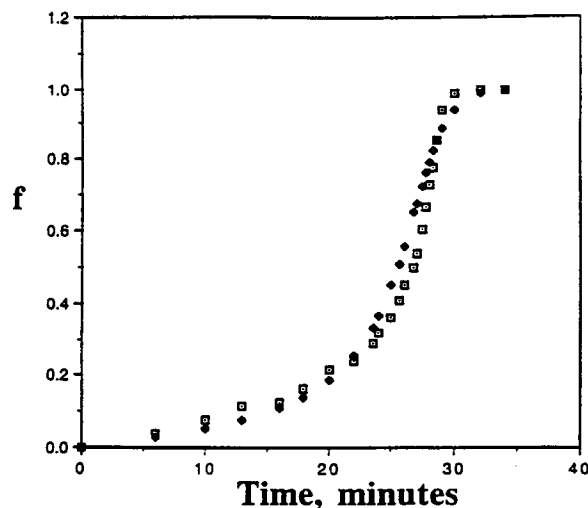
**Figure 3** (■) Experimental data and (◆) fitted eq. (4) for a copolymer with 30 wt % styrene.

**Table I   Kinetic Constants for Deprotection of Copolymers as Represented by Eq. (4)**

| Wt. Fraction of Styrene in Copolymer | $1000 \times k_1$ $(\text{min}^{-1})$ | $100 \times k_3$ $[(\text{L/mol})^2$ $\text{min}^{-1}]$ | $100 \times r$ $= k_1/k_3 A_0^{2a}$ |
|---|---|---|---|
| 0 | 7.79 | 3.52 | 4.02 |
| 0 | 8.07 | 3.29 | 4.46 |
| 0 | 5.89 | 4.08 | 2.63 |
| 5 | 5.08 | 4.24 | 2.29 |
| 10 | 5.83 | 4.28 | 2.75 |
| 15 | 4.85 | 4.52 | 2.75 |
| 20 | 4.38 | 6.01 | 1.65 |
| 25 | 4.34 | 6.24 | 1.68 |
| 30 | 4.83 | 5.54 | 2.26 |
| 40 | 5.62 | 6.01 | 2.84 |
| 50 | 5.42 | 7.23 | 2.71 |

[a] $A_0 = 5.5 \, (1 - \text{wt. fraction of styrene})$, mol/L.

## COPOLYMERS

A series of copolymers of the protected unit with styrene was made. The deprotection of each copolymer was studied at 150°C. To fit rate constants to the various samples, eq. (4) was used even though eq. (5) was a slight improvement for the homopolymer. The rationale for choosing the simpler model was the difficulty of deriving an analytical solution incorporating the variable shrinkage, $\beta$, for intermediate values between $-0.5$ and 0.

The fit for samples with 30 and 50 wt % styrene are reasonably represented by eq. (4) (Figs. 3 and 4). The values for the fitted constants are summa-
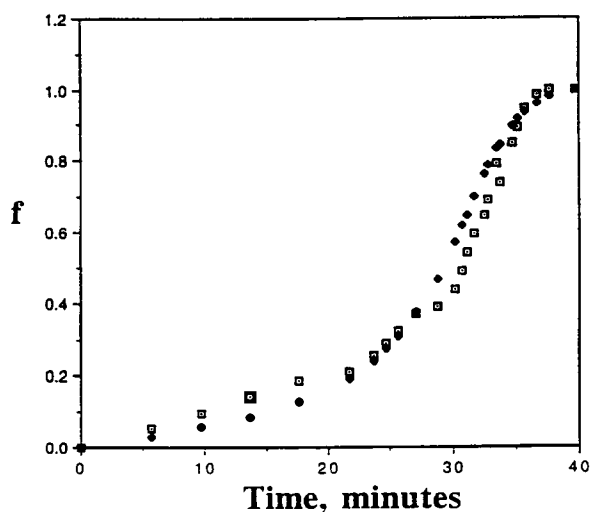
rized in Table I. There appears to be no consistent trend in the values of $k_1$. Since the first-order decomposition should not depend on the accessibility of groups, the constancy is realistic. On the other hand, the third-order constant, $k_3$, appears to increase more or less directly as the styrene content increases. Intuition predicts the opposite trend. The interposition of blocking groups should cause the combination of individual phenolic groups to become less likely rather than more likely. However, the presence of styrene moieties could conceivably allow the protected groups to be closer to each other by removing steric barriers to rotation. This would make cooperation easier and increase $k_3$. At any rate, the change in $k_3$ with styrene content is not dramatic enough either to justify or to abandon the third-order hypothesis.

## ENERGY OF ACTIVATION

The data for isothermal deprotection of the homopolymer at various temperatures have been found to be superimposable (Fig. 5) when plotted as conversion vs. reduced time defined by eq. (6). The implication of the superposition is that the same value of $R'$ is applicable at every temperature. The half-lives are inversely proportional to $k_1$. If $R'$ does not change much with temperature, then $k_3$ must vary with temperature in almost the same way as does $k_1$. Thus, the energy of activation, $(E_a)_1$, which is about 30 kcal/mol for the first-order decomposition reaction, must be similar to the energy of activation, $(E_a)_3$, for the third-order decomposition reaction.
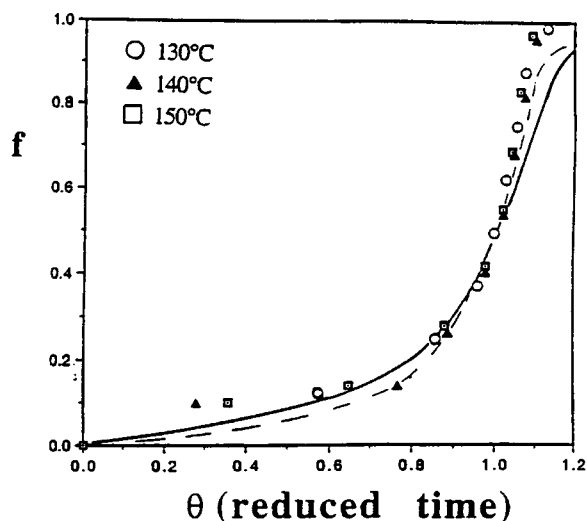
**Figure 4** (□) Experimental data and (◆) fitted eq. (4) for a copolymer with 50 wt % styrene.

**Figure 5**   Data at three temperatures are superposed on reduced coordinates. The solid line is eq. (4) fitted for 150°C ($R' = 130$). The dashed line (with $R' = 300$) is added for comparison.

The value of 30 kcal/mol is not unlike the values for decomposition of many peroxides and azo compounds.[1]

## DERIVATIONS

### Second Reaction Is Second Order

This is the classical autocatalytic model. The derivation of an equation in terms of conversion, $f$, as a function of time, $t$, is as follows:

We write the usual rate equations in terms of reactant concentrations (brackets omitted) and rate constants[7]:

$$-dA/dt = k_1A + k_2AB \quad \text{and} \quad B = A_0 - A \quad (7)$$

where $A_0$ is the initial concentration of $A$. Let $f$ = conversion, i.e.:

$$f = B/A_0 = (A_0 - A)/A_0 \quad (8)$$

Then,

$$-(1/A_0)dA/dt = k_1A/A_0 + k_2(A/A_0)(B/A_0)A_0 \quad (9)$$

Or

$$df/dt = k_1(1 - f) + k_2A_0f(1 - f) \quad (10)$$

Let

$$k = k_2A_0 \quad \text{and} \quad R = A_0k_2/k_1 = 1/r \quad (11)$$

Then,

$$df/dt = (1 - f)(k_1 + kf) = k(1 - f)(r + f) \quad (12)$$

To integrate, we rearrange to

$$\int_0^f \frac{df}{(f + r)(1 - f)} = \int_0^t kdt = kt \quad (13)$$

and

$$-\left[\frac{1}{(1 + r)}\right]\left\{\ln \frac{(1 - f)}{(f + r)} + \ln r\right\} = kt \quad (14)$$

This is the same as eq. (1). Also,

$$r\left\{\frac{r(1 - f)}{(f + r)}\right\} = \exp\{-(1 + r)kt\} \quad (15)$$

Then,

$$f = \frac{r[1 - \exp\{-(1 + r)kt\}]}{[\exp\{-(1 + r)kt\} + r]} \quad (16)$$

It is convenient to express conversion in terms of a *parametric* time, $z = (1 + r)kt$:

$$f = r[1 - \exp(-z)]/[r + \exp(-z)] \quad (17)$$

so that

$$f/(1 - f) = \{r/(1 + r)\}\{\exp(z) - 1\} \quad (18)$$

Similarly, an equation in terms of a *reduced* time, $q = z/z_h = t/t_{1/2}$, can be obtained in several steps:

$$\{f(1 + r)\}/\{r(1 - r)\} + 1 = \exp(z) \quad (19)$$

and

$$z = \ln(f + r) - \ln(r) - \ln(1 - f) \quad (20)$$

At $f = \frac{1}{2}$, $z = z_h$ and

$$z_h = \ln(1 + 2r) - \ln(r),$$

$$\text{which is approximately} = -\ln(r) \quad (21)$$

At a reduced time $q$,

$$q = 1 - [\ln\{(f + r)/(1 - f)\}]/\ln(r) \quad (22)$$

In other words, $q$ is a function only of $f$ and $r$. This can be put in a form which is explicit in $f$ by starting with eq. (14) rewritten as

$$\ln\left[\frac{f(1+r)}{r(1-f)} + 1\right] = z \qquad (23)$$

Divide by $-z_h/\ln r$ which is $= 1$:

$$\ln\left[\frac{f(1+r)}{r(1-f)} + 1\right] = -\left(\frac{z}{z_h}\right)\ln r = -\theta \ln r \qquad (24)$$

Now

$$\left[\frac{f(1+r)}{r(1-f)} + 1\right] = \exp(-\theta \ln r) = r^{-\theta} \qquad (25)$$

Or

$$\frac{f}{(1-f)} = \left\{\frac{r}{(1+r)}\right\}\{r^{-\theta} - 1\} \qquad (26)$$

### Volume Change During Reaction

The PBOCST system loses about 45% of its initial volume during deprotection. The concentration of $A$ can be written as $N/V$, where $N$ is the number of moles of $A$. Eqs. (7)–(9) are now modified to be

$$-dA/dt = -(1/V)dN/dt$$
$$= \{-A_0/(1 + \beta f)\}df/dt = k_1A + k_2AB \qquad (27)$$

$$BV = A_0V_0 - AV \qquad (28)$$

$$A/A_0 = (1 - f)/(1 + \beta f) \qquad (29)$$

Combining these yields

$$A_0df/dt = k_1A_0(1 - f) + k_2A_0(1 - f)$$
$$\times \{A_0 - A_0(1 - f)\}/(1 + \beta f) \qquad (30)$$

$$df/dt = k_1(1 - f) + k_2A_0(1 - f)f/(1 + \beta f) \qquad (31)$$

Let $f = 1 - x$ and, again, $R = k_2A_0/k_1$:

$$(-1/k_1)dx/dt = x + Rx(1 - x)/(1 + \beta - \beta x)$$
$$= x\{1 + R(1 - x)/(1 + \beta - \beta x)\} \qquad (32)$$

Also,

$$-k_1dt = dx/[x\{1 + R(1 - x)/(1 + \beta - \beta x)\}] \qquad (33)$$

Integration between limits of conversion 1 to $x$ as time goes from 0 to $t$ gives the somewhat lengthy result previously presented as eq. (3). In the case of PBCOST, $\beta = -0.45$.

### Second Reaction Is Third Order

$$-dA/dt = k_1A + k_3AB^2 \qquad (34)$$

$$df/dt = k_1(1 - f) + k_3A_0^2f^2(1 - f) \qquad (35)$$

Let

$$x = 1 - f \text{ again, but, now, } R' = k_3A_0^2/k_1$$

Then,

$$(-1/k_1)dx/dt = x(1 + R') - 2R'x^2 + R'x^3 \qquad (36)$$

Manipulation is simplified if we substitute $X = (1 + R') - 2R'x + R'x^2$. Then, integration and conversion of $x$ back to $f$ yields previously presented eq. (4).

### Volume Change with Third-order Reaction

In this case, we combine the third-order reaction with the real fact of variable volume. Using the same definitions as before, we can derive an equation in $x$ (which is $1 - f$ as before):

$$-(1/k_1)dx/dt$$
$$= x + R'x(1 - x)^2/(1 + \beta - \beta x)^2 \qquad (37)$$

The integration of this is simplified greatly if $\beta = -0.5$, which is very close to the actual value for the deprotection reaction. Even then, the result is the somewhat cumbersome eq. (5).

### Estimation of Kinetic Rate Constants

The commercial optimization package used to fit equations to experimental data was Excel™ Solver for Windows. Each equation [eqs. (1) and (3)–(5)] is put in a form explicit in a residual, Res:

$$\text{Res} = F(f_i, t_i, k_1, R_j) \qquad (38)$$

In eqs. (1) and (2), $R_j$ is $A_0k_1/k_2$, and in eqs. (34) and (36), it is the same as $R' = A_0^2k_1/k_2$. Also, the subscript $i$ refers to an individual experimental point. For example, eq. (1) becomes

$$\text{Res} = \{1/(R + 1)\}\ln\{(f_iR + 1)/$$
$$(1 - f_i\} - k_1t_i \quad (39)$$

The objective function to be minimized is the sum of the squares of Res.

The optimization program minimizes the objective function for a given set of data points, thus producing values of $k_1$ and $R_j$, which are the closest fit to all the data. This kind of "least-squares" fit is familiar for linear equations. The same caveats that are observed for linear systems apply here also. Of course, the values for the constants will be influenced greatly by the data set entered into the spreadsheet in the first place. For the present examples, 20–25 points were used, with approximately equally spaced values of $f_i$. Another feature of the program is that good initial guesses are needed for the parameters to be estimated. Initial values of $k_1 = 0.01$ and $R_j = 100$ were employed together with the constraint that both be positive numbers.

## CONCLUSIONS

The inclusion of variable volume in the classical autocatalytic model definitely improves agreement with experimental data. Whether the higher-order fast reaction is a real mechanism or merely an artifact, the improvement in rationalizing the data is rather dramatic.

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