

Applying Tikhonov Regularization to Process the Kinetic Data of Polymerization

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ABSTRACT: Most experimental polymerization kinetic data are in the form of degree of polymerization versus time plots. However, to explore kinetic models it is more useful to have the data as polymerization rate versus degree of polymerization plots. Converting degree of polymerization into rate is an ill-posed problem in that if inappropriate methods are used the noise in the data will be amplified, leading to unreliable results. This paper describes a procedure, based on Tikhonov regularization, to perform this conversion. The procedure is independent of kinetic models and keeps noise amplification under control. Its performance is demon-

strated using several sets of published polymerization kinetic data. In each case the computed rates are used to determine the parameters in the rate expression proposed in the original papers. Modified rate expressions will also be explored. The ease with which such investigations can be performed highlights the advantages of this new procedure. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1625–1633, 2004

Key words: kinetics (polym.); degree of polymerization; modeling; Tikhonov regularization; integral equation

INTRODUCTION

In a typical polymerization kinetic investigation the progress of the reaction is monitored by measuring the degree of polymerization $X(t)$ as a function of time t . Guided by prior experience or knowledge of the likely mechanism, a rate expression is then proposed that relates the polymerization rate $r(t) = dX(t)/dt$ to $X(t)$ and other relevant experimental conditions. The next step is to determine the numerical values of the kinetic parameters in the rate expression from the experimental data. The general method for doing this is to treat the rate expression as a differential equation and integrate it to give the computed degree of polymerization $X(t)$ as a function of time with the kinetic parameters appearing as unknowns to be determined. Typically these parameters are found by least-squares regression between the computed degree of polymerization and its experimentally observed counterpart.

The polymerization rate expression can take the form of a differential equation of such complexity that it can only be integrated numerically. Determination of the kinetic parameters in the rate expression by least-squares regression requires repeated numerical integration of the equation, making the entire process very time consuming. There is often another problem. Because of the generally complex form of the inte-

grated rate expression, there may be several locally optimum kinetic parameter sets. It is also possible that the minimum of the least-squares regression computation may not be sufficiently sharp to allow the kinetic parameters to be determined to the degree of accuracy required.

The present investigation adopts a different approach. Instead of integrating the rate expression and then matching the computed $X(t)$ with the experimental observations, the experimental data are converted into polymerization rate $dX(t)/dt$. This is compared directly with the proposed rate expression. The rate expression is usually a simpler expression, compared to the form of the integrated $X(t)$ profile, and allows the parameters in the expression to be determined with greater ease and possibly also to a higher degree of certainty.

Thus, the key step in this new procedure is the differentiation of the experimentally measured $X(t)$ data. Direct differentiation of experimental data usually does not lead to reliable polymerization rates because differentiation amplifies the unavoidable noise in the data.¹ Special procedures were developed to perform this task.² Recently Yeow et al. showed that Tikhonov regularization is a reliable yet simple procedure for obtaining reaction rates from the time-concentration data for a wide class of chemical reactions.³ They demonstrated that the procedure is successful in keeping noise amplification under control and has the added advantage that it does not require the assumption of a rate expression to describe the

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original experimental data. The aim of this paper is to demonstrate that this procedure is equally applicable to the kinetic data of polymerization and the advantages observed in its application to simple chemical reactions are also retained in polymerization reactions.

For this purpose a number of sets of polymerization kinetic data are taken from the published literature. These are converted into rate profiles and compared with generally accepted kinetic models to illustrate the simplicity of the computation involved. Since the models are either as proposed by the originators of the data or minor modifications thereof, no attempt will be made to justify them. The experimental conditions and methods used in generating these data can be found in the original literature. Apart from a brief mention, such details will be omitted.

THE GOVERNING EQUATION

The relationship between the polymerization rate $r(t) = dX(t)/dt$ and the degree of polymerization $X(t)$ can be rewritten as

$$X(t) = \int_{t'=0}^t r(t') dt'. \quad (1)$$

This is an integral equation of the first kind for the unknown polymerization rate $r(t)$ and reveals clearly the ill-posed nature of the problem.² If inappropriate methods are used to solve this integral equation the noise in the experimental degree of polymerization data will be amplified, leading to inaccurate results.

Following Yeow et al.,³ eq. (1) is transformed into

$$\begin{aligned} X^C(t) &= \int_{t'=0}^t \left[\frac{dt' r(t')}{dt'} - t' f(t') \right] dt' = t' r(t') \Big|_{t'=0}^t \\ &- \int_{t'=0}^t t' f(t') dt' = tr(t) - \int_{t'=0}^t t' f(t') dt' = t \left(\int_{t'=0}^t f(t') dt' + r_0 \right) \\ &- \int_{t'=0}^t t' f(t') dt' = \int_{t'=0}^t (t - t') f(t') dt' + tr_0, \quad (2) \end{aligned}$$

where $f(t) = dr(t)/dt$ and $r_0 = r(0)$. Equation (2) is an integral equation of the first kind for $f(t)$. Tikhonov regularization is used to obtain an approximate nu-

merical solution for the unknown function $f(t)$ and the constant r_0 . The superscript C is used to distinguish the computed degree of polymerization given by this equation from its experimentally measured counterpart which will be denoted by the superscript M.

Once $f(t)$ and r_0 are known, $r(t)$ and $X(t)$ can be obtained by direct numerical integration. Since the integration process averages out noise, the $r(t)$ thus obtained can be expected to be relatively free from the influence of experimental noise.

Equation (2) is the starting point of the present investigation. Inputs to this equation are the experimentally measured degree of polymerization data points: $(t_1, X_1^M), (t_2, X_2^M), (t_3, X_3^M), \dots, (t_{N_D}, X_{N_D}^M)$. N_D is the number of points in the set. It is usually a relatively small number, typically around 10 to 50, and the data points may or may not be regularly spaced out in time. From the way eq. (2) was obtained it is clear that this equation is independent of the nature of the polymerization reaction.

TIKHONOV REGULARIZATION

To apply Tikhonov regularization to eq. (2), $f(t)$ for $0 \leq t \leq t_{N_D}$ is discretized into N_K uniformly spaced points $(f_1, f_2, \dots, f_{N_K})$. Typically N_K is a large number of the order of 401 or 601 or larger. The unknowns of the problem are $(f_1, f_2, \dots, f_{N_K}, r_0)$. These unknowns can, in principle, be determined so that they

(i) minimize the sum of squares of the difference between the measured and computed degrees of polymerization to ensure accuracy;

(ii) minimize the sum of squares of the second derivatives $d^2f(t)/dt^2$ at the internal discretization points to ensure a smooth $f(t)$.

In Tikhonov regularization, instead of minimizing (i) or (ii) a linear combination of these two requirements is minimized. It can be shown that the set of $(f_1, f_2, \dots, f_{N_K})$ and r_0 that minimize the linear combination is³

$$\mathbf{g} = (\mathbf{A}^T \mathbf{A} + \lambda \boldsymbol{\beta}^T \boldsymbol{\beta})^{-1} \mathbf{A}^T \mathbf{X}^M. \quad (3)$$

\mathbf{g} is used to represent the column vector of the unknowns, i.e., $(f_1, f_2, \dots, f_{N_K}, r_0)$. \mathbf{A} and $\boldsymbol{\beta}$ are known matrices arising, respectively, from the discretization of the integral in eq. (2) and the finite difference approximation of the second derivative $d^2X(t)/dt^2$ at the internal discretization points.³ λ is an adjustable weighting/regularization factor. A large λ favors (ii), resulting in a very smooth $f(t)$. On the other hand a small λ favors (i), leading to a close match with the experimental data but the resulting $f(t)$ may exhibit excessive and physically unrealistic fluctuations. In practice λ is chosen so that the average deviation between the measured and computed $X(t)$ is of the same order as the experimental error bar of $X^M(t)$.

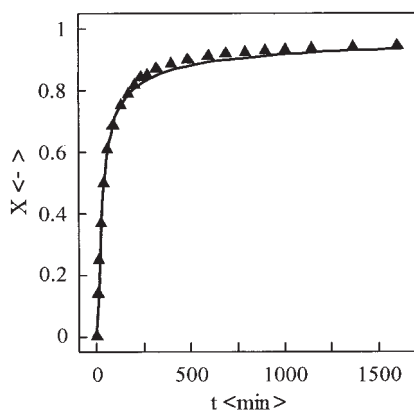


Figure 1 Polyesterification of diethylene glycol with adipic acid. Points are the data of Flory.⁴ The continuous curve is back calculated from the best-fit rate expression given by eq. (4).

POLYMERIZATION DATA AND KINETIC PARAMETERS

Self-catalyzed polyesterification of adipic acid with diethylene glycol

In his investigation of the kinetics of polyesterification Flory reported the polymerization reaction between adipic acid and diethylene glycol at 166°C⁴. His experimental data are presented in Figure 1 as a plot of $X(t)$ against t instead of the common practice of plotting $1/[1-X(t)]^n$ against t with n variously set equal to 1, 3/2, 2.⁴⁻⁶ Each value of the exponent n was found to be appropriate only for a restricted subinterval in the range $0 \leq X \leq 1$.

Equation (3) is now applied directly to convert the discrete $X(t)$ data in Figure 1 into $f(t) = d^2X(t)/dt^2$. In this and in subsequent examples the $f(t)$ is then integrated numerically to give $dX(t)/dt$, which is in turn integrated to give $X(t)$. Since $f(t)$ is well behaved and is known at a large number of regularly spaced discretization points, the two numerical integration steps are very straightforward and can be performed using any of the well-tested numerical integration procedures. The outcome is shown in Figure 2 as a plot of $dX(t)/dt$ versus $X(t)$. In this particular computation $N_K = 1601$ but, for clarity, only every eighth point is shown. The very large N_K used here is atypical and is needed to capture the very rapid increase in $X(t)$ observed for small t (see Fig. 1).

Instead of assuming a rate expression with a different exponent n for different subintervals of $X(t)$, it is proposed that the simple rate expression

$$\frac{dX(t)}{dt} = \frac{k(1 - X(t))^3}{1 + \alpha(1 - X(t))^3} \quad (4)$$

be used to describe the kinetics of this polyesterification reaction. k and α are the two parameters to be determined. The exponent $n = 3$ in eq. (4) is based on

the outcome of numerical experimentation with $n = 2, 2\frac{1}{2}, 3$. Clearly, unless a physically plausible explanation can be put forward to justify both this exponent and the factor in the denominator, eq. (4) should be treated as an empirical model. $n = 3$ and its departure from 3 have been discussed by a number of investigators.⁴⁻⁶ The factor in the denominator can, for example, be regarded as an empirical factor introduced to allow for the change in the rate constant of the reaction as the polymerization progresses toward completion.

Numerical values of the parameters in eq. (4) and that in the rate expressions in all the subsequent examples are obtained using standard least-squares regression to minimize the difference between the model-independent rate given by eq. (3) and the model-dependent rate given by eq. (4).^{1,7} The resulting values of these parameters are $k = 0.07341 \text{ min}^{-1}$ and $\alpha = 2.5563$. Several methods of numerical minimization were used in the least-squares regression computation and all of them converged to essentially the same set of parameters.¹ The resulting best-fit model-based rate curve is shown as a continuous curve in Figure 2. There is clearly a very satisfactory agreement between the experimentally based and the model-based rate curves. This is confirmed by the array of statistical measures of goodness-of-fit generated by the least-squares regression computation. Such statistical measures will not be reproduced in this paper.

Instead, as a quick check of the reliability of the best-fit eq. (4), it is integrated, with $X(0) = 0$ as the initial condition, to give the model-based back-calculated degree of polymerization $X(t)$. This $X(t)$ is shown as a continuous curve in Figure 1. The good agreement of the two rate curves in Figure 2 ensures that there is very good general agreement between the back-calculated $X(t)$ and the experimental data.

Bulk thermal polymerization of styrene

Arai et al. investigated the thermal polymerization of styrene in glass ampoules and followed the progress

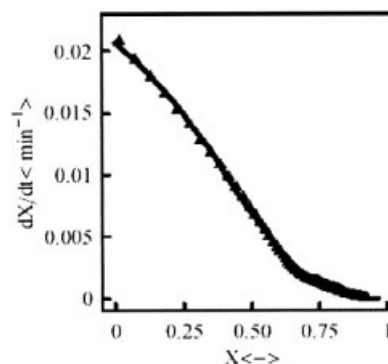


Figure 2 Rate of polyesterification. The \blacktriangle -curve is the model-independent rate given by eq. (3) and the continuous curve is the best-fit eq. (4).

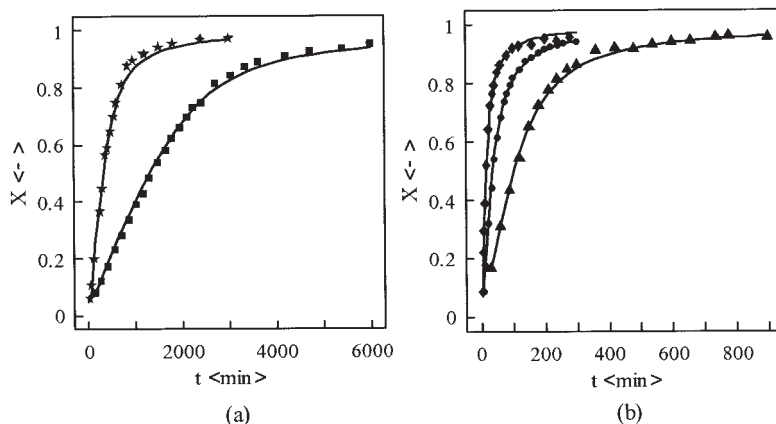


Figure 3 Polymerization of styrene. Discrete points are the data of Arai et al.⁸ at different temperatures and the continuous curves are back calculated from the best-fit rate expression in eq. (5). $T = 100.1^{\circ}\text{C}$ (■), 120.4°C (★), 140.2°C (▲), 160.8°C (●), and 179.5°C (◆).

of the reaction gravimetrically.⁸ Their experimentally measured $X(t)$, for five different temperatures, are shown as discrete points in Figure 3. The polymerization rate $dX(t)/dt$ versus $X(t)$ computed by eq. (3) from these data are shown in Figure 4 as marked curves. $N_K = 401$ in these computations. Again, for clarity, only a reduced set of the computed rate points is shown.

The kinetics of thermal polymerization of styrene has been studied extensively.^{9,10} It is generally accepted that the polymerization process can be treated as a second-order reaction, i.e., $dX(t)/dt = k(1-X(t))^2$. However, it is also widely observed that the rate constant k does not remain constant for the entire range of the experimental data.¹⁰ As in the previous example, this variation of k can be accommodated by the introduction of a $X(t)$ -dependent factor in the denominator of the modified second-order rate expression,

$$\frac{dX(t)}{dt} = \frac{k(1 - X(t))^2}{1 + \alpha(1 - X(t))^2}. \quad (5)$$

Standard least-squares regression computation between this equation and the model-independent rate curves in Figure 4 allows the parameters k and α in eq. (5) to be determined. These are summarized in Table I and the corresponding model-based best-fit rate curves are shown as continuous curves in Figure 4. For each temperature eq. (5) is integrated to give the model-based $X(t)$ curve. These are shown as continuous curves in Figure 3. On each of these curves the experimentally measured $X(t)$ at the smallest t is used as the initial condition. Comparing the model-based and the experimental curves in Figures 3 and 4, it can be seen that agreement exhibited by the model-based $X(t)$ curves appear to be, in general, more satisfactory than that exhibited by the model-based $dX(t)/dt$ curves. This is observed in most of the kinetic data investigated, suggesting that regression between the rate data given by eq. (3) and the assumed rate expression may provide a more sensitive route to the kinetic

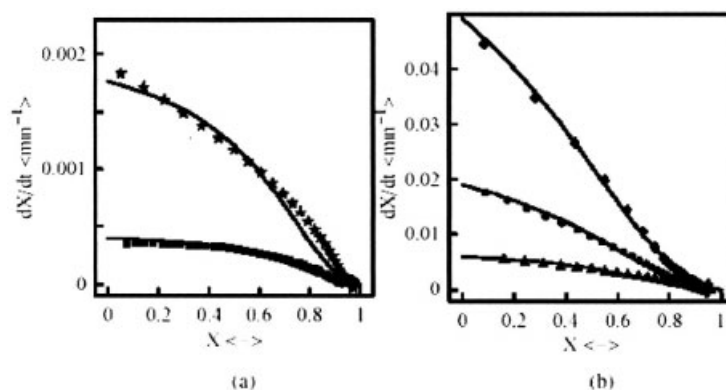


Figure 4 Polymerization rates of styrene. Marked curves are model-independent rates given by eq. (3). The continuous curves are the best-fit rate expression in eq. (5). $T = 100.1^{\circ}\text{C}$ (■), 120.4°C (★), 140.2°C (▲), 160.8°C (●) and 179.5°C (◆).

TABLE I
Kinetic Parameters of eq. (5) for Styrene Polymerization

Temperature (°C)	k (min ⁻¹)	α (-)
100	0.003784	8.3977
120	0.01146	5.5104
140	0.03115	4.2080
160	0.06162	2.2344
180	0.12428	1.5231

parameters than regression between the integrated model-based $X(t)$ and the measured $X(t)$.

Catalytic synthesis of poly(4-oxybenzoate)

Mathew et al. investigated the kinetics of catalytic synthesis of poly(4-oxybenzoate) by melt polymerization of 4-acetoxybenzoic acid (ABA).¹¹ They performed the reaction in a specially constructed reactor and followed the progress of the reaction by condensing and measuring the volume of the acetic acid produced as a function of time. The volume of the polymerizing melt is not measured and consequently the concentration of ABA and that of other reacting species are not known. The volume of acetic acid collected, expressed as a fraction of the expected stoichiometric amount, is taken as the degree of polymerization $X(t)$. A typical set of their results, with dibutyltin oxide as catalyst, at different temperatures is shown as discrete points in Figure 5. The rate curves generated by eq. (3) from these data are shown in Figure 6 as marked curves. N_K varied between 301 and 401 in these computations.

Mathew et al. assumed that polymerization of ABA can be regarded as a second-order reaction and plotted as $1/[1-X(t)]$ against t to obtain a linear plot.¹¹ Instead of a single straight line these authors observed

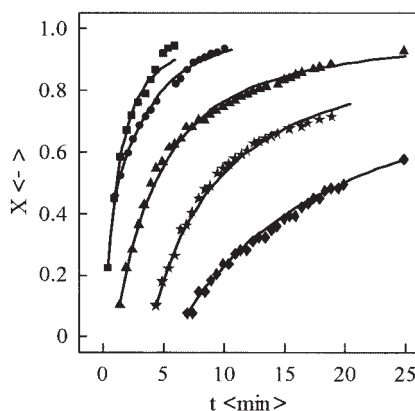


Figure 5 Polymerization of ABA. Points are the experimental data of Mathew et al.¹¹ and the continuous curves are back calculated from the best-fit rate expression in eq. (6). $T = 250^\circ\text{C}$ (◆), 275°C (★), 300°C (▲), 325°C (●), and 350°C (■).

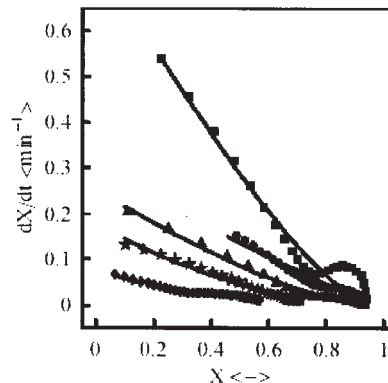


Figure 6 Polymerization rates of ABA. Marked curves are model-independent rates given by eq. (3) and the continuous curves are the best-fit rate expression in eq. (6). $T = 250^\circ\text{C}$ (◆), 275°C (★), 300°C (▲), 325°C (●), and 350°C (■).

that, at 300°C and above, the $1/[1-X(t)]$ plots are made up of two straight lines with significantly different slopes. This is an indication that the kinetics of this reaction is not adequately described by a second-order rate model with a unique rate constant k . To accommodate this a modified second-order rate expression of the form

$$\frac{dX(t)}{dt} = \frac{k(1 - X(t))^2}{1 + \alpha[1 - X(t)]} \tag{6}$$

is used to describe the ABA data. The effective rate constant is now a function of $X(t)$. In this case it was found that the exponent of the empirical factor in the denominator equal to unity provides marginally more satisfactory description of the experimental data. But other exponents such as 2 or 3/2 also provide a reasonably satisfactory description of both the rate and the degree of polymerization curves. With the data available the regression computation is unable to discriminate between these physically plausible exponents. The values of k and α for eq. (6) are summarized in Table II and the resulting model-based rate curves are shown as continuous curves in Figure 6. The back-calculated $X(t)$ curves using the k and α in Table II are shown as continuous curves in Figure 5. Again, it can be seen that even though the agreement between the model-based and the model-independent rate curves

TABLE II
Kinetic Parameters of eq. (6) for ABA Polymerization

Temperature (°C)	k (min ⁻¹)	α (-)
250	0.07034	0
275	0.19257	0.09739
300	0.53110	1.10173
325	3.98214	12.6526
350	2.22326	1.88085

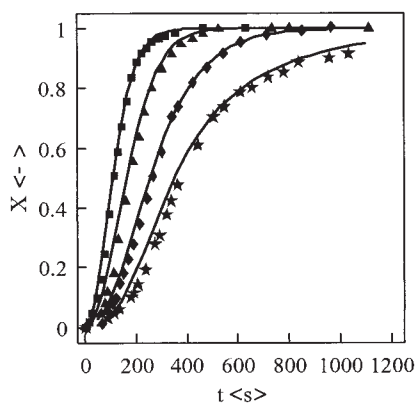


Figure 7 Polymerization of hexyl methacrylate at different initiator concentration. Points are the experimental data of Morgan et al.¹² and the continuous curves are back calculated from the best-fit least-squares eq. (8). Initiator concentration = 0.326 mM (■), 0.159 mM (▲), 0.092 mM (◆), and 0.042 mM (★).

in Figure 6 is not completely satisfactory, the agreement between their counterparts in Figure 5 is reasonably satisfactory. The relatively large deviation of the back-calculated $X(t)$ curve for $T = 350^\circ\text{C}$ is a consequence of the inability of eq. (6) to describe the polymerization rates given by eq. (3) when the degree of polymerization is high.

Microemulsion polymerization of hexyl methacrylate

Morgan et al. investigated the polymerization of hexyl methacrylate in a mixed cationic surfactant microemulsion system.¹² A typical set of their $X(t)$ versus t data are reproduced as discrete points in Figure 7. The concentrations of the initiator, azobis (amidinopropane) hydrochloride, for these data are shown in Figure 7.

The polymerization rates $dX(t)/dt$ extracted by eq. (3) from the experimental data are shown as marked $dX(t)/dt$ versus $X(t)$ curves in Figure 8. $N_K = 401$ but for clarity only every fifth point is shown. Morgan et al. obtained the $dX(t)/dt$ curves by an entirely different technique.¹² They fitted spline curves through the discrete $X(t)$ data in Figure 7 and obtained $dX(t)/dt$ by differentiating the spline curves. There is very good agreement between their rate curves (not shown) and the marked curves in Figure 8. This is rather surprising but reassuring as differentiating spline curves tends to amplify noise.

Based on a number of simplifying assumptions, such as no bimolecular termination and fast radical capture, Morgan et al. arrived at the rate expression¹²

$$\frac{dX(t)}{dt} = (1 - X(t)) \sqrt{-2A \log_e (1 - X(t))}. \quad (7)$$

A is the only kinetic parameter. For each initiator concentration this parameter is determined by least-squares regression between eq. (7) and the model-independent rate curve in Figure 8. The resulting parameters are summarized in Table III. The parameters obtained by Morgan et al. from their spline-based $X(t)$ curves are also shown in Table III.¹² In view of their entirely different origin, the agreement between the two set of parameters can be regarded as very satisfactory. The rates curves based on the best-fit eq. (7) of the present investigation are shown as marked curves in Figure 8a.

It is clear from Figure 8a that eq. (7) provides a satisfactory description of the experimentally observed rates except in the neighborhood of X close to unity where it consistently overestimated the rate. This observation has also been reported by Morgan et al.¹² The performance of eq. (7) can be improved by introducing a simple correction factor. Numerical ex-

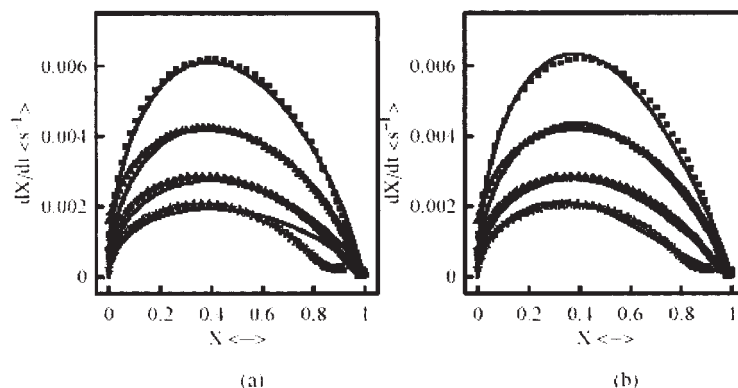


Figure 8 Polymerization rates of hexyl methacrylate. The marked curves are model-independent rates given by eq. (3) and the continuous curves in (a) are best-fit eq. (7) and that in (b) are best-fit eq. (8). Initiator concentration = 0.326 mM (■), 0.159 mM (▲), 0.092 mM (◆) and 0.042 mM (★).

TABLE III
Kinetic Parameters of eqs. (7) and (8)

Initiator concentration (mM)	eq. (7)	eq. (7)	eq. (8)	
	(this investigation) A (s^{-2})	Morgan et al. ¹² A (s^{-2})	(this investigation) A (s^{-2})	β
0.326	1.012×10^{-4}	1.0×10^{-4}	1.104×10^{-4}	0.3412
0.159	4.876×10^{-5}	5.0×10^{-5}	5.205×10^{-5}	0.2575
0.092	2.013×10^{-5}	1.9×10^{-5}	2.143×10^{-5}	0.6264
0.042	1.002×10^{-5}	9.8×10^{-6}	1.319×10^{-5}	2.6334

perimentation shows that greatly improved agreement can be achieved if the rate expression of Morgan et al. is modified to

$$\frac{dX}{dt} = \frac{(1-X)\sqrt{-2A \log_e(1-X)}}{1 + \beta X^4} \quad (8)$$

β is the second parameter of this new rate expression and the introduction of the correction factor is, as in previous examples, to allow for the fact that A may not be strictly a constant but changes with X . The best-fit eq. (8) is shown as continuous curves in Figure 8b. There is now good agreement over the entire range of X for all the experimental data. The numerical values of A and β given by least-squares regression are shown in Table III.

The back-calculated $X(t)$ curves based on the best-fit eq. (8) are shown as continuous curves in Figure 7. The agreement is satisfactory for the entire range of the experimental data. If the best-fit eq. (7) is used instead of eq. (8) the agreement is generally less satisfactory and deteriorates markedly for the curve with the lowest initiator concentration for large X . This has also been observed by Morgan et al.¹² Despite the improvement achieved, unless a theoretical justification can be put forward to explain the additional factor in eq. (8), this rate expression can only be regarded as an empirical equation.

Bulk polyesterification between *o*-phthalic anhydride and neopentyl glycol

Cudero et al. examined the suitability of the polyester formed by the polymerization of *o*-phthalic anhydride and neopentyl glycol as a binder for printing ink.¹³ As part of their investigation they studied the kinetics of this polymerization process and followed the progress of the reaction by different NMR analyses and standard volumetric analysis. In one set of their data these authors presented the concentration of the ester group $[-COO-]$ formed as a function of time. These data are shown as discrete points in Figure 9. As in the previous examples, eq. (3) is applied to convert these data into a model-independent reaction rate curve and this is shown in Figure 10 as a marked curve. $N_K = 401$ in

the Tikhonov regularization computation and only selected points are shown.

Cudero et al. used the following rate expression to describe the kinetics of this polyesterification reaction:¹³

$$\frac{d[-COO-]}{dt} = k(a - [-COO-])^m(b - [-COO-])^n \quad (9)$$

a and b are the initial concentration of the acid group $[-COOH]$ and that of the alcohol group $[-OH]$ in the reacting mixture and the corresponding terms on the RHS of eq. (9) are their respective concentrations at time t . For the data in Figure 9, $a = 3.19 \text{ mol kg}^{-1}$ and $b = 5.98 \text{ mol kg}^{-1}$.¹³ Apart from the rate constant k , the exponents m and n in eq. (9) have also been left as kinetic parameters to be determined. Following Cudero et al., m and n are restricted to integer values and simple fractions such as $1/2$ and $3/2$.¹³ Least-squares minimization between eq. (9) and the rate curve in Figure 10 resulted in $k = 0.006024 [-COO-][COOH]^{-m}[OH]^{-n} \text{ min}^{-1}$ with $m = 1.0$ and $n = 0.5$. The more general optimum parameters are $k = 0.01131[-COO-][COOH]^{-m}[OH]^{-n} \text{ min}^{-1}$, $m = 1.248$ and $n = 10^{-11}$. The model-based rate curve

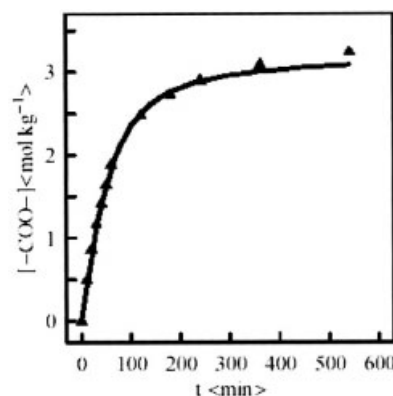


Figure 9 Polymerization of *o*-phthalic anhydride and neopentyl glycol. Points are the data of Cudero et al.¹³ and the continuous curve is back calculated from the best-fit eq. (10) with $m = 2$ and $n = 0$.

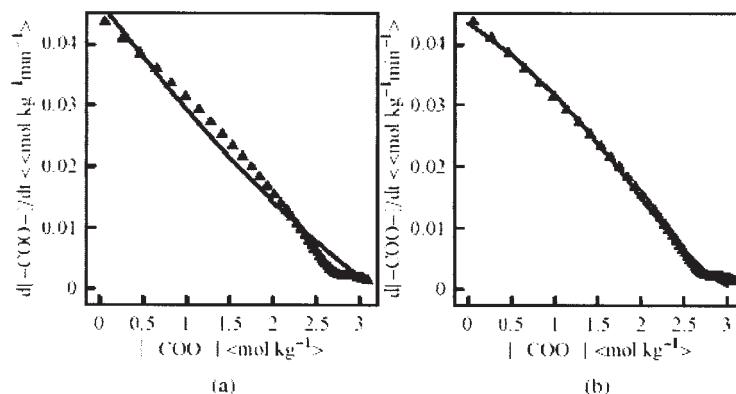


Figure 10 Polymerization rate of *o*-phthalic anhydride and neopentyl glycol. \blacktriangle -curves in (a) and (b) are the model-independent rate given by eq. (3). The continuous curves in (a) is the best-fit eq. (9) with $m = 1$, $n = 0.5$ and that in (b) is the best-fit eq. (10) with $m = 2$ and $n = 0$.

with $m = 1.0$ and $n = 0.5$ is shown as a continuous curve in Figure 10a.

It is clear that the fit in Figure 10a is generally acceptable. The corresponding back-calculated $X(t)$ curve (not shown) is also in acceptable agreement with the experimental data in Figure 9. However, it is also clear from Figure 10a that the curvature of the model-based rate curve is the reverse of that of the model-independent rate data. To rectify this situation, eq. (9) is modified empirically to

$$\frac{d[-\text{COO-}]}{dt} = \frac{k(a - [-\text{COO-}])^m(b - [-\text{COO-}])^n}{1 + \alpha(a - [-\text{COO-}])^m(b - [-\text{COO-}])^n} \quad (10)$$

Least-squares regression is again applied to determine the kinetic parameters of this model.

The new parameters are $k = 0.01430[-\text{COO-}][-\text{COOH}]^{-m}[-\text{OH}]^{-n} \text{ min}^{-1}$, $\alpha = 0.2384[-\text{COOH}]^{-m}[-\text{OH}]^{-n}$, $m = 2$ and $n = 0$ (the more general set is $k = 0.01417[-\text{COO-}][-\text{COOH}]^{-m}[-\text{OH}]^{-n} \text{ min}^{-1}$, $\alpha = 0.2274[-\text{COOH}]^{-m}[-\text{OH}]^{-n}$, $m = 1.9448$ and $n = 0$). It is interesting to note that n turned out to be zero in this more general rate expression. The best-fit rate curve based on eq. (10) with $m = 2$ and $n = 0$ is shown as a continuous curve in Figure 10b. This curve shows the correct curvature and is clearly, even visually, an improvement over that in Figure 10a. The $X(t)$ back calculated from this more general rate expression is shown as a continuous curve in Figure 9. The agreement with the experimental data is, as expected, very good but the improvement over the corresponding back-calculated curve based on eq. (9) (not shown) is not visually perceptible.

Cudero et al. followed the standard procedure, i.e., integrating eq. (9) numerically and then applied least-squares regression between the integrated curve and the concentration data in Figure 9, to determine the

kinetic parameters.¹³ Their regression computation did not result in a unique set of rate parameters. The optimum combinations of $\{m, n\}$ observed by these authors include $\{1, 1\}$, $\{1, 3/2\}$, $\{1, 2\}$, $\{3/2, 0\}$, $\{3/2, 1/2\}$, etc. In view of this lack of uniqueness, the $\{m, n\}$ of the present investigation reported above can be regarded to be in acceptable agreement with their findings. The back-calculated $X(t)$ curves based on all their near-optimum parameter sets are visually indistinguishable from one another. This has long been the difficulty encountered when applying regression between the integrated rate expression and experimental degree of polymerization data. The problem is less serious when the regression computation is between the assumed rate expression and the model-independent rate data generated by eq. (3).

DISCUSSION

The procedure based on Tikhonov regularization has successfully converted the degree of polymerization data $X(t)$ into polymerization rates $dX(t)/dt$. It is applicable to kinetic data irrespective of the types of polymerization reactions. The same equation, eq. (3), is used to perform the data conversion. It is a simple equation and all the numerical operations in setting up the matrices and their subsequent manipulations can be performed using standard commercial computer software.⁷ The computation time required, even when N_K is as large as 10^3 , on the current generation of PCs is less than a minute or two.

The data as generated by eq. (3) take the form of a discrete set of closely spaced polymerization rate data points. Without assuming any rate model, these data points can be used to back calculate the degree of polymerization curves. Because of the nature of the Tikhonov regularization computation, good agreement with the original experimental data is observed

in each case. As the back calculations were performed using commercial software⁷ independent of that developed specifically for the present investigation, they provide a quick check against possible errors introduced during the derivation and numerical solution of eq. (3).

The discussion up to this point is independent of the reaction kinetic model. As can be seen from all the examples, the regularization parameter λ has ensured that each set of the rate data given by eq. (3) traces out a relatively smooth curve. Such curves, even in the absence of a rate model, can be used directly in process engineering calculations. For example, they can be used in the sizing calculations of reactors when a satisfactory rate expression is not available.

If a rate expression is proposed for the polymerization process in question, the $X(t)$ versus $dX(t)/dt$ curve generated by eq. (3) can be used to determine the parameters in the model. The key step involved here is the least-squares regression between the relatively simple rate expression and the well-behaved rate data. This can be performed using standard regression or least-squares minimization routines found in most commercial software packages. As mentioned above, using the computed $X(t)$ versus $dX(t)/dt$ curve rather than the integrated degree of polymerization curve to determine the kinetic parameters can be expected to simplify the regression calculations significantly and lead to more reliable results. These gains have been demonstrated by some of the examples shown above.

These examples also demonstrate how the testing of modified rate expressions is greatly simplified. Regression computation can be carried out directly each time the rate expression is modified. There is no need to repeat the computation in eq. (3). There is also no need to integrate the rate expression each time it is modified. In contrast, in the widely adopted procedure of performing the regression between the experimental data and the model-based degree of polymerization curve, repeated integration is required each time the rate expression is modified.

The success of Tikhonov regularization requires an appropriately chosen regularization parameter λ . In the present investigation this choice has been guided by the simple expectation that the average and maximum deviation between X^C and X^M must be physically realistic, i.e., they must be comparable with the estimated magnitude of the error bars of the kinetic data while ensuring that the resulting polymerization rate curve is sufficiently smooth. This is referred to as the Morozov Principle in some mathematical texts.² For all the polymerization processes investigated, this principle appears adequate as a guide for locating the appropriate λ . As long as λ is of the appropriate order

of magnitude, changes of λ within this range do not greatly affect the final results. Fine tuning of λ is generally not required. For an example of the effects of changing λ see Yeow et al.³ As λ is neither a property of the reaction under investigation nor that of the experimental technique used to monitor the polymerization process, it is therefore not very useful, and in fact rather misleading, to tabulate the values of λ associated with the reactions investigated in this paper. There are alternative methods for selecting λ such as the L-curve method¹⁴ and the method of generalized cross validation.¹⁵ See Engl et al.² for further discussion of this issue.

CONCLUSION

Tikhonov regularization provides a reliable way of converting the degree of polymerization data into polymerization rates. The procedure is independent of any assumed rate expression and is applicable to different types of polymerization reactions. As noise amplification is kept under control, the resulting large set of rate data allows the kinetic parameters in any proposed kinetic model of the polymerization reaction to be determined with relative ease and reliability.

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