

Optimal Designs for Constant-Heating-Rate Differential Scanning Calorimetry Experiments for Polymerization Kinetics: n th-Order Kinetics

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ABSTRACT: Optimal designs have been constructed for differential scanning calorimetry (DSC) experiments conducted under constant-heating-rate conditions for materials that are *a priori* assumed to follow n th-order kinetics. Two different operating scenarios are considered, including single-scan and multiscan DSC experiments for eight different kinetic parameter combinations representing a range of typ-

ical polymeric curing reactions. The resulting designs are studied to determine which kinetic model parameters are influential in determining the optimal design. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2133–2139, 2010

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INTRODUCTION

Differential scanning calorimetry (DSC) is a well-known experimental thermal analysis technique that can be used to investigate a range of thermal events. Very briefly, DSC experiments compare the difference in the input energies required by an inert reference and the sample under investigation to maintain a specified temperature or heating rate. When the sample undergoes an exothermic event (e.g., a polymerization reaction), it requires less energy input than the reference, whereas the sample undergoing an endothermic event (e.g., a phase change) requires more energy input than the reference. When the sample is stable, the energy input difference between it and the reference remains constant and is a function of the heat capacity and mass of the two.

There are two common modes of operation for DSC experiments: isothermal and constant heating rate. In isothermal experiments, the temperature of the sample and reference is quickly changed to the desired test temperature, and then it is maintained there for the duration of the experiment. This approach has the appeal of simple data analysis, but multiple experiments must be conducted if temperature effects are to be determined. Isothermal experiments can also be used to confirm kinetic parameters estimated from

constant-heating-rate experiments. In constant-heating-rate experiments, the temperatures of the sample and the reference are kept equal but are raised at a predetermined constant rate. This approach has the advantage of being able to determine temperature effects and can also require less time than isothermal experiments. Data analysis^{1–4} for constant-heating-rate experiments is more difficult than for isothermal experiments, but modern computing techniques have eliminated this worry for the most part. In this article, we are concerned only with the constant-heating-rate mode of DSC operation.

One common use for constant-heating-rate DSC experiments is the determination of the kinetics of polymerization reactions. Because polymerization reactions are seldom, if ever, simple reactions amenable to analysis from first principles, simplified kinetic expressions in terms of the extent of reaction are used to model the reaction chemistry. The most common and simplest is first-order kinetics:

$$\frac{\partial \alpha}{\partial t} = k(1 - \alpha) \quad (1)$$

where α is the extent of reaction (unitless), t is the time (s), and k is the rate constant (s^{-1}). The latter is usually assumed to have an Arrhenius temperature dependence:

$$k = Ae^{-\left(\frac{E}{RT}\right)} \quad (2)$$

where A is the pre-exponential factor (s^{-1}), E is the activation energy (J/mol), R is the gas constant (8.3145 J/mol K), and T is the temperature (K).

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For most polymerization reactions, first-order kinetics does not adequately describe the reaction chemistry, and so other expressions, albeit arbitrary, are sometime assumed to be suitable. In order of increasing complexity, four of these expressions are⁵

- n th-order kinetics, a three-parameter model given by

$$\frac{\partial \alpha}{\partial t} = k(1 - \alpha)^n \quad (3)$$

- mn autocatalytic kinetics, a four-parameter model given by

$$\frac{\partial \alpha}{\partial t} = k(1 - \alpha)^n \alpha^m \quad (4)$$

- m autocatalytic plus n th-order kinetics (which we refer to as $m_n n$ kinetics), a six-parameter model given by

$$\frac{\partial \alpha}{\partial t} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (5)$$

- lmn kinetics, a seven-parameter model given by

$$\frac{\partial \alpha}{\partial t} = k_1(1 - \alpha)^n + k_2 \alpha^m (1 - \alpha)^l \quad (6)$$

In all these models, l , m , and n are model parameters and the rate constants (k , k_1 , and k_2) are all assumed to have an Arrhenius temperature dependence as given by eq. (2). However, the values of A and E determined for the rate constant for one form of the kinetic model cannot be used for another form. Also, the two rate constants used in the $m_n n$ and lmn kinetic models have separate and distinct values of A and E ; that is, values of A_1 , E_1 , A_2 , and E_2 must be determined.

The design of constant-heating-rate DSC experiments for both first-order and n th-order kinetic models has already been discussed.⁶⁻⁸ In this article, our interest is designing constant-heating-rate DSC experiments for the n th-order kinetic model, that is, Figure 3. When designing an experiment, we explicitly mean the specification of the level(s) and independent factor(s) that will be used when the experiment is being conducted; that is, we do not mean the experimental procedure or equipment design. For constant-heating-rate DSC experiments, there are two independent factors that must be specified: the heating rate(s) and extent(s) of reaction. The necessity of specifying the heating rate(s) is obvious, and

with today's computer-controlled apparatus, it is common to specify the frequency with which the data are recorded and then to use all that data (there could be hundreds of data points) in the analysis. However, as shown earlier,⁶ the judicious selection of a few points from each scan results in more reliable estimates of the kinetic parameters. Thus, the challenge in designing these DSC experiments is to determine the best heating rate(s) and extent(s) of reaction to provide the most accurate estimates of the kinetic parameters. This can be accomplished with a design technique known as D-optimal design.⁹⁻¹¹

The general formulation for D-optimal experimental design for continuous designs¹⁰ begins by the *a priori* specification of a specific functional relationship between the independent factor(s) and the dependent response factor(s):

$$\mathbf{y} = f(\mathbf{x}, \boldsymbol{\beta}) \quad (7)$$

where \mathbf{y} is the vector of dependent factors, \mathbf{x} is the vector of independent factors, and $\boldsymbol{\beta}$ is the vector of model parameters. On the basis of this model selection, the information matrix (\mathbf{M}) is formed as follows:

$$\mathbf{M} = \sum_{i=1}^N \left\{ \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \left[\frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \right]^T \right\} \quad (8)$$

where the summation is taken over N data points and \mathbf{x}_i explicitly refer to the set of independent factors for the i th experiment. For the case of three model parameters, which is shown for the sake of illustration, \mathbf{M} becomes

$$\mathbf{M} = \sum_{i=1}^N \left\{ \begin{array}{ccc} \left[\frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_1} \right]^2 & \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_1} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_2} & \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_1} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_3} \\ \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_1} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_2} & \left[\frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_2} \right]^2 & \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_2} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_3} \\ \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_1} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_3} & \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_2} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_3} & \left[\frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_3} \right]^2 \end{array} \right\} \quad (9)$$

The extension of this to a larger number of model parameters is straightforward. The D-optimal design is then given by the set of independent factors that minimize the determinant of the inverse of \mathbf{M} .

D-OPTIMAL FORMULATION

\mathbf{M} for the case of n th-order kinetics studied with a constant-heating-rate DSC experiment can now be formulated. First, $\boldsymbol{\beta}$ is given by

$$\boldsymbol{\beta} = (A_1, E_1/R, n)^T \quad (10)$$

where the first two factors are the pre-exponential and activation energy values for rate constant k and n has its usual meaning. The normalization of E_1

TABLE I
Eight-Run 2³ Factorial Design in Coded Factor Levels

Run	A ₁	E ₁ /R	n
1	1	1	1
2	-1	1	1
3	1	-1	1
4	-1	-1	1
5	1	1	-1
6	-1	1	-1
7	1	-1	-1
8	-1	-1	-1

was done to enhance the stability of the numerical solutions discussed later.

Before the independent and dependent factors are defined, DSC data analysis needs to be discussed. A typical DSC scan is plotted with the temperature as the independent factor and the input energy difference as the response factor. A linear baseline is then constructed from the beginning of the reaction to the completion of the reaction. For simplicity, we have assumed that the baseline is horizontal; that is, that the heat capacities of the reactant and the product are the same. Once this is done, α can be obtained as follows:

$$\alpha = \frac{\int_{T_0}^{T_\alpha} (C - B)dT}{\int_{T_0}^{T_e} (C - B)dT} \tag{11}$$

where T₀ and T_e are the initial and end temperatures of the reaction (K), T_α is the temperature (K) at extent of reaction α, and C and B represent the DSC and baseline curves, respectively. This gives an explicit relationship between the temperature and the extent of reaction. For simplicity, the baseline is assumed to be identically equal to zero; that is, there is no difference in the thermal mass (the product of the mass and heat capacity) for the sample and the reference. In the following analysis, simple linear interpolation is used to compute both α and T_α on the basis of tabular data computed for the incremental integration of eq. (5) based on uniform time steps. In the rest of the development, we have elected to treat α as the independent factor and T_α as the dependent response factor. Given this, x is determined as follows:

$$\mathbf{x}_i = (h_i, \alpha_i)^T \tag{12}$$

where h_i is the heating rate (K/min). A design, or a measure, is then obtained as follows:

$$\xi_{r,j} = (x_1, x_2, \dots, x_j)^T \tag{13}$$

where subscripts r and j refer to the run number and the number of points in the design, respectively. To further simplify the design calculations, it has been assumed that the heating rate is bounded

between 1 and 10 K/min and must be an integer. It has also been assumed that the response temperature is determined for discrete values of the extent of reaction ranging from 10 to 90% in 5% steps.

As for the examination of the effects of the model parameters on the resulting D-optimal design, the large number of parameters prohibits us from examining all possible combinations of them in some systematic manner. However, because a systematic manner of investigating these effects was desired, we used a classic eight-run 2³ factorial design capable of detecting main effects.¹² The values of the parameters for the eight runs are given in terms of coded levels in Table I, and the coded levels for each factor are given in Table II.

For the current problem statement, the jkth element of M is given by

$$\mathbf{M}_{jk} = \sum_{i=1}^N \left[\frac{\partial T_\alpha(\mathbf{x}_i, \beta)}{\partial \beta_j} \frac{\partial T_\alpha(\mathbf{x}_i, \beta)}{\partial \beta_k} \right] \tag{14}$$

For each run in the factorial design, the derivatives needed to calculate M were calculated with a central difference scheme for each admissible extent of reaction and at each possible heating rate. These 510 points (3 derivatives, 17 extents of reaction, and 10 heating rates) for each combination of the model parameters were calculated and stored for subsequent use in determining the optimal design.

To determine the optimal design, a pick-and-exchange algorithm was used.¹⁰ This algorithm has six distinct steps: (1) specify all the points at which the experiment could be conducted; (2) randomly select N of these points as the initial design; (3) compute the standardized variance at all points (those included in the design and those omitted from the design); (4) find the point with the smallest standardized variance of the design points and the point with the largest standardized variance of the omitted points; (5) exchange these two points to create a new design; and (6) if the new design is more efficient than the previous design, that is, has a larger determinant of M, continue the process starting with step 3, but otherwise restore the previous design and terminate the process. Because the final design selected may depend on the initial points selected at step 2, steps 2–6 are repeated many times, and the solution at the end of each iteration is recorded. From these multiple solutions, the most efficient are selected as the final designs.

TABLE II
Low and High Levels of the Model Parameters

Level	A ₁ (s ⁻¹)	E ₁ /R (K)	n
-1	1.00 × 10 ⁴	7.00 × 10 ³	1
+1	5.00 × 10 ⁴	1.00 × 10 ⁴	2

TABLE III
Optimal Designs for the Single-Scan Constant-Heating-Rate DSC Experiments Using Three Points To Determine the Model Parameters for n th-Order Kinetics

Run	Design measure
1	$\xi_{1,3} = \{(6,0.10), (6,0.60), (6,0.90)\}^T$
2	$\xi_{2,3} = \{(6,0.10), (6,0.60), (6,0.90)\}^T$
3	$\xi_{3,3} = \{(6,0.10), (6,0.60), (6,0.90)\}^T$
4	$\xi_{4,3} = \{(6,0.10), (6,0.60), (6,0.90)\}^T$
5	$\xi_{5,3} = \{(6,0.10), (6,0.55), (6,0.90)\}^T$
6	$\xi_{6,3} = \{(6,0.10), (6,0.55), (6,0.90)\}^T$
7	$\xi_{7,3} = \{(6,0.10), (6,0.55), (6,0.90)\}^T$
8	$\xi_{8,3} = \{(6,0.10), (6,0.55), (6,0.90)\}^T$

RESULTS AND DISCUSSION

Two experimental strategies were considered, and the appropriate D-optimal designs were generated for both. The first strategy was that of a single DSC scan, in which the optimal heating rate and extents of reaction needed to be determined. The second strategy was that of multiple scan rates with one or more extents of reaction from each scan used in the determination of the kinetic constants. Each of these strategies is discussed.

Single-scan designs

To compute the D-optimal designs for single-scan experiments, the pick-and-exchange algorithm was used to determine the optimal design for each of the possible heating rates. The optimal design consisted of the three extents of reaction that minimized the determinant of the inverse of \mathbf{M} at that heating rate. From these 10 designs, the one with the smallest determinant was selected as the D-optimal design. This process was repeated for each combination of kinetic parameters as specified in Tables I and II.

TABLE IV
Optimal Designs for the Single-Scan Constant-Heating-Rate DSC Experiments Using Eight Points To Determine the Model Parameters for n th-Order Kinetics

Run	Design measure
1	$\xi_{1,8} = \{(6,0.10), (6,0.15), (6,0.50), (6,0.55), (6,0.60), (6,0.65), (6,0.85), (6,0.90)\}^T$
2	$\xi_{2,8} = \{(6,0.10), (6,0.15), (6,0.50), (6,0.55), (6,0.60), (6,0.65), (6,0.85), (6,0.90)\}^T$
3	$\xi_{3,8} = \{(6,0.10), (6,0.15), (6,0.50), (6,0.55), (6,0.60), (6,0.65), (6,0.85), (6,0.90)\}^T$
4	$\xi_{4,8} = \{(6,0.10), (6,0.15), (6,0.50), (6,0.55), (6,0.60), (6,0.65), (6,0.85), (6,0.90)\}^T$
5	$\xi_{5,8} = \{(6,0.10), (6,0.15), (6,0.45), (6,0.50), (6,0.55), (6,0.60), (6,0.85), (6,0.90)\}^T$
6	$\xi_{6,8} = \{(6,0.10), (6,0.15), (6,0.45), (6,0.50), (6,0.55), (6,0.60), (6,0.85), (6,0.90)\}^T$
7	$\xi_{7,8} = \{(6,0.10), (6,0.15), (6,0.45), (6,0.50), (6,0.55), (6,0.60), (6,0.85), (6,0.90)\}^T$
8	$\xi_{8,8} = \{(6,0.10), (6,0.15), (6,0.45), (6,0.50), (6,0.55), (6,0.60), (6,0.85), (6,0.90)\}^T$

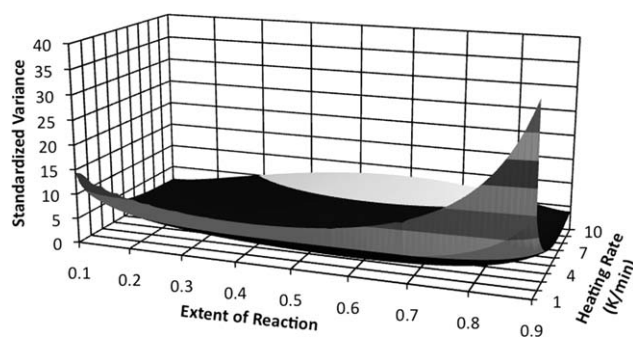


Figure 1 Standardized variance for the design measure $\xi_{8,3}$.

The results for the single-scan DSC D-optimal designs using just three extents of reaction, the minimum number necessary to estimate the three kinetic parameters in the model, are presented in Table III for all eight kinetic parameter combinations. From the data in Table III, it is immediately apparent that there are only two unique experimental designs and that those two designs vary only slightly. Both designs use an optimal heating rate of 6 K/s and points at the extremes of allowable extents of reaction, that is, at $\alpha = 0.10$ and $\alpha = 0.90$. The center point in the design is either $\alpha = 0.60$ or $\alpha = 0.55$, depending on the run. It is also apparent from a comparison of the results in Table III and the design presented in Table I that the extent of reaction for the center point depends on the level of exponent n : $\alpha = 0.60$ is appropriate for $n = 1$, whereas $\alpha = 0.55$ is used for $n = 2$.

An additional variation on the single-scan strategy that was examined was the effect of using more than the minimum of three points from a scan in the design (as would be the most likely application in practice). Optimal designs for up to eight points were determined for all eight combinations of the kinetic parameters being considered here. For all cases except one, as was just seen when three points were

TABLE V
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used To Determine the Model Parameters for n th-Order Kinetics

Number	Design measure
3	$\xi_{1,3} = \{(1,0.90), (10,0.15), (10,0.90)\}^T$
4	$\xi_{1,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{1,5} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.90)\}^T$
6	$\xi_{1,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{1,7} = \{(1,0.10), (1,0.85), (1,0.90), (9,0.90), (10,0.30), (10,0.35), (10,0.90)\}^T$
8	$\xi_{1,8} = \{(1,0.10), (1,0.85), (1,0.90), (8,0.90), (9,0.90), (10,0.30), (10,0.35), (10,0.90)\}^T$

The kinetic parameters for run 1 in Tables I and II were used.

TABLE VI
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for *n*th-Order Kinetics

Number	Design measure
3	$\xi_{2,3} = \{(1,0.90), (10,0.20), (10,0.90)\}^T$
4	$\xi_{2,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{2,5} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.90)\}^T$
6	$\xi_{2,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{2,7} = \{(1,0.10), (1,0.85), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
8	$\xi_{2,8} = \{(1,0.10), (1,0.85), (1,0.90), (8,0.90), (9,0.90), (10,0.30), (10,0.35), (10,0.90)\}^T$

The kinetic parameters for run 2 in Tables I and II were used.

used, only two unique designs were determined, and the difference between these two designs was only a single point. This is shown in Table IV for the case for which eight points were used in the design; for designs with five, six, or seven points, similar results were obtained, but they are not reported here. The exceptions to this were the designs with four points at a single scan rate. For this case, seven of the eight designs followed the anticipated pattern, but the design for run 4 did not. Instead of being identical to either of the other designs, the design for run 4 used one interior point that was unique to this set of kinetic parameters. The reason for this is still under investigation.

The quality of the experimental design can be considered by an examination of the standardized variance (d_i) for predicted values over the entire experimental region of interest. d_i is determined as follows:

$$d_i = N \left[\frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \right]^T M \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \quad (15)$$

TABLE VII
Optimal Designs for Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for *n*th-Order Kinetics

Number	Design measure
3	$\xi_{3,3} = \{(1,0.90), (10,0.20), (10,0.90)\}^T$
4	$\xi_{3,4} = \{(1,0.10), (1,0.90), (10,0.45), (10,0.90)\}^T$
5	$\xi_{3,5} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.40), (10,0.90)\}^T$
6	$\xi_{3,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{3,7} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.45), (10,0.50), (10,0.90)\}^T$
8	$\xi_{3,8} = \{(1,0.10), (1,0.15), (1,0.85), (1,0.90), (9,0.90), (10,0.45), (10,0.50), (10,0.90)\}^T$

The kinetic parameters for run 3 in Tables I and II were used.

TABLE VIII
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for *n*th-Order Kinetics

Number	Design measure
3	$\xi_{4,3} = \{(1,0.90), (10,0.20), (10,0.90)\}^T$
4	$\xi_{4,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{4,5} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.90)\}^T$
6	$\xi_{4,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{4,7} = \{(1,0.10), (1,0.85), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
8	$\xi_{4,8} = \{(1,0.10), (1,0.85), (1,0.90), (8,0.90), (9,0.90), (10,0.30), (10,0.35), (10,0.90)\}^T$

The kinetic parameters for run 4 in Tables I and II were used.

where N is the number of experimental points and point \mathbf{x}_i may or may not be a point at which the experiment was conducted. For illustration purposes, the standardized variance is plotted in Figure 1 for the single-scan design measure $\xi_{8,3}$ presented in Table III. The general equivalence theorem requires for a D-optimal design that the standardized variance be less than or equal to the number of parameters in the model. It is apparent that this criterion is not satisfied by this design and that, in general, predictions for slow heating rates will have a great deal of uncertainty associated with them as a result of the experimental design, even though this design minimizes the volume of the joint confidence interval of the parameter estimates. To more accurately predict the behavior at slower heating rates, a different experimental strategy must be considered.

Multiscan designs

A more general experimental strategy is to select the best N experimental points from the 510 possible

TABLE IX
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for *n*th-Order Kinetics

Number	Design measure
3	$\xi_{5,3} = \{(1,0.90), (10,0.15), (10,0.90)\}^T$
4	$\xi_{5,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{5,5} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.90)\}^T$
6	$\xi_{5,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.30), (10,0.35), (10,0.90)\}^T$
7	$\xi_{5,7} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
8	$\xi_{5,8} = \{(1,0.10), (1,0.15), (1,0.85), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$

The kinetic parameters for run 5 in Tables I and II were used.

TABLE X
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for n th-Order Kinetics

Number	Design measure
3	$\xi_{6,3} = \{(1,0.10), (10,0.40), (10,0.90)\}^T$
4	$\xi_{6,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{6,5} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
6	$\xi_{6,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{6,7} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
8	$\xi_{6,8} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.45), (10,0.90)\}^T$

The kinetic parameters for run 6 in Tables I and II were used.

points and not constrain the experiment to a single heating rate. The results of these calculations for $N = 3, 4, \dots, 8$ for all eight combinations of the kinetic parameters are presented in Tables V–XII. Generally, designs using four points add a point to the three-point designs that fills a corner of the experimental region that is not covered in the three-point design. As additional points are added to the four-point design, however, they cluster near the existing points until the eight-point design is very similar to a two-fold replication of the four-point design. This is also illustrated in Figure 2, in which all 64 points from the eight 8-point designs have been plotted to show the portion of the experimental space used in the designs. In Figure 2, there are only 13 unique points, of which 8 would be used by any particular design. The points are grouped in four clusters, each cluster containing one of the points from the four-point designs. This then suggests that perhaps instead of using eight distinct points, using a four-

TABLE XI
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for n th-Order Kinetics

Number	Design measure
3	$\xi_{7,3} = \{(1,0.10), (10,0.40), (10,0.90)\}^T$
4	$\xi_{7,4} = \{(1,0.10), (2,0.90), (10,0.45), (10,0.90)\}^T$
5	$\xi_{7,5} = \{(1,0.10), (2,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
6	$\xi_{7,6} = \{(1,0.10), (1,0.15), (2,0.90), (10,0.45), (10,0.50), (10,0.90)\}^T$
7	$\xi_{7,7} = \{(1,0.10), (1,0.15), (2,0.90), (9,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
8	$\xi_{7,8} = \{(1,0.10), (1,0.15), (2,0.90), (9,0.90), (10,0.40), (10,0.45), (10,0.50), (10,0.90)\}^T$

The kinetic parameters for run 7 in Tables I and II were used.

TABLE XII
Optimal Designs for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for n th-Order Kinetics

Number	Design measure
3	$\xi_{8,3} = \{(1,0.10), (10,0.40), (10,0.90)\}^T$
4	$\xi_{8,4} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.90)\}^T$
5	$\xi_{8,5} = \{(1,0.10), (1,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
6	$\xi_{8,6} = \{(1,0.10), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.90)\}^T$
7	$\xi_{8,7} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.40), (10,0.45), (10,0.90)\}^T$
8	$\xi_{8,8} = \{(1,0.10), (1,0.15), (1,0.90), (9,0.90), (10,0.35), (10,0.40), (10,0.45), (10,0.90)\}^T$

The kinetic parameters for run 8 in Tables I and II were used.

point design and replicating it would be more efficient. The design efficiency scaled for the number of points used in the experiments (p_i) is determined as follows:

$$p_i = \frac{N_j}{N_i} \left(\frac{|\mathbf{M}_i|}{|\mathbf{M}_j|} \right)^{1/p} \quad (16)$$

where N is the number of experimental points in the design, \mathbf{M} is the information matrix for the design, p is the number of model parameters (i.e., $p = 3$ for this study), and subscripts i and j indicate the design. For all comparisons, we selected $j = 8$. The scaled design efficiencies comparing the i -point designs and the eight-point designs are given in Table XIII. For all cases, either the three- or four-point designs were the most efficient when scaled by the number of points. However, this is slightly misleading because a three-point design cannot be replicated $2\frac{1}{3}$ times to be equivalent in effort to an eight-point design. The four-point designs, which were the most efficient 75% of the time and the second most efficient the remaining 25% of the time,

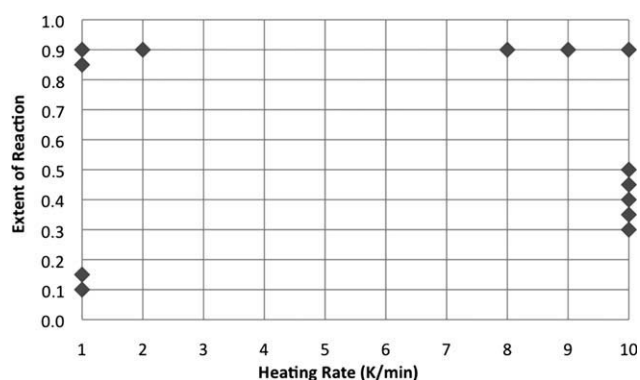


Figure 2 Location of experimental points for all 8 runs for the multiscan $\xi_{r,8}$ design measures.

TABLE XIII
Scaled Efficiencies for the Multiscan Constant-Heating-Rate DSC Experiments Used to Determine the Model Parameters for n th-Order Kinetics

Number	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
3	109.3	109.7	107.3	110.0	101.7	95.5	99.4	95.6
4	107.4	107.3	108.4	107.2	106.7	104.1	102.5	104.1
5	105.2	105.1	105.3	105.0	103.0	101.9	101.3	101.9
6	103.1	103.1	104.2	103.0	102.6	100.9	101.0	100.9
7	101.7	101.7	102.0	101.7	101.6	101.5	101.0	101.5
8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The kinetic parameters in Tables I and II were used.

can be exactly replicated twice to require the same effort as the eight-point designs, which would result in a 2.5% to 8.4% increase in efficiency.

The improvement with the multiscan strategy compared to the single-scan approach can be seen by a comparison of the standardized deviations for the former (given in Fig. 2 for run 8) and the latter (already given in Fig. 1). Most notable in this comparison is that the maximum standardized variance in the experimental region has decreased from 35.7 to 3.2; this is a significant improvement in the ability to predict the model response. We also note that this surface is supported equally at the four support points, that is, the four points at which the experiment was conducted. This design is not quite D-optimal because the maximum standardized variance is still greater than 3; however, this is most likely due to the limitations placed on allowable heating rates and extents of reaction; that is, this is not a continuous design.

CONCLUSIONS

In this study, D-optimal designs were constructed for both single-scan and multiscan constant-heating-rate DSC experiments for which it had been assumed *a priori* that n th-order kinetics were appropriate. The designs were developed for kinetic parameters typical of polymerization reactions. For the single-scan experiments, it was shown that for all

cases the optimal heating rate was 6 K/min, and only two unique, though very similar designs were developed for the eight combinations of kinetic parameters studied. It was also shown that this was not a highly effective design for estimating the kinetic parameters. For the multiscan experiments, it was shown that the optimal heating rates were 1 and 10 K/min, and the assumed extremes were experimentally realizable. It was also shown that the general development of the design as experimental points were added involved the placement of the additional points near those that were included in the four-point design. Furthermore, it was shown that it would be more efficient to replicate the four-point design than to conduct an eight-point design. Therefore, it is recommended that when n th-order kinetics is assumed (or known) to be appropriate, constant-heating-rate DSC experiments should be conducted at 1 and 10 K/min with as many replicates as possible to provide the most reliable estimates of the kinetic parameters for polymerization reactions.

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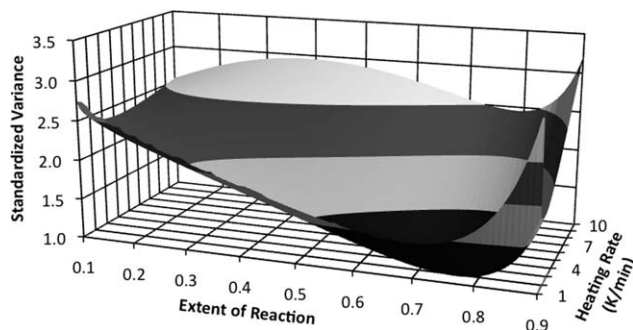


Figure 3 Standardized variance for the design measure $\xi_{8,4}$.