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The NPK method
An innovative approach for kinetic analysis of data from thermal analysis and calorimetry

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Abstract

The basic theory of the ''non-parametric kinetics,'' NPK method is exposed. This procedure for the kinetic analysis of data from thermal analysis is applied the thermal decomposition of dicyclohexylidene diperoxide and to the mass polymerisation of methyl methacrylate catalysed by AIBN. The first case could be described using a simple kinetic model and is an example to show how it is possible to obtain its parameters using NPK. The second one corresponds to a complex kinetics. It is used to show the capability of NPK of predicting data without using any kinetic model, not even requiring the Arrhenius law.

Keywords: Kinetic analysis; NPK; Polymerisation; Thermal decomposition

1. Introduction

It is possible to make use of the kinetic analysis in thermal analysis with two different purposes. The first one is to obtain conclusions about the mechanism of a reaction or to extract reference values of certain parameters, such as activation energies. The second purpose is just to obtain a model to predict the behaviour of a reaction under certain conditions. In this case, it is not intended to obtain a mechanistic model, but an operative one.

Classical methods are based on assuming a possible kinetic model and fitting its parameters [1]. Usually, they assume that the rate of change of conversion or reaction rate can be described using two independent functions: $f(T)$ representing the influence of the temperature and $g(\alpha)$ representing the influence of the conversion.

$$\dot{\alpha} = f(T)g(\alpha) \tag{1}$$

$f(T)$ is commonly accepted to correspond to the Arrhenius law and $g(\alpha)$ is usually associated to an a priori established equation. Some new methods, such as ''model free'' [2–4], avoid the use of explicit kinetic models, but remain tied to the Arrhenius law. The use of a method completely free of a priori established models, seems that it should be the natural next step. The ''non-parametric kinetics'' NPK method was developed to fit this objective [5,6]. In this paper the basic theory of the NPK method and its application to two different chemical systems are exposed.

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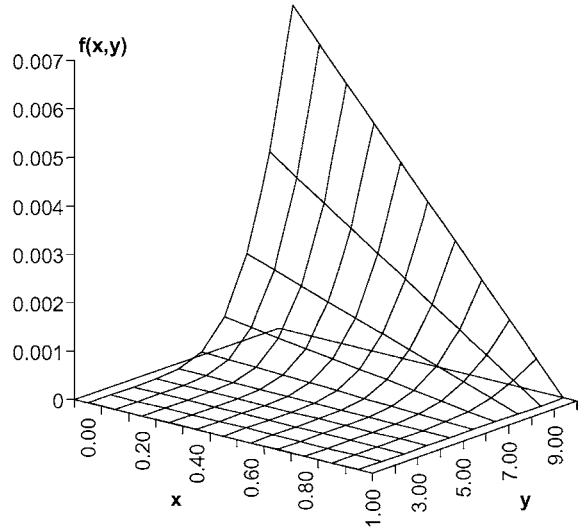

Fig. 1. Spatial representation of the values of Eq. (2).

2. Theory

Consider a bidimensional ($\Re^2 \rightarrow \Re$) function $f(x,y)$ that corresponds to the product of two independent functions $f_1(x)$ and $f_2(y)$. Fig. 1 shows the values for the function:

$$\left.\begin{aligned} f_1(x) &= \mathrm{e}^{-50/x} \\ f_2(x) &= (1-y) \end{aligned}\right\},$$
$$f(x,y) = f_1(x) f_2(y) = \mathrm{e}^{-50/x}(1-y) \qquad (2)$$

Take into account that only the values at the crosses of the graphic are known. They can be represented as a table or a matrix, $\boldsymbol{A}$, as shown in Table 1. If a singular value decomposition (SVD) a common method of decomposition of matrices is applied on the data of $f(x, y)$ contained in the $M \times N$ matrix $\boldsymbol{A}$, three matrices are produced: an $M \times N$ orthogonal matrix $\boldsymbol{U}$, a diagonal matrix $\boldsymbol{W}$ with N elements and an $N \times N$ orthogonal matrix $\boldsymbol{V}$. The original matrix, $\boldsymbol{A}$, can be then obtained through the product $\boldsymbol{A} = \boldsymbol{U}\boldsymbol{W}\boldsymbol{V}^{\mathrm{T}}$. The elements of the diagonal of $\boldsymbol{W}$ are called "singular values" of $\boldsymbol{A}$. The singular value in i place determines the weight of the product of the i row of $\boldsymbol{U}$ and the transpose of the i row of $\boldsymbol{V}$ in the above product of matrices. Due to the algorithm that is used to perform the SVD the singular values appear in decreasing order. Obviously, only those pairs of rows of $\boldsymbol{U}$ and $\boldsymbol{V}$ that correspond to different from zero singular values have significance to reconstruct the original matrix $\boldsymbol{A}$.

Table 1
Some values of Eq. (2)

x	y		
	0.00	0.10	0.20
1.00	1.93×10^{-22}	1.39×10^{-11}	5.78×10^{-8}
2.00	1.74×10^{-22}	1.25×10^{-11}	5.20×10^{-8}
3.00	1.54×10^{-22}	1.11×10^{-11}	4.62×10^{-8}

In the example, the matrix $\boldsymbol{A}$ has been obtained through the product of two vectors, one corresponding to the values of $f_1(x)$ and the other containing values of $f_2(y)$. As a consequence, only one singular value of $\boldsymbol{A}$, $\boldsymbol{w}$, is different from zero. Then, only the first row of the matrices $\boldsymbol{U}$ and $\boldsymbol{V}$ are necessary to describe the data matrix $\boldsymbol{A}$. These rows are called vectors $\boldsymbol{u}$ and $\boldsymbol{v}$, respectively. The first one, $\boldsymbol{u}$, is proportional to the values of $f_2(y)$ and the second one, $\boldsymbol{v}$, proportional to the values of $f_1(x)$ at the given values of x and y. Table 2 and Fig. 2 show the values of $\boldsymbol{u}$ and $\boldsymbol{v}$. The value of w also provided by the SVD is used as a scaling in order to make possible the reconstruction of the original data:

$$\boldsymbol{u}\boldsymbol{w}\boldsymbol{v}^{\mathrm{T}} = \boldsymbol{A} \qquad (3)$$

So, the value of $f(x, y)$ at a given pair of co-ordinates (x, y) can be obtained interpolating for the value of y on the table formed by the values of $\boldsymbol{u}$ and for x on $\boldsymbol{v}$ and

Table 2
Results of the SVD of the matrix containing values of Eq. (2) at the indicated x and y points[a]

x	v	y	u
1.00	2.40×10^{-20}	0.00	5.10×10^{-1}
2.00	1.73×10^{-9}	0.10	4.59×10^{-1}
3.00	7.18×10^{-6}	0.20	4.08×10^{-1}
4.00	4.63×10^{-4}	0.30	3.57×10^{-1}
5.00	5.64×10^{-3}	0.40	3.06×10^{-1}
6.00	2.99×10^{-2}	0.50	2.55×10^{-1}
7.00	9.82×10^{-2}	0.60	2.04×10^{-1}
8.00	2.40×10^{-1}	0.70	1.53×10^{-1}
9.00	4.80×10^{-1}	0.80	1.02×10^{-1}
10.00	8.37×10^{-1}	0.90	5.10×10^{-2}
		1.00	0.00

[a] $\boldsymbol{w} = 1.58 \times 10^{-2}$.

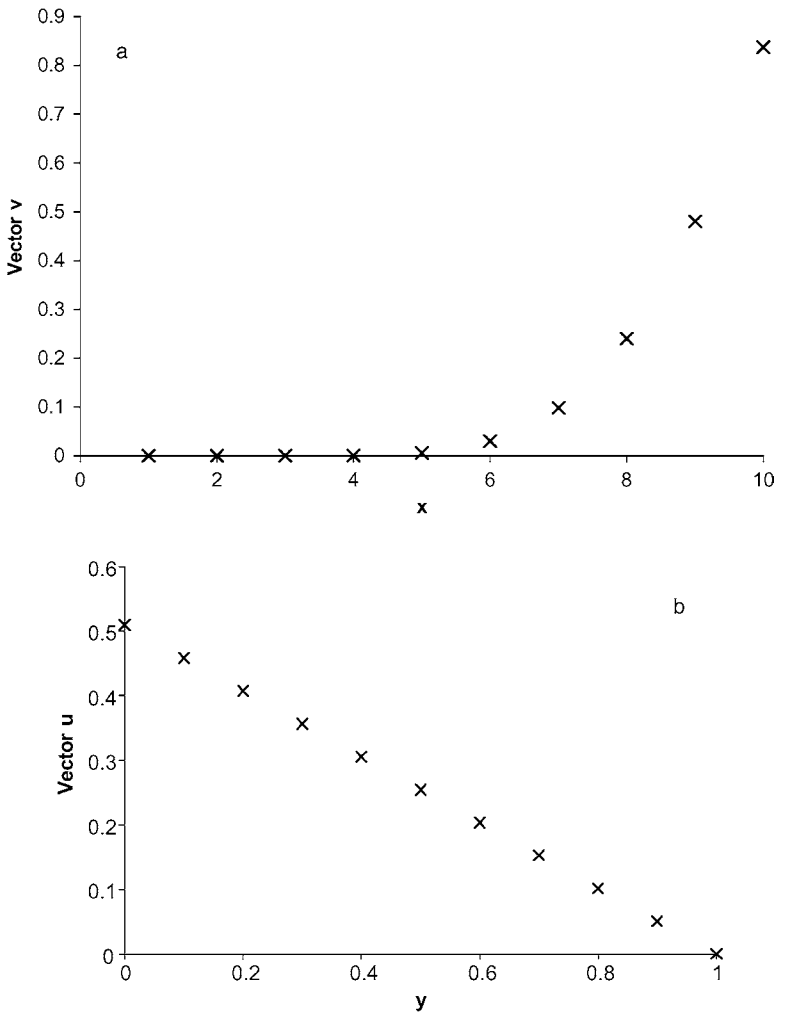

Fig. 2. Vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ resulting from the SVD decomposition of the values of Eq. (2) represented in Fig. 1.

multiplying then together with the scaling factor. As an example, the interpolated value for $x = 5.50$ is 1.40×10^{-2} and the interpolated value for $y = 0.55$ is 2.29×10^{-1}. Thus, the estimated value of $f(5.50, 0.55)$ is

$$(1.40 \times 10^{-2})(1.58 \times 10^{-2})(2.29 \times 10^{-1}) = 5.06 \times 10^{-5}$$

Which is an excellent approximation to the expected value (5.07×10^{-5}). This procedure allows predicting the values of an unknown function using only its values at certain points.

In the case of a set of records of isothermal calorimetry, the same procedure can be applied on the experimental data. As a first step, data of reaction rate, α are tabulated in front of temperature, T and degree of conversion, α. Then, the obtained matrix, $\boldsymbol{A}$, is decomposed using SVD. If the reaction can be well enough described using Eq. (1), only one singular value, $\boldsymbol{w}$, is different from zero. One $\boldsymbol{u}$ vector and the corresponding $\boldsymbol{v}$ vector are enough to reproduce the data matrix. The results contained in the vector $\boldsymbol{v}$ are proportional to the function of temperature, $f(T)$, at the given temperatures, and those in the vector $\boldsymbol{u}$ are proportional to the function of conversion, $g(\alpha)$.

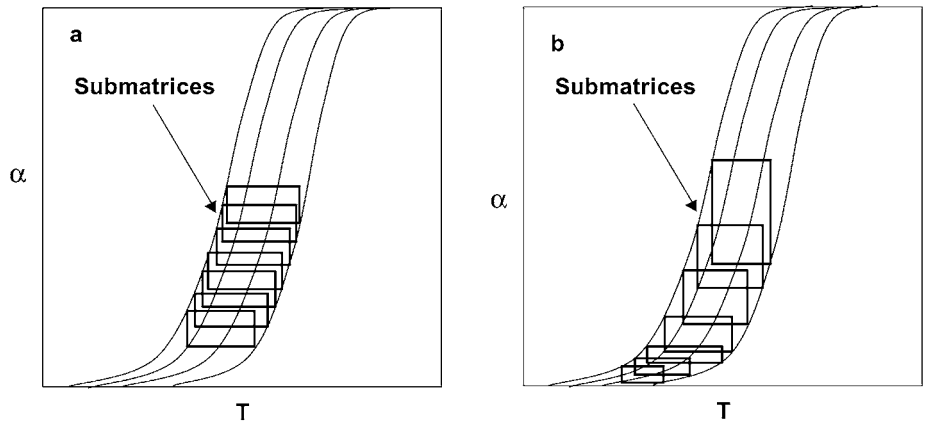

Fig. 3. Example of the evolution of the recursive algorithm as used by NPK. Each rectangle corresponds to a submatrix, which is decomposed by SVD: (a) rigid NPK and (b) adaptive NPK.

The shape of $g(\alpha)$ should be the same that those of all isothermal records. Then, the vector $\boldsymbol{v}$ might be called ''isothermal vector''.

When a set of records of dynamic DSC is used, it is necessary to reconstruct the whole data set using the available data. A recursive calculation based in the creation and SVD of a set of full submatrices and a continuity criterion is used to obtain the $\boldsymbol{U}$, $\boldsymbol{W}$ and $\boldsymbol{V}$ matrices, as stated in reference [5] (Fig. 3a). A recent improvement is the development of a variable step procedure that allows extending the evaluation to very low and very high conversions (Fig. 3b). Again, if only one singular value of each submatrix is taken into account, the result is a pair of vectors, $\boldsymbol{u}$ and $\boldsymbol{v}$, with the same meaning as stated above.

The NPK method has been applied also to adiabatic calorimetry [6], showing good robustness despite of the error introduced by the derivation of the original data.

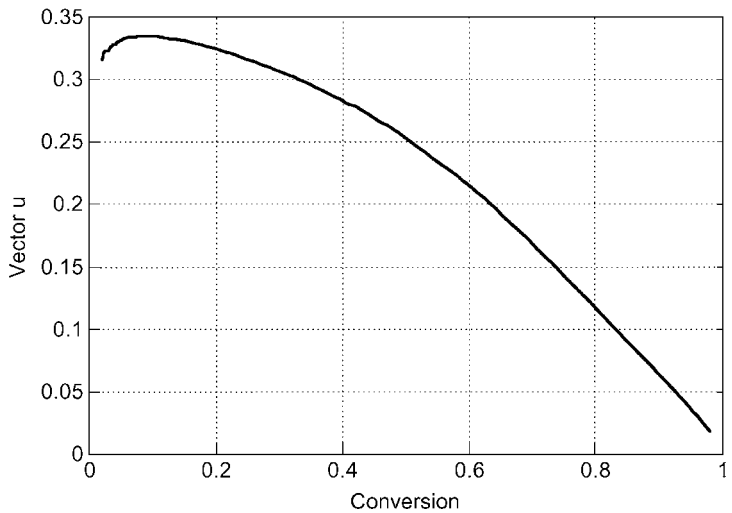

Fig. 4. Vector $\boldsymbol{u}$ produced from the experimental data of the thermal decomposition of the dicyclohexylidene diperoxide, containing information on the influence of conversion.

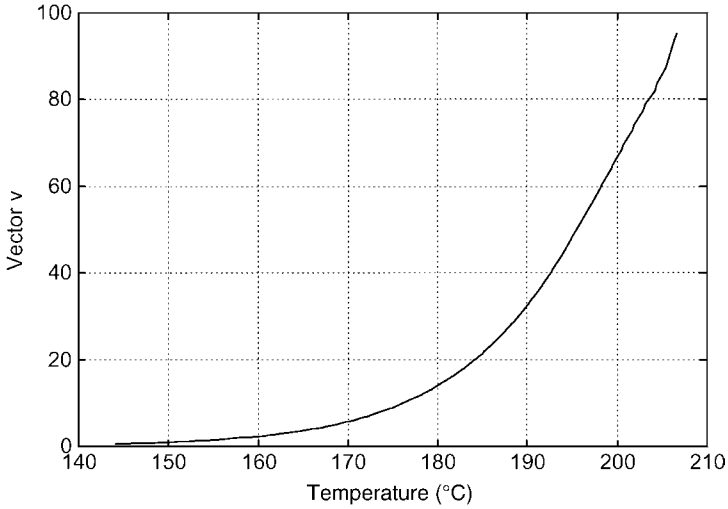

Fig. 5. Vector $\boldsymbol{v}$ produced from the experimental data of the thermal decomposition of the dicyclohexylidene diperoxide, containing information on the influence of temperature.

3. Experimental

Dicyclohexylidene diperoxide is prepared according to the method described by Sanderson et al. [7]. DSC curves are obtained using a Mettler-Toledo Star^e system with a DSC821 cell, using standard aluminium crucibles (ME-51119870) with a perforated lid (ME-51140832) under a flow of 80 ml min^{-1} of nitrogen. Samples from 2 to 4 mg are recorded at 1, 2, 5 and 7 K min^{-1}.

A 1% (w/w) of AIBN solution in freshly distilled methyl metacrylate is prepared and stored at 4 °C. DSC curves are obtained using a Mettler-Toledo Star^e system with a DSC30 cell, using medium pressure crucibles

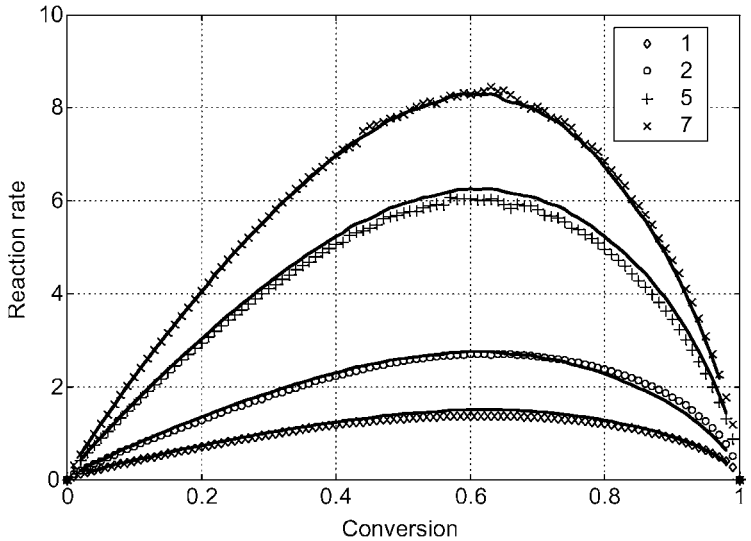

Fig. 6. Reconstruction of the experimental data set using the NPK results for the thermal decomposition of the dicyclohexylidene diperoxide: (◇) 1 K min^{-1}; (○) 2 K min^{-1}; (+) 5 K min^{-1} and (×) 7 K min^{-1}.

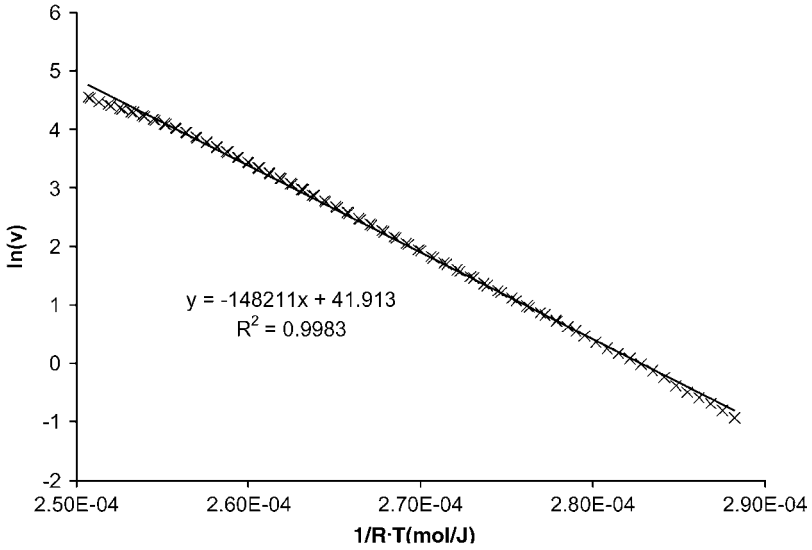

Fig. 7. Arrhenius plot of the $\boldsymbol{v}$ vector corresponding to the thermal decomposition of the dicyclohexylidene diperoxide.

(ME-29990) sealed under nitrogen [8]. Samples from 4 to 6 mg are recorded at 2, 4, 6, 8 and 10 K min^{-1}.

4. Results

The application of the NPK algorithm to the decomposition of dicyclohexylidene diperoxide gives the results shown in Figs. 4 and 5. In this case, the vector $\boldsymbol{u}$ seems to correspond to a simple kinetic model, and the Arrhenius plot of $\ln(u)$ versus $1/T$ gives a value of 148 kJ mol^{-1} for the activation energy. The shape of vector $\boldsymbol{u}$ could be identified as a SB model $(g(\alpha) = \alpha^n(1-\alpha)^m)$. Their parameters are easily obtained by direct regression of the elements of $\boldsymbol{u}$ versus conversion. However, the produced values

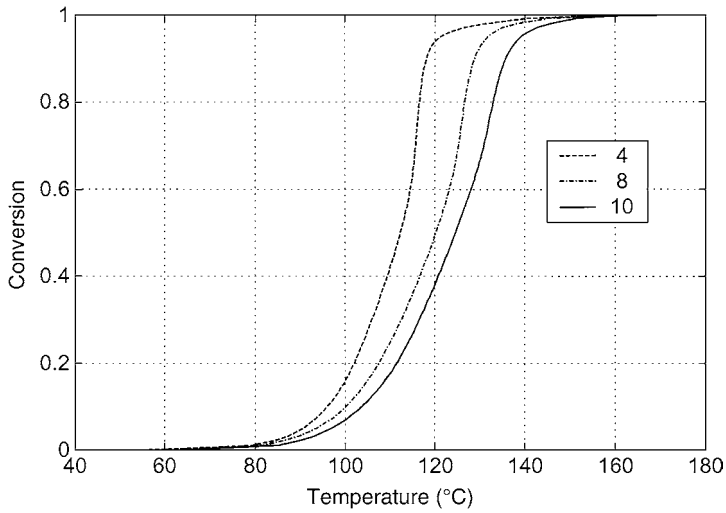

Fig. 8. Shape of some DSC curves corresponding to the mass polymerisation of methyl methacrylate: (- - -) 4 K min^{-1}; (- · -) 8 K min^{-1} and (—) 10 K min^{-1}.

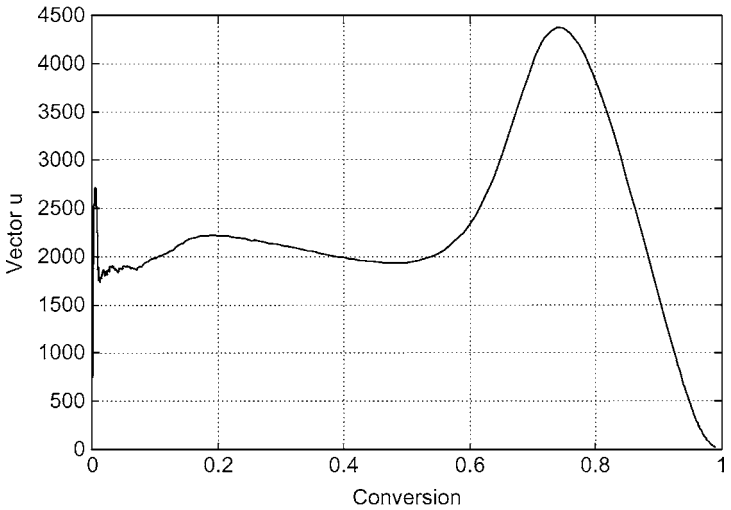

Fig. 9. Vector ***u*** produced from the experimental data of the mass polymerisation of methyl methacrylate, containing information on the influence of conversion.

($n = 0.092$; $m = 0.80$) have no clear meaning, and suggest that fitting a more complex model might be necessary to carry out predictions. On the other hand, the results of the NPK method allow the direct reconstruction of the experimental data with an excellent accuracy, but not using any model, as shown in Figs. 6 and 7.

The case of the mass polymerisation of methyl methacrylate (Fig. 8) is more complex due to the presence of the Trommsdorf or gel effect [9–11]. An autoacceleration of the reaction is observed as shown in Fig. 9, corresponding to the ***u*** vector produced by the NPK algorithm. As described in literature, the onset of the autoacceleration takes places

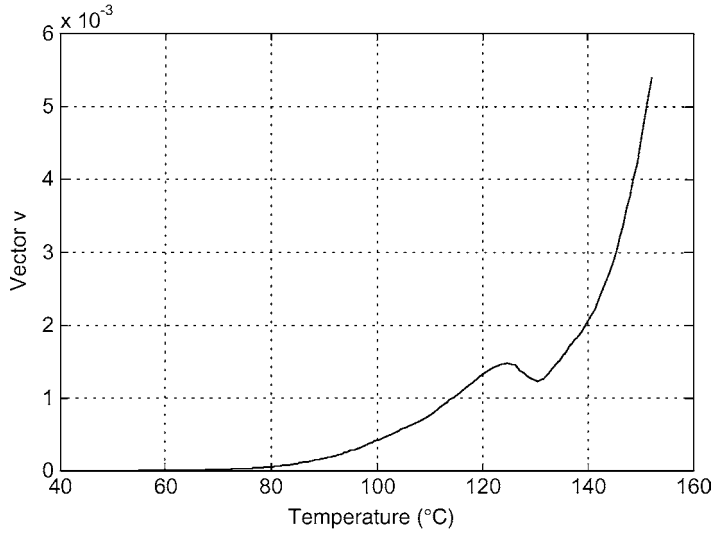

Fig. 10. Vector ***v*** produced from the experimental data of the mass polymerisation of methyl methacrylate, containing information on the influence of temperature.

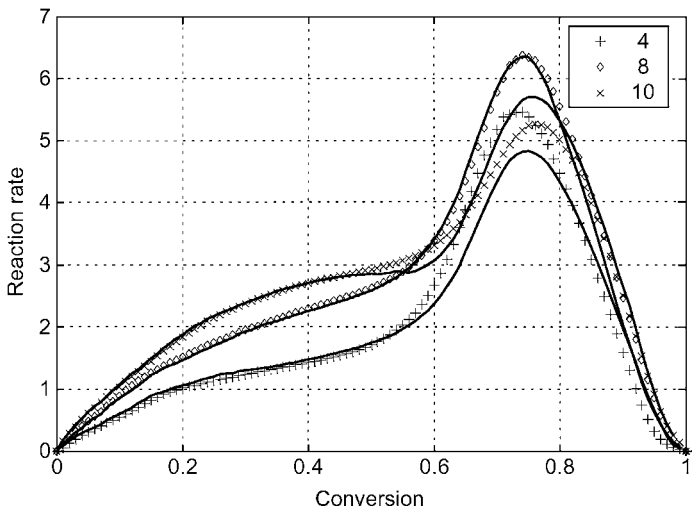

Fig. 11. Reconstruction of the experimental data set using the NPK results for the mass polymerisation of methyl methacrylate: (+) 4 K min^{-1}, (◇) 8 K min^{-1} and (×) 10 K min^{-1}.

around sixty percent of conversion. Fig. 10 displays vector $\boldsymbol{v}$. It shows two different segments, corresponding to the normal polymerisation and the accelerated process due to the gel effect.

Although, the difficulty of describing such a process using a simple model, the results of the NPK algorithm again allow to reproduce the experimental data set with pretty good accuracy (Fig. 11) and to predict the behaviour of the reaction under other conditions within the studied range of temperature.

It must be taken into account that the direct prediction of the behaviour of the system is performed by integration of the differential Eq. (1), obtaining the values of $f(T)$ and $g(\alpha)$ interpolating in the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$. The prediction outside the explored temperature range requires the use of extrapolation. In this case it would be better to use the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ to deduct and parameterise a traditional model.

5. Conclusions

The NPK method applied to simple processes can be used to identify a kinetic model, and to obtain their kinetic parameters. Moreover, using the NPK method itself does not make necessary any model to carry out predictions, even in the case of complex chemical behaviour.

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