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Factor Analysis of the Styrene Polymerization Kinetics Statistical Verification of the Procedure

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Introduction- Statistical verification of operations used earlier for kinetics experimental data treatment of the styrene suspension polymerization performed on the one of known kinetics model. Internal standard times matrix for different conversions found to have only two statistically significant eigenvalues. Therefore, they may be considerate as plains and easily described to give equation for its dependence from initial condition needed for dimensionless time scale definition. Conversion vectors dependence on the later forms sets of very closely curves. They may be considerate as stochastic realization of the one common curve what follows from its non parametric statistical comparison. Final single curve finds by uniting and sorting operation of its values. That operation gives one plain common curve described by empirical equation with small set of the empirical parameters needed, considerably less than in existing models. Procedure is convenient and robust.

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I. Introduction

Statistical verification of operations used earlier for kinetics experimental data treatment of the styrene suspension polymerization performed on the one of known kinetics model. Internal standard times matrix for different conversions found to have only two statistically significant eigenvalues. Therefore, they may be considerate as plains and easily described to give equation for its dependence from initial condition needed for dimensionless time scale definition. Conversion vectors dependence on the later forms sets of very closely curves. They may be considerate as stochastic realization of the one common curve what follows from its non parametric statistical comparison. Final single curve finds by uniting and sorting operation of its values. That operation gives one plain common curve described by empirical equation with small set of the empirical parameters needed, considerably less than in existing models. Procedure is convenient and robust.

We have recently found [1] that the styrene dispersion polymerization kinetics described by simple semi empirical equation with only six empirical constants:

$$x_M = 1 - 0.5\left[\exp(-a\theta) + \exp(-b\theta^c)\right], \qquad (1)$$

where:

x_M – monomer conversion,

a,b,c - empirical constants,

θ - dimensionless time defined as

$$\theta = \frac{\tau}{\tau_{0.6}} \qquad (2)$$

τ – astronomical time,

$\tau_{0\cdot6}$ – the internal standard time (IST) defined as the time of 60% conversion of the monomer.

The dimensionless time found to be the linear function of the initial conditions: temperature T, and initial initiator concentration I_0 with the quite practically acceptable standard deviation 8.123.10^{-3}:

$$\ln\tau_{0.6} = A + BT^{-1} + C\ln I_0\,. \qquad (3)$$

These equations we have obtained in the frame of the new procedure, which consist of the *a priori* experiment design for following factor analysis using. Our experiment space have been created by the quadratic matrix 5x5 non coincidental combinations of the initial 5 temperatures and 5 initiator concentrations. Experiment results have given us 25 kinetics curves, *i.e.* monomer conversion dependence on the astronomical time. That way the experiment space created. That space than transformed in the dimensionless form by transition from astronomical time to dimensionless one by formula (2) after Dilman and Polanin [2]. Basic conversion needed chosen equal to 0.6 because at that point gel effect initiates [1,3]. Internal standard time matrix have found to be plane in the limits of the experiment accuracy and described by the equation (3). The kinetics curves in the new coordinates x_M - θ found very close one to the other and seems to belong to the only one curve. For finding the later we used the new procedure: uniting them by the placing corresponding arrays one top to the other bottom. The resulting common array values than sorted in ascending order. Because of the large number of experimental points such procedure was performed initially to the 5 initial condition matrix columns giving 5 corresponding united and sorted arrays, and then performing the same operation to all them. Uniting and sorting operation used also to find dimensionless time vector. This way one common array for dependence of the conversion from dimensionless time have derived, which have been excellently seen, corresponds qualitatively to the reaction with the pronounce gel effect described by the equation (1). However, such procedure had two indefinites to proving. The first is indefinites in the basic conversion choosing, and the second – statistically not based uniting and sorting operations with the arrays. These indefinites proving is current communication task.

Verification performed by numerical experiment on the kinetics model close qualitatively to our experimental data, namely – Santos *et al* [3]. That model bases on the classical radical polymerization scheme in terms of quasi steady state approximation and quadratic active chains termination [4] corrected by introducing initiator affectivity factor (cage effect supposed constant – f =0.5) and empirical gel effect description.

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The last used exponential multiplier for termination rate constant, containing regression third order equation with linear dependence its coefficients on temperature. That multiplier contains six purely empirical constants.

Kinetics curves produced by numerical integration that model at the initial condition identical to matrix in the real investigation [1], *i.e.* temperatures 78, 81, 84, 87, and 91C, and initiator concentrations 0.021, 0.033, 0.045, 0.058, and 0.070 mol/l. Ten equidistant points from interval {0, 1} chosen to form the points of the simulated "kinetics curves". The 25 kinetics curves was the result, which formed the experimental space in time and initial conditions coordinates. Space cross section at conversions 0.2, 0.3, 0.4, 0.5, 0.6 and 0.8 produced corresponding internal standard time matrixes. All they found to have rank 5. Factor analysis [5] demand their centering and normalization, but we ignored these operations. The first of them needed for matrix rotation and the later standardized values by the variances that may differ in time. We considerate all curves as the section at the same conversion what did the later operation excessive. The matrix centering we applied only for excluding large number in calculating because rotation will lead to emergence of new variable - linear combination of the initial, and all description serious complication.

Results of the matrixes eigenvalues calculation given in the Table 1, from which seen that all them have only two first significant values. Information content in them practically not differs from 1. To these eigenvalues corresponds two eigenvectors which defines space dimension created by matrix. Therefore, cross sections at any conversion may be considerate as planes, provided that experimental error taken into consideration. Fig. 1 demonstrates that visually.

Table 1 : Centered IST matrixes eigenvalues* at various monomer conversions

	Basic monomer conversion					
	0.2	0.3	0.4	0.5	0.6	0.8
Eigenvalues λ	2.937 1.25 1.381×10^{-5} 2.533×10^{-7} 1.179×10^{-10}	2.854 1.3 2.951×10^{-6} 5.806×10^{-7} 1.355×10^{-6}	2.77 1.347 2.815×10^{-6} 6.209×10^{-7} 1.198×10^{-8}	2.688 1.394 4.516×10^{-6} 7.911×10^{-7} 2.624×10^{-10}	2.623 1.43 1.892×10^{-6} 8.067×10^{-7} 7.615×10^{-8}	2.623 1.43 1.892×10^{-6} 8.067×10^{-7} 7.615×10^{-8}
Matrix rank	5	5	5	5	5	5
R**	1	1	1	1	1	1

) centering performed referring to the central matrix value instead of the mean one.*

*)** the information fraction of the first two values:* $(\lambda_1 + \lambda_2)/\Sigma\lambda$.

The planes only slightly curved, and curving induces by initiator. This is seen from correlation coefficients for matrix columns and rows: for temperature ones they all strictly are 1, and only close to 1 for initiator concentration (*ca*. 0.985).

These results mean that equation (3) may be applied for the IST dependence from initial condition full description. Table 2 confirms that conclusion. It must be noted that in that case the better correlation obtained with the modified form of this equation (3) where initial initiator concentration used instead of its logarithm, *i.e.*

$$\ln\tau_x = A + BT^{-1} + CI_0\,. \qquad (4)$$

Table 2 : Regression coefficients of the equation (4)

Coefficient	Basic monomer conversion					
	0.2	0.3	0.4	0.5	0.6	0.8
A B C	25.755 -6548 19.386	26.387 -6667 19.073	27.589 -7015 18.743	28.707 -7356 18.406	28.831 -7353 18.121	29.778 -7.654 17.818
Standard deviation	0.045	0.045	0.047	0.049	0.050	0.053

One may see from table 2 that equation (4) describes planes rather well but regression coefficients vary with the basic conversion. *A* and *B* increase while the *C* diminishes noticeably. One may see also increasing of the standard deviation. Thus, in the whole, such description seems to be acceptable - especially for practical purposes. All six matrixes shown on the Fig. 1 form visually coplanar plains - that seen visually very well.

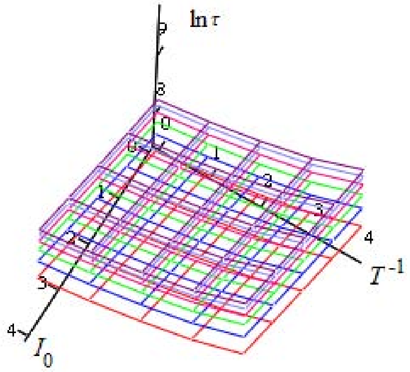

Figure 1 : IST dependence on initial conditions at monomer conversions: 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 (down to up)

Results of the uniting and sorting operation application to the vectors artificially produced (kinetics curves) shown on the Fig 2. The common curve seen very well. Diverging observed at high conversions (more than 0.95 – see Fig.3) and has order approximately 0.01-0.02 in the maximum. This diverging depends on the basic conversion chosen for dimensionless time determination and diminishing the later increase it noticeably. 60% conversion have been chosen in [1] rather well. From Fig. 3 one may see also that uniting and sorting operation are equivalent, in some sense, to meaning all curves.

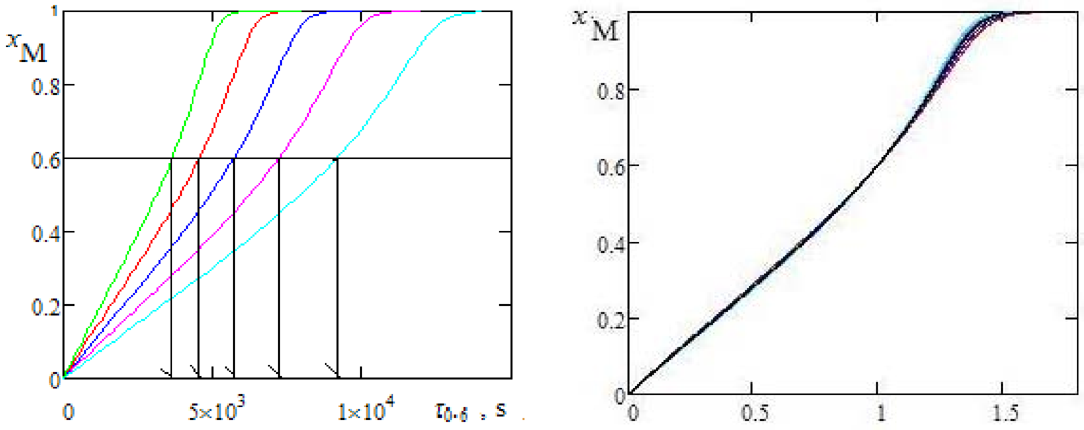

Figure 2 : Kinetics curves, and times of the 60% conversion determination (shown by arrows) for temperature series (78, 81, 84, 87 and 90 C) at the initiator concentration 0.07 mol/l – left. Kinetics curves in the dimensionless time scale and operation result of its uniting and sorting (black curve) – right

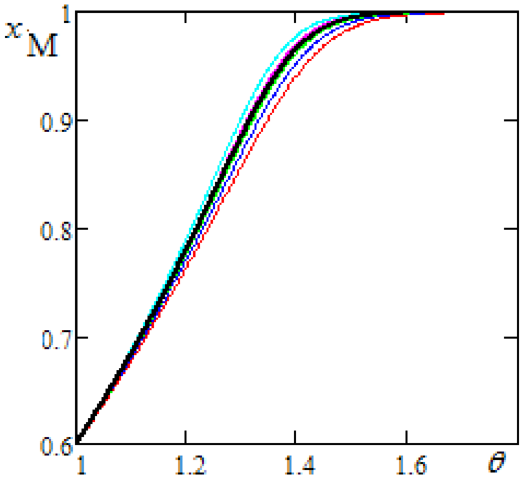

Figure 3 : Conversion *vs*. dimensionless time curves from Fig.2 at high conversions. There is no full coinciding. Fat black curve is the result of uniting and sorting operation on all five individual curves

Operation of experimental vectors uniting and sorting needs special attention because not only its role in the resulting equation obtaining but its amazing effectiveness also. One may see that if compares initial experimental curves and final one in [1]. Just that gives us base consider it earlier justified *a posteriori* [6]. We prove that operations on the model in two ways: in the reproducibility “runs”, and in one series treating. Fig.4 represents results of the simulation data treatment with “experimental error”. The last modeled by addition to calculated values of conversion normal distributed random variable with null mean and variance 0.04 (standard deviation 0.2!). Initial model kinetics curve reproduces quite well, providing that dimensionless time vectors treat by the same procedures uniting and sorting. Fig. 4 demonstrates how these operations works for serial data. Initial curves do not indentify even its form which seen well on the united and sorted vector. Fig. 5 demonstrates that procedure for reproducibility five runs. Common vector curve reproduced model curve quite well.

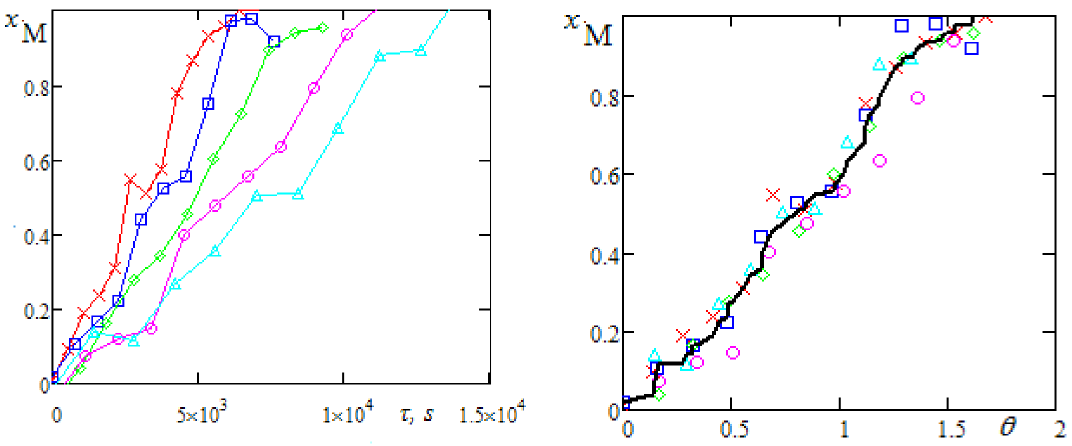

Figure 4 : Simulated kinetics curves at initiator concentration 0.070 mol/l, and different temperatures. Standard deviation equals 0.2. Five "experimental" curves – on the left. United and sorted common vector – on the right

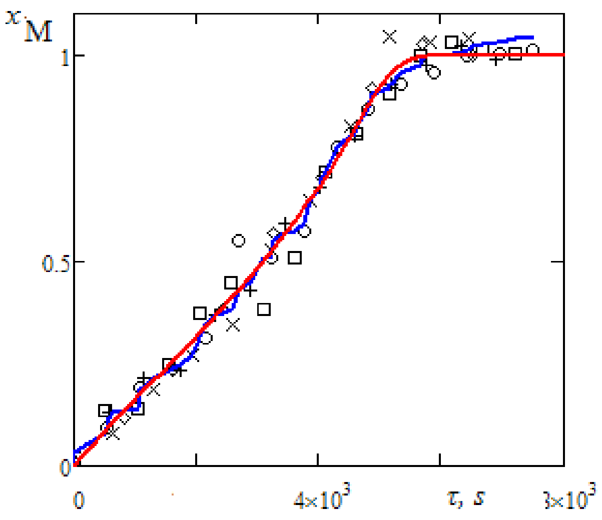

Figure 5 : Stack and sort operations illustration for simulated reproducibility runs. Points are individual five "runs" results with standard deviation 0.2, blue line is result of uniting and sorting operations, and red line is the model. Unreal conversions, larger than 1.0, are included intentionally for procedure demonstration

The procedure used bases on the postulate that all experimental curves are stochastic realization of only one common curve. One may see that from Fig. 3 and this statement have to prove. Small experimental points we have exclude using of any parametrical criterion and nonparametric one from Wilcoxson (Mann-Witney) was used [7]. For proving, we take border curves having maximum differences, namely at 78C and 90C (initiator concentration 0/07 mol/l). The procedure [7] include generating one common vector from two vectors compared, its sorting in ascending order, and ranging its values by natural number sequence. Then rank sum calculated for the initial vectors for criterion values calculation. The smaller one compared with critical one from statistical table, which must be smaller than calculated in the case of the difference insignificancy of the two vectors compared. The following example also gave vectors uniting and ranging operation illustration.

In our case, vectors compared are (two temperatures at initiator concentration 0.07 mol/l):

xm51 (0, 0.105, 0.206, 0.306, 0.409, 0.521, 0.650, 0.804, 0.955, 0.997, 1.000)

xm55 (0, 0.086, 0.169, 0.253, 0.340, 0.433, 0.537, 0.661, 0.817, 0.967, 0.999)

United and sorted vector is:

Xm5 (0,0,0.086, 0.105,0.169, 0.206, 0.253,0.306, 0.340, 0.409,0,433, 0.521,0.537,0.650,0.661, 0.804, 0.817, 0.955,0.967, 0.997, 0.999, 1.000),

and corresponding rank vector is:

RXm5 (1, 1, 2, 3 … 21)

Initial vectors ranks and their rank sum:

Rxm51 (1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21) SRxm51=121
Rxm55 (1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20) SRxm55=131

Criteria calculated in such way [6]

$$U5i = \sum Rxm5i - \frac{Ni(Ni+1)}{2},$$

where Ni is i-vector length. The smaller criterion calculated is 55. Critical criterion value is 25 on the 1% significance level [6]. All other calculated criteria are more than that value. Thus, all five vectors are indistinguishable statistically and may considerate as stochastic realization of the one common vector. This conclusion justifies procedure described above – uniting all five vectors in common one and sorting its values in ascending order.

II. CONCLUSION

The procedure developed basis on consciously experiment design for subsequent factor analysis methods using. It results in the substantial simplification of the kinetics description for styrene polymerization in full interval of monomer conversion. The experiment space found to need for full description only six empirical parameters when literature models include 13 (and more!) such parameters. The new operations in the data treatment, *i.e.* internal time standard introduction for time dimentionlessing and subsequent uniting and sorting conversion and time vectors values leads to one common two-dimensional kinetics curve. Its empirical description is pure technical task. All these operation are statistically valid as numerical experiment on the one of kinetics model demonstrated even without stochastic experimental error. The initial kinetics curves reproduce well. The procedure seems to be robust, simple and convenient - especially with contemporary PC program using. The single restriction is that only ascending (or descending) experimental curves may be treated.

The procedure includes some interesting features needed feather investigation. The vectors uniting and ranging operation high efficiency remain incomprehensible. Perhaps, there is united and sorted conversion and dimensionless time vectors autocorrelation because of its determination from the same experimental curves set. Resulting two dimensional curve empirical descriptions definitely demands two different functions sum using. It is possible that in reality we have two different polymerization mechanisms – diffusion complicated and classical in macromolecular globules and monomer phases, existing really up to glass effect point. It is seems interesting to note that the second term in equation (1) has form typical for process of crystallization. Finally, it is possible that procedure will be useful for searching empirical dependencies from experimental data [7] - not only for kinetics time series.

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