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Quantitative Description of Polymerization Reactions by Means of Multiparameter Equations

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ABSTRACT

Linear free energy relations are successfully extended to the principle of polylinearity when propagation is the predominant rate-determining step and others (e.g., initiation, termination) can be neglected. The cationic polymerization of vinyl ethers and p-substituted styrenes provides improved insight into the mechanism. On the other hand, the overall rate of the homopolymerization or the relative reactivity of the cross-propagation step in copolymerization can be controlled by means of multiparameter equations. Some examples are given where multiparameter correlation analysis with rather empirical parameters are shown useful for controlling industrial processes as well as for definite product formation.

INTRODUCTION

Correlation analysis is an empirical method for modeling structure-reactivity and structure-property relationships. Starting from the basic work by Hammett [1] and Taft [2], this method is well established and outlined for different fields of organic chemistry [3]. The method—generally known as linear free energy relationship

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(LFER)–is based on the assumption that in a data set of interest the change in the value of reactivity or of some property which results from a given structural change is proportional to the change of reactivity or in a property of a reference data set caused by the structural change. Thus,

$$(\partial y_i/\partial X)V_j = a_1$$

$$y_{i,X} = a_1 x_{1,X} + a_0$$

where y is the reactivity (lg k or lg K); i and 1 designate the set of interest and the reference set, respectively; X is the structural change; a_1 and a_0 are constants; $x_{1,X}$ is the sensibility of the structural change; and V_j are variables which are kept constant when y is determined (e.g., T, P, solvent).

In modeling structural effects on reactivity, various kinds of structural parameters may be required. They represent electrical, steric, polarizability, and interaction contributions to the overall structural effect. Additional parameters which must be taken into consideration are so-called control parameters: Temperature, pressure, solvent, catalyst, variation of concentration of components.

If independent linear relations exist between the reactivity parameters of one reaction set and parameters of different structural influences (and/or control parameters), the quantitative description should be possible by linear combination of different parameters x_i (or functions of these parameters):

$$y_i = \sum a_i x_i$$

This method was developed by Palm [4, 5], and extensive studies were done concerning the cationic polymerization and copolymerization of styrenes by our group [6-11]. When we started our investigation into multiparameter correlation analysis, only a few papers had been published which correlated the overall rate of the cationic polymerization (lg k_{ov}) and the copolymerization parameters (lg $1/r_1$ or lg $1/r_2$) with electrical [12] and steric substituent effects [13] of the monomers used, with quantum chemical reactivity data of the monomers [14], with the solvent polarity [15], with the activity of initiators [16], and with the variation of monomer concentration and initiator concentration [17]. In addition to some other aims (e.g., exhaustive experimental data sets, standard reaction conditions), we were most interested in multiparameter correlations which would show the complex behavior of cationic polymerization resulting from the overlap of various kinds of initiation, propagation, and chain limiting processes [18].

METHODIC DEVELOPMENT

The lg k_{ov} data were determined either by dilatometry [7] or by rest monomer detection by means of gel permeation chromatography [9, 10]. In the case of copolymerization, the relative reactivities of M_1 and M_2 could be successfully represented by lg r_1/r_2. The derivation of this parameter based on a free-energy model of propagation steps in cationic copolymerization was published in Ref. 10. Some advantages of this parameter in comparison with lg $1/r_1$ or lg $1/r_2$ are reported in Ref. 11. The computation of copolymerization parameters (r_1 and r_2) was reported by the author [19], and a detailed understanding of the mathematical equations, models, and computer programs used is available from earlier papers [20, 21].

In the general case the structure of a data set may be written XRY, where X is the variable substituent, Y is the reaction center (double bond of the monomers), and R is a skeletal group to which X and Y are bonded. Various kinds of structural parameters were used:

1. Empirical parameters; i.e., substituent values by Hammett (σ_p) or Taft (σ_I), steric substituent constants (E_S).
2. Molecule parameters obtained by spectroscopic methods; i.e., λ_{max} values of the UV absorption of the monomer double bonds or their IR absorption peaks.
3. Values calculated by quantum chemistry; i.e., stabilization energy (ΔE_{ij}^{π}), π-electron density, etc.

Our investigation has shown that empirical parameters gave the best results in all cases expressed in computer terms: Regression coefficients (r, or R in multiple regression analysis), scale of exactness (B), rest deviation (S_R; least squares method). That is why we used only parameters of the Type 1 which are quasi-justified in real reaction systems. For the correlation analysis of the copolymerization of p-substituted styrenes, the structural effect on reactivity was expressed by the difference of the two σ_p values ($\Delta\sigma_p$).

Besides structural effects on reactivity, the following external influences on the reactivity were investigated (control parameters):

1. The solvent effect, represented by the dielectric constant or some empirical scales of solvent polarity (e.g., Z values, Y values, E_T values). Our best result could be obtained by use of the E_T values by Reichardt [22].
2. The initiator activity, represented by a scale of empirical parameters determined by high-frequency conductivity measurements

[7, 9]. The parameters (χ_{Kat} or $\epsilon_{Glas/Kat}$) include the Lewis acid activity as well as the acidity of the initiator/coinitiator system (e.g., MtX_n/HX) under standard conditions. The coinitiator effect was represented by $\chi_{Cokat}/\chi_{SnCl_4}$ [7, 9].

3. The reaction temperature [9, 23].
4. Variation of monomer and initiator concentrations [9, 24].

Basic requirements for successful correlation analysis experiments are standard conditions for the purification of all reaction components, solvents, etc. [11]. The same holds for the accuracy of the determination of y (e.g., lg k_{ov} or lg r_1/r_2) in dependence on x_i. The other variables are kept constant within the range of x_i, which should be as wide as possible.

When more than one independent variable x_i is included in regression models, statistical problems with colinearities arise. There are some ways of solving this problem, but in the case of cationic polymerization the structural and external influences on reactivity are rather complex so that it was not possible to introduce meaningful correction terms into a multiparameter equation. Thus we applied step-wise regression analysis to determine the so-called "monolinearities" (x_1, x_2, x_3 . . ., etc.), and only when the LFER was valid were the parameters used for multiparameter correlation of the general type $Y_i = \sum a_i x_i$.

Computer programs for regression analysis are available at any computer center [20]. According to the mechanistic interpretation of cationic polymerization [6, 18], some parameters showed nonlinear functions (e.g., Lewis acid activity [9], or monomer concentration [9, 24]). Therefore the computer program was extended to nonlinear functions (e.g., time-conversion curves ran through a maximum). Successful investigations, including nonlinear functions, are referred to in more detail in Refs. 9-11 and 21.

RESULTS OF CORRELATION ANALYSIS AND DISCUSSION OF MECHANISTIC ASPECTS

Some results of the kinetic analysis of the cationic polymerization of alkyl vinyl ethers initiated with I_2 at room temperature and with $BF_3.OEt_2$ at -78°C are shown in Table 1. The regression data are as follows:

TABLE 1. Kinetic Data of Alkyl Vinyl Ether Polymerization by Initiation with I_2 at 25°C in 1,2-Dichloroethane[a] and with $BF_3.OEt_2$ at -78°C in Toluene[b]

R in R–O–CH=CH_2	k_{ov}[a] ($J \cdot L^2 \cdot s^{-1} \cdot mol^{-2}$)	lg k_{ov}	k_{ov}[b] ($s^{-1} \cdot mol^{-1} \cdot L$)	lg k_{ov}	$\overline{M}_n$[a]	$\overline{M}_n$[b]	σ_I	E_S (R–CH_2–CO_2R')
t-Butyl	1630.0	3.21	-	-	420	-	-0.3	-1.74
i-Propyl	175.0	2.24	4.73×10^{-4}	-3.33	450	1,610	-0.19	-0.91
Cyclohexyl	80.1	1.90	2.4×10^{-4}	-3.62	380	3,750	-0.15	-0.95
n-Butyl	16.6	1.22	-	-	334	-	-0.13	-0.38
Ethyl	16.3	1.21	3.53×10^{-5}	-4.45	506	11,250	-0.10	-0.34
n-Propyl	11.1	1.05	2.25×10^{-5}	-4.65	380	2,000	-0.12	-0.36
i-Butyl	7.8	0.89	2.47×10^{-5}	-4.61	348	18,000	-0.13	-0.34
Methyl	-	-	1.53×10^{-6}	-5.82		18,000	0.0	0.0

[a] Determined by the thermokinetic method by means of an anisothermic calorimeter; referred to in detail in Ref. 25. [Mon] = 6.0×10^{-2} mol/L; [I_2] = 8.9×10^{-5} mol/L; [H_2O] 2.7×10^{-3} mol/L.

[b] Determined by dilatometry [25]. [Mon] = 1.5 mol/L; [$BF_3.OEt_2$] = 2×10^{-2} mol/L; [H_2O] $\approx 2.7 \times 10^{-3}$ mol/L.

1) (I_2 as initiator):

$\lg k_{ov} = -11.73\sigma_I - 0.19$; $n = 7$; $r = 0.96$

$\lg k_{ov} = -1.55E_S + 0.56$; $n = 7$; $r = 0.98$

2) ($BF_3.OEt_2$ as initiator):

$\lg k_{ov} = -13.27\sigma_I - 5.9$; $n = 6$; $r = 0.96$

$\lg k_{ov} = -2.28E_S - 5.52$; $n = 6$; $r = 0.96$

In both cases the high negative slope of ρ_I (reaction constant a_i in Taft equation) indicates that cation formation (initiation and propagation) seems to be the rate-determining step within this electrophilic mechanism. The sensibility of steric effects is only 1/5 or less compared with the polar effect on the reaction center.

The next step was to determine two-parameter equations by multiple linear regression analysis [20, 21]. We obtained the following data (in principle, extended Taft equations):

1) $\lg k_{ov} = -1.24\sigma_I - 1.4\,E_S + 0.48$

$R = 0.98$; $S_R = 0.195$; $B = 0.96$

2) $\lg k_{ov} = -6.47\sigma_I - 1.31\,E_S - 5.78$

$R = 0.99$; $S_R = 0.16$; $B = 0.98$

While the slope of the two structural parameters is also negative in the two-parameter equations, the ratio for the sensibility (approximately 1/5 for ρ_I/ρ_{E_S}) of the structural effects is nearly the same for $BF_3.OEt_2$-initiated polymerization. In the case of I_2 initiation, the ratio is approximately 1. Though the computer data are relatively good for both cases, the results seem to be doubtful for a mechanistic interpretation with respect to transition state formation as the rate-determining step. As to be seen from Table 1, the molecular weights are quite different. In Case 1, only oligomerization occurs. That includes a stronger overlap of the transition state formation for at least three reaction steps (initiation, propagation, and chain limitation by termination and transfer). In the case of real polymerization ($BF_3.OEt_2$ initiated), the transition state formation of the propagation step seems to be dominant; this means that $\lg k_{ov}$ preferably consists of this rate-determining step. If correlation analysis data are applied to the elucidation of the reaction mechanism, the concept of an immutable transition state structure within a data set will be one premise to be made. Therefore, we propose that only in the case of polymerization reactions with the dominant propagation step in the measured $\lg k_{ov}$ will the former assumption be valid, and multiparameter equations provide improved insight into a detailed understanding of the reaction mechanism and thus into control of these elementary events.

In order to get more comprehensive data sets, we applied this method to a series of p-substituted styrenes. Table 2 lists the results and the reaction conditions used in our investigation. With the exception of monomer concentration, in all cases linear behavior was obtained when plotting lg k_{ov} versus x_1. The B values are quite good. After linear transformation of the curve which represents the influence of monomer concentration [21], the resulting function serves for the determination of multiparameter equations.

We obtained the following four-parameter equation:

$$\lg k_{ov} = -2.98\sigma_p + 0.11E_T + 0.0034\chi_{Kat} + 6.66\chi_{cokat}/\chi_{Kat} - 12.84$$

$$B = 0.97;\ S_R = 0.13$$

In our experimental programs the temperature was kept constant (0°C). The monomer concentration was eliminated by the "test of significance" of the computer program [3, 4, 24].

On the basis of the above-mentioned equation for varied reaction conditions, experimentally obtained and calculated lg k_{ov} values are compared (Table 3). As shown in Table 3, the empirical parameters which influence the dominant transition state formation adequately reflect the mechanistic model of cationic polymerization. We infer from this fact that these parameters can be applied to quantitative investigations.

Using the above empirical parameters, we were able to show that lg r_1/r_2 derived from a free-energy model [10] reflects the selectivity of the cross-propagation step of cationic copolymerization. Table 4 lists the correlation data of some monolinear relationships.

We also examined correlation analysis of lg $1/r_1$ or lg $1/r_2$ with the above parameters; however, the best correlation was obtained by using lg r_1/r_2. An additional advantage of this parameter is its universality within a series of monomers which have a similar structure. If lg $1/r_1$ or lg $1/r_2$ is used, one of the monomers must be kept constant [26].

The following four-parameter equation was obtained:

$$\lg r_1/r_2 = -4.9\,\Delta\sigma_p + (-1)^{\Delta\sigma_p}[-53.7 + 2.87\,E_T/(1 + b_1E_T^2) + 0.015\,\chi_{Kat}/(1 + b_2\,\chi_{Kat}^2) + (305.61)(1/T)]$$

TABLE 2. LFE Equations of the Cationic Polymerization of p-Substituted Styrenes of the General Type: $y = a_0 + a_1x_1$

Varied parameter	y	x_1	a_0	a_1	B	Conditions
Substituent	$\lg k_{ov}$	σ_p	-0.40	-3.16	0.95	$SbCl_5/CH_2Cl_2$/0°C
Solvent	$\lg k_{ov}$	E_T	-5.9	0.1	0.99	Styrene/$BF_3.OEt_3/CH_2Cl_2$/0°C
Initiator	$\lg k_{ov}$	χ_{Kat}	0.003	-2.4	0.99	p-Cl-Styrene/CH_2Cl_2/0°C
Coinitiator	$\lg k_{ov}$	$\frac{\chi_{Cokat}}{\chi_{SnCl_4}}$	-8.32	6.65	0.96	p-Br-Styrene/$CH_2Cl_2/TiCl_4$/0°C
Temperature	$\lg k_{ov}$	1/T	2.78	-683	0.98	p-Me-Styrene/$CH_2Cl_2/SnCl_4$/0°C
Monomer concentration	$\lg k_{ov}$	$c_M \exp (bc_M)$	0.06	0.86	0.94	p-Me-Styrene/$CH_2Cl_2/SnCl_4$/0°C

TABLE 3. Comparison of Experimental and Calculated Data of a Four-Parameter Equation

Monomer	Solvent	Initiator[a]	lg k_{ov} (exptl)	lg k_{ov} (calc)	Deviation, %
Styrene	$(CH_2)_2Cl_2$	$BF_3.OEt_2$	-1.94	-1.65	14.5
Styrene	CH_2Cl_2	$SnBr_4$	-1.70	-1.61	4.9
p-Cl-styrene	CH_2Cl_2	$AlBr_3$	-1.79	-1.90	6.0
p-PhO-styrene	CH_2Cl_2	$BF_3.OEt_2$	-0.54	-0.50	7.3
p-CN-styrene	CH_2Cl_2	$SbCl_5$	-2.19	-2.14	2.8

[a] Standard conditions: 0°C; $C_{H_2O} \approx 3 \times 10^{-3}$ mol/L.

TABLE 4. LFER Equations of the Cationic Copolymerization of p-Substituted Styrenes of the General Type: $y = a_0 + a_1x_1$

Varied parameter	y	x_1	a_0	a_1	B	Conditions
Substituent	lg r_1/r_2	σ_p	-0.09	-4.92	0.91	$TiCl_4/CH_2Cl_2$/-78°C
Solvent	lg r_1/r_2	E_T	2.23	-0.042	0.90	St/p-Cl-St/$TiCl_4/CH_2Cl_2$/-78°C
Initiator	lg r_1/r_2	$\chi_{Kat}/(1 + b\ \chi_{Kat}^2)$	-0.14	0.015	0.97	St/p-Cl-St/CH_2Cl_2/-78°C
Temperature	lg r_1/r_2	1/T	-0.62	311.4	0.97	St/p-Cl-St/$TiCl_4/CH_2Cl_2$/-78°C
Monomer concentration	lg r_1/r_2	lg $([M_1]_0 \cdot [M_2]_0)$	1.02	0.22	0.98	St/p-Cl-St/$TiCl_4/CH_2Cl_2$/-78°C

$$B = 0.98; \quad b_1 = 7.716 \times 10^{-4}$$

$$S_R = 0.243; \; b_2 = 6.4 \times 10^{-4}$$

The sign factor $(-1)^{\Delta\sigma_p}$ results from empirical considerations. It refers to the intersection of the curves with the abscissa when $\Delta\sigma_p$ changes its sign [10]. The direct plot of E_T and χ_{Kat} led to curves which pass through a maximum. On that account they were transformed as shown in the above equation [21]. However, for a mechanistic understanding, their direct functions hint at the role of a different charge separation in the transition state structure, which results from the cross-propagation step of the copolymerization. The parameters of catalyst activity (χ_{Kat}) were determined from conductivity measurements, and the parameters of solvent polarity (E_T) were determined from spectroscopic data which express the solvation of a positively and negatively charged N-phenol-pyridinium betaine. Thus they reflect the degree of charge separation, and one can expect that the variation of charge separation depending on the reaction conditions will also change the selectivity of the cross-propagation step. Evidence for this hypothesis is shown in several papers [9-11, 19]. The application of lg r_1/r_2 as a selectivity parameter representing the influence of reaction conditions (solvent, Lewis acid, temperature) on the cationic copolymerization of isobutene and α-methylstyrene has been investigated in detail [27]. Convincing proof was shown from these results that the variation of charge separation of the cross-propagation step leads to different sequential compositions of the copolymers.

The author's papers [9, 10] include some results on a comparison of experimental and calculated data for the cationic copolymerization of p-substituted styrenes. They do not correspond as well as in the case of the homopolymerization (Table 3). Obviously, the copolymerization mechanism is even more complex, and events such as specific monomer solvation within the active species, displacement of solvent by the monomers, etc. [19, 27, 28] are not clearly understood. Great differences between experimental and calculated data (up to 90%) were obtained when one of the comonomers was tert-butylstyrene [9]. It appears possible that monomer solvation of this bulky monomer at the propagating cation is more hindered and, in turn, the gain of solvation energy is not as perfect as in the case of other monomers.

Our investigation of multiparameter correlations led to the following comprehensive conclusions:

1. The extension of linear free energy relations (LFER) to the principle of polylinearity (PPL [4, 5]) was found to be fruitful when the initiation and the chain limiting step (termination or transfer) follow the same mechanism, so that they can be neglected in comparison with the predominant rate-determining propagation step.

2. The negative slope of the structural parameters shows that the overall rate (lg k_{ov}) is determined by increasing positive charge formation at the reaction center, i.e., the formation of propagating cations.
3. Multiparameter equations meet the quantification of structural and control parameters. Empirical parameters which are justified at the experimental conditions of polymerization show better correlation data as do theoretical parameters [29, 30].
4. The investigation led to a better understanding of the mechanism of cationic olefin polymerization and in particular to an understanding of the cross-propagation step of copolymerization. Some of the novel mechanistic aspects that resulted from these studies, in principle, allow reaction-controlled processes which lead to products of special properties.
5. Experiments involving olefins of quite different structures (aromatic, aliphatic, cyclic) fail, which shows the limitation of correlation analysis [11].

APPLICATION OF MULTIPARAMETER CORRELATION TO DEVISE NEW PROCESSES AND PRODUCTS

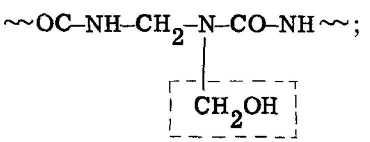
For the production of special adhesive materials, poly(ethylene-co-vinyl acetate), EVA, is bound to other polymers, e.g., with copolymers obtained by cationic polymerization of styrene with components from a technical C_4-fraction [31]. Japanese workers have shown that the total properties depend on the content of styrene in the copolymer and on the total molecular weight. Both parameters which influence the properties of the copolymers fit the following two-parameter equation:

$$sp = 1.24\ stc + 0.007\ M_w - 35.1;\ n = 13;\ B = 0.8$$

where sp = soften point and stc = styrene content.

Some other results are referred to in the literature, e.g., where the microstructure of polybutadiene via anionic polymerization was controlled by the temperature and the nucleophilicity of donors which were added in various ratios with respect to the initiator used [32].

An interesting application of correlation analysis was reported by Dietrich and co-workers [33] concerning the control of the optimized properties of amino plastic resins by polycondensation reaction. Properties, e.g., shrinking, CH_2O-degradation, E-module, etc., show a strong dependence on the ratio of methylene group content and methylol group content, as seen from the following formula sequences:



$$\sim\!\!\sim OC{-}NH{-}CH_2{-}\underset{\boxed{CH_2OH}}{\underset{|}{N}}{-}CO{-}NH\sim\!\!\sim; \qquad \sim\!\!\sim CO{-}NH{-}\boxed{CH_2}{-}O{-}\boxed{CH_2}{-}NH{-}COO\sim\!\!\sim$$

On the basis of a three-parameter equation containing the pH value (which represents the effective acidity), the reaction temperature, and the time of reaction, the reaction could be controlled.

Multiparameter correlation analysis was also shown to be a reliable diagnostic tool to control the degradation of nylon 6 in ethylene glycol in order to get definite oligoamides [34]:

$$\text{nylon 6} + (CH_2)_2(OH)_2 \xrightarrow{\Delta T}$$

$$H_2N{-}(CH_2)_5{-}\!\!\left[CO{-}NH{-}\!\left(CH_2\right)_5\right]_n COO{-}CH_2{-}CH_2{-}OH$$

The following equation was determined

$$y = 240.8 - 0.553T - 0.734t_d + 63.3s - 0.29\ Ts$$

where $y = f(t_d, T, s)$ is the percentage yield of oligoamides, and

$$t_d = \frac{\overline{M}_n - 50{,}053 + 154.7T + 28{,}890s - 89.7Ts}{3.4T - 1{,}107}$$

is the degradation time in hours, s is the percentage catalyst ($HO\!-\!(CH_2)_2\!-\!ONa$), T is the temperature, and $\overline{M}_n$ is the molecular weight of nylon 6. The parameters were varied within the following ranges:

$T = 200\text{-}300°C$

$t_d = 4\text{-}24$ h

$s = 0\text{-}1\%$

In order to obtain oligoamides with $\overline{M}_n = 1000$ in proper yields up to 75-80%, the optimized conditions were calculated by means of the above three-parameter equation: $T = 250°C$; $t_d = 16$ h; $s = 1\%$.

Industrial application of multiparameter correlation is focused on product properties and how they are affected by various processing

TABLE 5. Optimization of Recipe Components and Conditions Used

Components and conditions, respectively	Variation range
x_1 = H_2O [m^3]	5.4-6.3
x_2 = Vinyl chloride (VC) [m^3]	2.5-3.4
x_3 = AIBN [%, with respect to VC]	0.031-0.0375
x_4 = Heat up time [h]	2.0-4.5
x_5 = Concentration of dispersing agent [%, with respect to H_2O]	0.1-0.2
x_6 = Concentration of electrolyte [%, with respect to H_2O]	0.065-0.150

parameters. Since the mathematical method is quite the same as that referred to in the preceding sections, the physical and chemical meanings of the parameters are often unknown. However, from a practical point of view, within a given range of parameter variation it is possible to find the optimum processing conditions in order to get desirable product properties. This is illustrated by the following examples.

For the production of special PVC types, the PVC formed by suspension polymerization requires constant particle quality. Therefore, experiments were carried out in a model reactor of 10 m^3 volume at 62°C to simulate the various control parameters of the procedure in order to get a stabilized aqueous suspension [35, 36]. Table 5 lists the variation range of the reaction components and the variation of reaction conditions used.

Applying a computer program of multiple linear correlation to the calculation of $y = \Sigma a_i x_i$, the effects of the parameters from Table 5 on some selected product properties are shown in Table 6.

The data in Table 6 which represent the effect of reaction components and reaction conditions on the product properties are normalized from +1 to -1. The normalizing conditions are [35]

$$x_{i,\text{norm.}} = \frac{2x_i}{x_h - x_l} - \frac{x_h + x_l}{x_h - x_l}$$

where x_i = value to be normalized
x_h = highest value
x_l = lowest value

TABLE 6. Computer Simulation of the Effect of Reaction Components and Reaction Conditions on Selected Product Properties

	Coefficients a_i in the general equation $y = \Sigma a_i x_i$					
Product properties [y]	x_1 H_2O	x_2 VC	x_3 AIBN	x_4 heat up time	x_5 dispersing agent	x_6 electrolyte concentration
Yield [%]		-5.8		+4.0	+7.7	
Volume-time yield [$kg/m^3 \cdot h$]						+4.8
Run time [h]			-1.3	+0.6		-1.3
K value		-1.0		+1.0	+5.4	-2.0
Bulk weight [g/L]						-21.6
Trickle ability [g/s]	+8.0		-13.6		-10.8	+6.5
Wet sifting [%] (63-200 nm)	-7.3					

The normalization should express the relative effect of the various parameters which are assumed to be essential for reaction control.

To improve the plastic properties of polyvinyl chloride by internal plasticization, copolymerization with vinyl acetate or formation of sequential copolymers by grafting of vinyl chloride on poly(ethylene-co-vinyl acetate) is often carried out.

These products show better flow properties in molding compositions processed by extrusion, calendering, etc. Again, the application of computer simulation to multiparameter correlations enables such essential parameters as vinyl acetate content in the copolymer, melting index of the copolymer, rest monomer content in the product, impact resistance, etc. to be optimized and thus a technical product to be formed. Further, some processing parameters for the creation of special plastic materials were elucidated with high efficiency [36]. Correlation analysis of the above empirical parameters led to the following three results:

1. Time optimum of a non-isobar, non-isotherm reaction (reduction of the polymerization cycle by 25%, relative to conventional processing).
2. Continuous adaptation of reaction parameters to the actual processing conditions (even in troublesome cases); therefore, high reproducibility with respect to the objective parameters (coefficient of variation $\nu \leq 5\%$ for $m_i \cong \pm 15$ kg/t of the product).
3. Full information on developing desirable objective parameters as a function of various processing parameters during the running process. This allows the possibility of type developing and type optimization in the technical reactor itself.

The final example belongs to a new application field of correlation analysis which may be termed "reaction morphometry." For the production of special filters, membranes, and some materials of high quality which are based on cellulose powders, the controlled hydrolytic degradation of such raw materials as paper pulp (cellulose), straw, and pine wood plays an important role. Enzymatic hydrolysis of cellulose as well as controlled acid-catalyzed degradation lead to cellulose powders which contain particles of different shapes. By special morphometric methods [37] the different shapes [e.g., convex structures (circles, ellipses, sticks) and nonconvex structures (worms, stars, crosses, popcorns)] are quantitatively classified. Table 7 contains an example of particle length classification and the quantitative distribution range of the particle lengths.

Empirical parameters which represent the particle length (L_i* [μm]) were derived from these data. They were correlated with some other parameters which also represent shape-dependent mean values (e.g., L_i [μm] = particle length obtained from light scattering, or the

TABLE 7. Particle Length and Distribution Latitude of the Particle Length of Ellipses

Length, μm	Particles[a]
5-10	17
10-16	25
16-23	16
23-33	10
33-46	13
46-63	22
63-85	14
85-114	8
114-151	4
151-200	2

[a] Total particle number: 191. Ellipses: 131; stars: 5; popcorns: 55.

specific fraction of meso- and macropores) on the one hand or with some reaction parameters on the other hand. The following relations were found [37]:

$L_i^* = 74 + 0.65\ L_i;\qquad r = 0.99,\ n = 14$

water retention volume (WRV) [%] = 1.3 + 111 macropores [cm^3/g]; $r = 0.82$; $n = 10$

residue enzymatic degradation (RED) [%] = 13 + 139U; $r = 0.7$; $n = 10$

where U = distribution range of particles

The industrial application of these correlations is beneficial, particularly for the following conditions:

1. Control of morphologically determined processes
2. Scale of regularity of different charges
3. Control of the product quality

We hope we have shown that correlation analysis, and in particular multiparameter equations, may serve either as a diagnostic tool for the elucidation of reaction mechanisms and thus, in proper cases, for controlling the route of the mechanism, or for useful analysis in the control of industrial processes and definite product formation.

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