Polym. Bull. (2010) 64:303–314
DOI 10.1007/s00289-009-0212-2

ORIGINAL PAPER

Optimization of synthesis parameters in interfacial polycondensation using design of experiments

Smaranda Iliescu · Ion Grozav · Simona Funar-Timofei · Nicoleta Plesu · Adriana Popa · Gheorghe Ilia

Received: 17 July 2009 / Revised: 10 September 2009 / Accepted: 20 November 2009 /
Published online: 27 November 2009

Abstract The reaction of phenylphosphonic dichloride with 4,4′-cyclohexylidenebisphenol by a gas–liquid interfacial polycondensation was investigated. The design of experiments (DoE) method is used for determination of the best reaction conditions. The correlation of simultaneous influence of the parameters (reaction time, reaction temperature, alkaline medium, reagents molar ratio) on yield and inherent viscosity was studied.

Keywords Gas–liquid · Interfacial polycondensation · Design of experiments

Introduction

Over the past few years, significant amount of research activities in the chemical community have been directed toward the development of new technologies for environmentally benign processes. This area of chemistry has

S. Iliescu · S. Funar-Timofei · N. Plesu · A. Popa · G. Ilia (✉)
Institute of Chemistry, Romanian Academy, 24 Mihai Viteazul Bvd, 300223 Timisoara, Romania
e-mail: ilia@acad-icht.tm.edu.ro

G. Ilia
Faculty of Chemistry-Biology and Geography, West University, 116 Pestalozzi Str, 300115 Timisoara, Romania

I. Grozav
POLITEHNICA University of Timisoara, 1 Mihai Viteazul Bvd., 300222 Timisoara, Romania

received extensive attention and is often referred to as "*green chemistry*." The principle of green chemistry can be applied to broad areas of chemistry including synthesis, catalysis, reaction conditions, separations, analysis, and monitoring. The reduction and/or optimization of the undesirable side reactions is one of the aims of green technology. Design of experiments (DoE) is an alternative way to the classical methods used in the optimization of the industrial processes [1–3].

The method of interfacial polycondensation or phase transfer catalysis follows the trend of green chemistry from which results the reduction of environmental pollution and steady development of chemistry [4].

In the last years, the peculiar advantages of this method raised as one of the most suitable in the organophosphorus chemistry. Various phosphorus containing polymers, respectively, polyphosphonates and polyphosphates have been obtained by this technique [5–10].

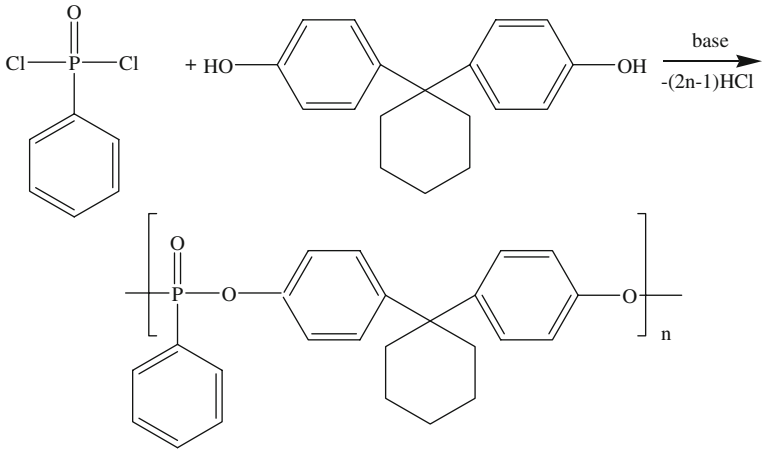
Studies made on phosphorus-containing polymers are steadily in development, taking into account the polymer range diversification and characterization and their use in various domains. One of the present preoccupations lies in the intensification of the efforts concerning fire proofing of macromolecular compounds which are in danger of ignition, although beneficial from technical and economical points of view.

Polyphosphonates have commercial interest because of their flame-retardant characteristics [11, 12] and their potential for use as high performance plastics [6].

In response to the need of development of phosphorus-containing polymers as biodegradable and flame-retardant materials, systematic studies on the synthesis of such polymers were performed.

In the last years, we have described the synthesis of polyphosphonates and polyphosphates by liquid–liquid interfacial polycondensation and gas–liquid interfacial polycondensation [13–16].

Due to the specific features of gas–liquid polycondensation and its advantages, respectively, the absence of solvent and catalyst, it should be considered as the most efficient and general green technology. The gas–liquid interfacial polycondensation of phosphoryldichlorides with diols takes place in aqueous solution. It is possible to obtain low-molecular-weight polymers. Reason for limitations of not achieving high-molecular-weights is the presence of the aqueous alkali. This causes several side-reactions that affect the formation of high-molecular-weight polymer, i.e., saponification of the phosphorylating agent, of oligomer end-group, and of the formed polymer. The rate of the propagation reaction must be of many orders of magnitude greater than the competing reactions. This article presents the simultaneous influence of various parameters: temperature (Temp), NaOH concentration (ConcNaOH), reaction time (ReacTime), and molar ratio (MolarRatio), on yield (Yield) and inherent viscosity (InhVisc) in the synthesis of a new polyphosphonate by gas–liquid interfacial polycondensation of phenylphosphonic dichloride (PPD) with 4,4′-cyclohexylidenebisphenol (bisphenol Z, BZ) (reaction I). The undesirable side reactions were minimized in order to optimize these parameters.



(I)

For correlation of the simultaneous influence of these parameters with the yield and inherent viscosity and for determination of the best reaction conditions, a DoE method was used.

Experimental

General procedure

The polyphosphonate was obtained by the gas–liquid interfacial polycondensation of PPD with BZ [15]. Since phosphoric dichlorides are more volatile than diols they are preferentially employed in the gas phase. The PPD was heated (90 °C) and a stream of nitrogen was carried out into a flask which contains aqueous 1 M sodium hydroxide solution and the diol. The solvent for diols is water. The nitrogen stream acts as carrier gas for the phosphoric dichloride, as reaction mixture protector from the atmospheric oxygen and for agitation of the reaction mixture. The resulted polymer, separated after 30 min from solution was washed with distilled water until free of chloride ion, dried at 50 °C, in vacuum and characterized by IR, ^{1}H-NMR and ^{31}P-NMR spectroscopies.

The infrared (IR) spectrum (film) exhibited absorption bands (cm^{-1}) at 1247 (P=O), 1142; 948 (P–O–C_{arom}), 1497 (P–C_{arom}), 3028; 1606; 1380 (Ph). The nuclear magnetic resonance (^{1}H-NMR) spectrum in $CDCl_3$, using TMS as internal standard, showed signals (δ) at 7.2–8.5 ppm (m, C_6H_5); 2.4 ppm (s, α, $\alpha'CH_2$); 1.6 ppm (s, β, β' and γ CH_2). The presence of phosphorus was confirmed by elemental analysis (Schoniger method: $P_{exp} = 7.2$) but also by ^{31}P-NMR analysis. The ^{31}P-NMR spectrum shows peaks at 15.6 ppm (P at chain end) and 12.0 ppm (P in the repeat unit).

Instruments

The IR spectra were recorded on a Jasco FT/IR 4200 spectrophotometer and ^{1}H-NMR and ^{31}P-NMR spectra on a Bruker DRX 400 MHz spectrometer. All NMR spectra

were recorded in $CDCl_3$ using TMS as internal standard. The polymer was characterized by inherent viscosity, on an Ubbelohde suspended level viscometer, at 30 °C.

Design of experiments

For interfacial polycondensation reactions, four parameters were considered as control factors and the results of the process have been measured with two output values: yield and inherent viscosity. Polyphosphonate synthesis needs to satisfy two functional requirements: high yield and inherent viscosity, respectively.

According to the axiomatic design [17], like in any other process, the design world consists in four domains: the customer domain, the functional domain, the physical domain, and the process domain (Fig. 1).

The customer domain is characterized by the customer needs {CA}. In the functional domain, the customer needs are specified by the functional requirements {FR} and constraints. To satisfy {FR}, one must consider the design parameters {DP}, included in the physical domain and finally to produce the product specified in terms of {DP}, a process will be developed that is characterized by process variable {PV}. In this article, we use only functional and physical domains and we note the {DP} terms as control factors {CF}, according to the notation of DoE mentioned in the literature [18–22].

We identified the customer needs, and then functional requirements {FR} as yield and inherent viscosity.

During the transposing process from the functional domain to the physical domain, in order to make the right decisions, the use of the independence axiom and the information axiom [17] is needed.

The independence axiom states that acceptable process must maintain the independence of the requirements in the functional domain. These functional requirements are obtained by using four parameters in the so-called physical domain. In an ideal synthesis, according to the independence axiom, the number of the parameters must be matched to the number of the functional requirements. The synthesis can be represented by the following equation:

$$\{\mathrm{FR}\}_m = [A]_{m\times n}\{\mathrm{CF}\}_n \tag{1}$$

where $\{\mathrm{FR}\}_m$ is a vector of m functional requirements, $\{\mathrm{CF}\}_n$ is a vector of n parameters, and $[A]_{m\times n}$ is an $m \times n$ syntheses matrix.

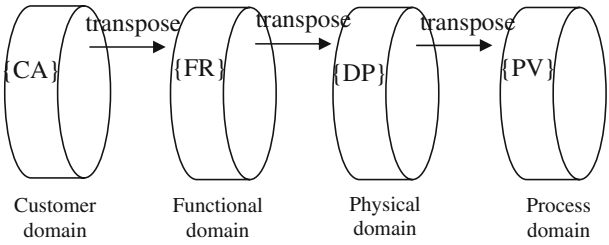


Fig. 1 The structure of domains

When $m = n$ (the case of the ideal synthesis), the synthesis is called uncoupled. In case of redundant synthesis, $m < n$, and when $m > n$ the synthesis is referred to as a coupled one.

In the ideal or uncoupled synthesis, every control factor modifies only one functional requirement and there are no interactions among parameters. In the coupled synthesis, there are interactions among the parameters. The modification of one control factor will modify many functional requirements and the optimization of the synthesis is difficult to be obtained. In the redundant synthesis, one must examine how it can be improved by proper choice of the parameters.

In the case of polyphosphonate synthesis, Eq. 1 can be transformed into:

$$\begin{Bmatrix} \text{Yield} \\ \text{InhViscosity} \end{Bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \end{bmatrix} \cdot \begin{Bmatrix} \text{Reaction\_time} \\ \text{Temperature} \\ \text{Conc\_NaOH} \\ \text{Molar\_ratio} \end{Bmatrix} \quad (2)$$

The elements of the synthesis matrix A_{ij} represent the transfer factors and they will be found using the DoE. In this study, the case of response surface design with four parameters has been chosen. For planning these experiments, the statistical MINITAB software [18–23] was used. The planned runs and the results of the experiments are presented in Table 1.

Table 1 The response surface experiment for $n = 4$ parameters

No.	Reaction time (min)	Temperature (°C)	Concentration of NaOH (%)	Molar ratio	Yield (%)	Inherent viscosity (dL/g)
1	40	30	2	1.2	15.4	0.8502
2	80	30	2	1.2	18	0.855
3	40	50	2	1.2	38.1	0.962
4	80	50	2	1.2	79.8	0.98
5	40	30	4	1.2	8.1	0.2105
6	80	30	4	1.2	10.2	0.1904
7	40	50	4	1.2	30	0.752
8	80	50	4	1.2	34.3	0.781
9	40	30	2	2.5	16.3	0.872
10	80	30	2	2.5	23	0.885
11	40	50	2	2.5	60.5	1.1
12	80	50	2	2.5	82.6	1.65
13	40	30	4	2.5	9.5	0.225
14	80	30	4	2.5	11.5	0.251
15	40	50	4	2.5	32.1	0.281
16	80	50	4	2.5	33.2	0.5215
17	60	40	3	2	38.7	0.586
18	60	40	3	2	37	0.552
19	60	40	3	2	35	0.5122
20	60	40	3	2	38.5	0.5

Table 2 Estimated regression coefficients of the parameters for the yield of reaction I

Term	Coeff.	SE coeff.	*T*	*P*
Constant	−151.657	48.3133	−3.139	0.014
ReacTime	**1.940**	1.1136	1.742	0.120
Temp	**2.219**	0.7889	2.813	**0.023**
ConcNaOH	**30.999**	8.8493	3.503	**0.008**
MolarRatio	**9.904**	13.7927	0.718	0.493
ReacTime*ReacTime	−0.013	0.0085	−1.581	0.153
ReacTime*Temp	0.017	0.0076	2.301	**0.050**
ReacTime*ConcNaOH	−0.199	0.0758	−2.623	**0.031**
ReacTime*MolarRatio	−0.090	0.1166	−0.775	0.460
Temp*ConcNaOH	−0.613	0.1515	−4.042	**0.004**
Temp*MolarRatio	0.169	0.2331	0.726	0.489
ConcNaOH*MolarRatio	−2.635	2.3314	−1.130	0.291

SE coeff. the standard error of the parameter's coefficients, *T* the values for *t*-distribution (Student test), *P* percentage values for the *t*-distribution

Table 3 ANOVA results for the yield

Source	df	Seq. SS	Adj. SS	Adj. MS	*F*	*P*
Regression	11	8297.63	8297.63	754.330	20.53	0.000
Linear	4	7069.76	609.67	152.417	4.15	0.041
Square	1	91.84	91.84	91.836	2.50	0.153
Interaction	6	1136.03	1136.03	189.339	5.15	**0.019**
Residual Error	8	293.95	293.95	36.743		
Lack-of-Fit	5	285.17	285.17	57.033	19.49	0.017
Pure Error	3	8.78	8.78	2.927		
Total	19	8591.58				

df the degrees of freedom, *SeqSS* the computed sum of square, *Adj. SS* the adjustable sum of square, *Adj. MS* the adjustable mean of square, *F* values for the Fischer distribution, *P* percentage values for the *F*-distribution

Results and discussion

The experimental results were analyzed by the MINITAB software. The regression coefficients for the yield of reaction I are presented in Table 2.

The significance of all calculations has been assigned in accordance to references [18–20, 22]. A significant effect of the parameters on the yield has the concentration of NaOH and the temperature (see Table 2 where $p < 0.05$).

Significant effects have, also, some interaction terms between parameters, like 'ReacTime*Temp,' 'ReacTime*ConcNaOH,' and 'Temp*ConcNaOH.' The significant influence on the yield of these interactions can be seen in Table 3, where the analysis of variance (ANOVA) is presented. These interactions give information on the nonlinear aspect of the yield surface.

In the case of inherent viscosity, the regression coefficients are presented in Table 4. For inherent viscosity, only the reaction time is nearby the limit of significance effect ($p = 0.05$), but there is an interaction that has significant effect in

Table 4 Estimated regression coefficients of the reaction parameters for the inherent viscosity

Term	Coeff.	SE coeff.	*T*	*P*
Constant	2.36291	1.27557	1.852	0.101
ReacTime	**−0.06441**	0.02940	−2.191	**0.060**
Temp	**−0.00187**	0.02083	−0.090	0.931
ConcNaOH	**−0.03833**	0.23364	−0.164	0.874
MolarRatio	**0.24560**	0.36416	0.674	0.519
ReacTime*ReacTime	0.00044	0.00022	1.955	0.086
ReacTime*Temp	0.00025	0.00020	1.271	0.239
ReacTime*ConcNaOH	−0.00097	0.00200	−0.485	0.641
ReacTime*MolarRatio	0.00384	0.00308	1.246	0.248
Temp*ConcNaOH	0.00143	0.00400	0.357	0.730
Temp*MolarRatio	−0.00047	0.00616	−0.077	0.940
ConcNaOH*MolarRatio	−0.14569	0.06155	−2.367	**0.045**

SE coeff. the standard error of the parameter's coefficients, *T* the values for *t*-distribution (Student test), *P* percentage values for *t*-distribution

Table 5 ANOVA calculated for the ConcNaOH*MolarRatio term calculated for the inherent viscosity

Source	df	Seq. SS	Adj. SS	Adj. MS	*F*	*P*
Regression	11	2.35675	2.356749	0.214250	8.37	0.003
Linear	4	2.02477	0.142288	0.035572	1.39	0.320
Square	1	0.09787	0.097868	0.097868	3.82	0.086
Interaction	6	0.23411	0.234108	0.039018	1.52	0.284
Residual error	8	0.20490	0.204901	0.025613		
Lack-of-fit	5	0.20029	0.200292	0.040058	26.07	0.011
Pure error	3	0.00461	0.004609	0.001536		
Total	19	2.56165				

df the degrees of freedom, *Seq. SS* computed sum of square, *Adj. SS* adjustable sum of square, *Adj. MS* adjustable mean of square, *F* values for Fischer distribution, *P* percentage values for *F*-distribution

case of the 'ConcNaOH*MolarRatio' term. The interactions calculated for the ConcNaOH*MolarRatio term in the case of the inherent viscosity have an insignificant effect ($p > 0.05$, see Table 5).

Using the regression coefficients for the principal factors from Tables 2 and 4, Eq. 2 is transformed into:

$$\begin{Bmatrix} \text{Yield} \\ \text{InhViscosity} \end{Bmatrix} = \begin{bmatrix} 1.940 & 2.219 & 30.999 & 9.904 \\ -0.06441 & -0.00187 & -0.03833 & 0.24560 \end{bmatrix} \cdot \begin{Bmatrix} \text{Reaction\_time} \\ \text{Temperature} \\ \text{Conc\_NaOH} \\ \text{Molar\_ratio} \end{Bmatrix} \quad (3)$$

If the regression coefficients are noted by *X* for the factors that have significant effect and with 0 for the factors with insignificant effect, the relation (3) becomes

$$\begin{Bmatrix} \text{Yield} \\ \text{InhViscosity} \end{Bmatrix} = \begin{bmatrix} 0 & X & X & 0 \\ X & 0 & 0 & 0 \end{bmatrix} \cdot \begin{Bmatrix} \text{Reaction\_time} \\ \text{Temperature} \\ \text{Conc\_NaOH} \\ \text{Molar\_ratio} \end{Bmatrix} \quad (4)$$

In this redundant synthesis, there are two parameters with significant effect on the yield and one on the viscosity. An important fact is that these parameters do not interfere in the same time on the yield and viscosity; therefore, this synthesis is an uncoupled one and can be optimized without more difficulties.

Figure 2 presents the contour plots for the yield and Fig. 3 for the inherent viscosity, respectively, realized by the MINITAB software for all combinations of parameters.

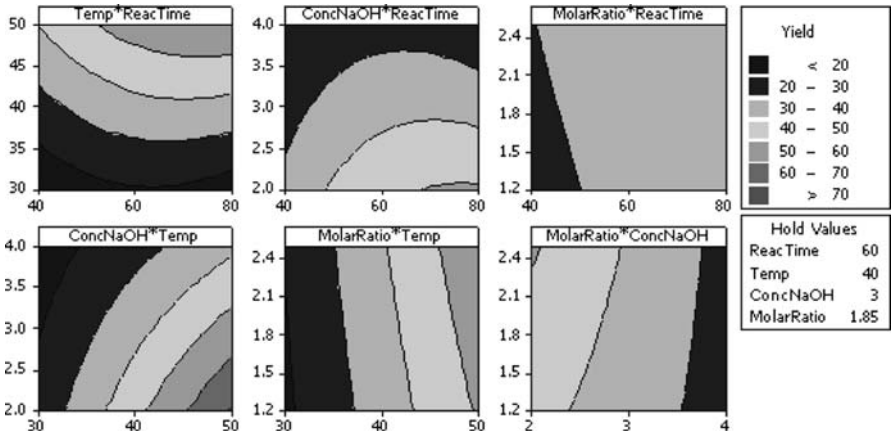


Fig. 2 Contour plot for the yield

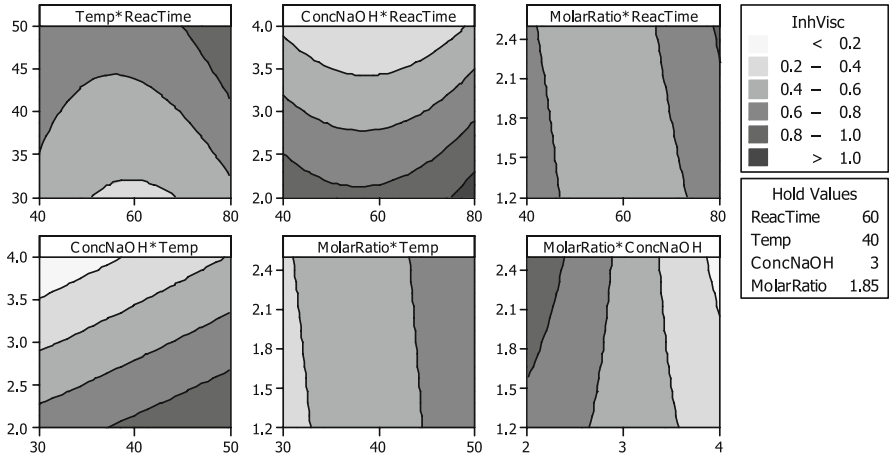


Fig. 3 Contour plot for the inherent viscosity

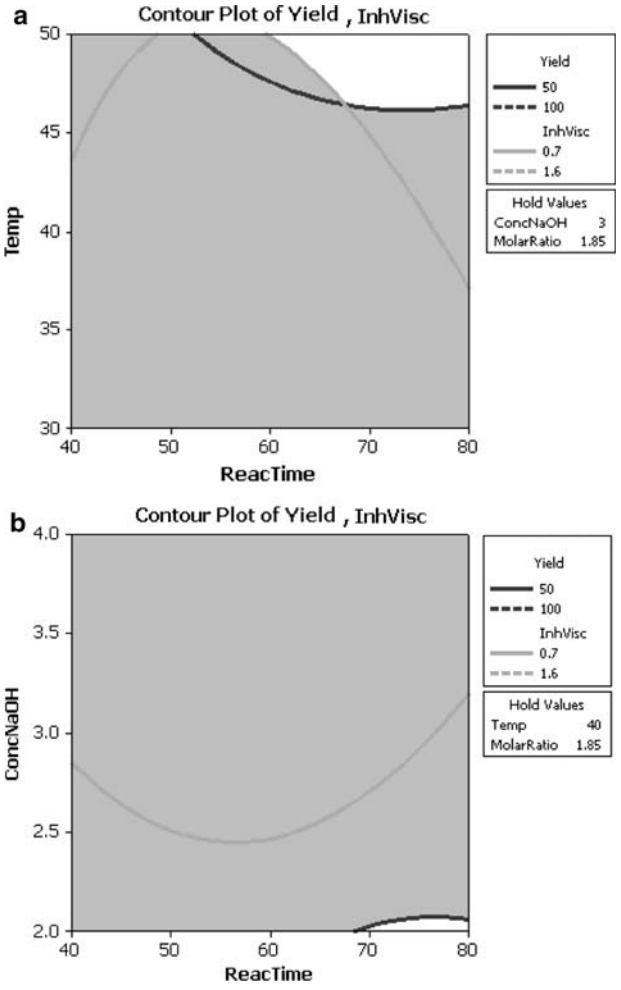


Fig. 4 **a** Effect of temperature and reaction time on the quality of yield and inherent viscosity characteristics of the synthesis. **b** Effect of concentration NaOH and reaction time on the quality characteristics of the synthesis

The nonlinear effect on the yield (see Fig. 2) is greater than the inherent viscosity (Fig. 3). In the next step, the best values of the parameters with important effect on the quality characteristics of the synthesis were looked for. This information can be found in Fig. 4a, b, in which the values of the parameters which give the maximum values for the yield and viscosity have been plotted. The dependence of the quality characteristics of the synthesis versus the effect of temperature, reaction time, and concentration of NaOH is presented in these figures.

Maximum values of the quality characteristics were obtained in case of reaction time, temperature, and minimum values for the NaOH concentration, respectively.

Using the optimization module of the MINITAB program, the optimum values of all parameters were found. These results are presented in Fig. 5 ("High" represents

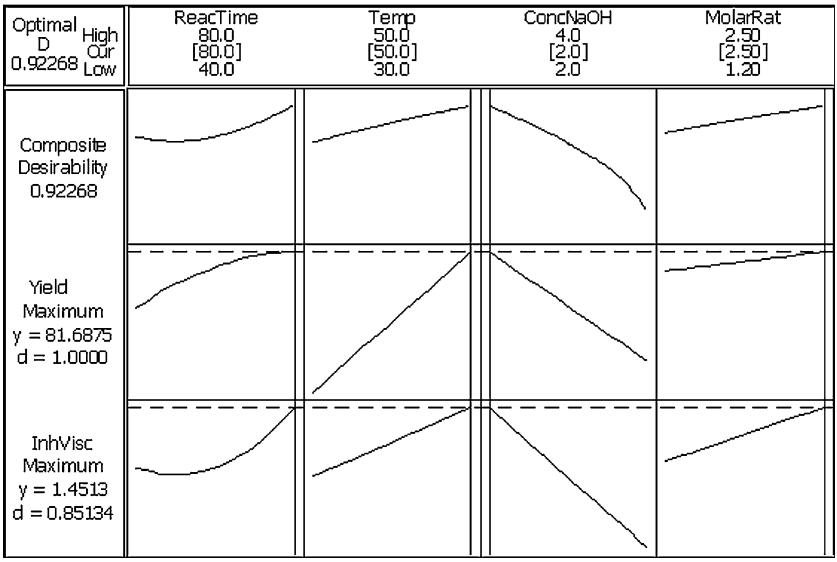


Fig. 5 Optimal values for parameters

Table 6 Optimal values for the yield and inherent viscosity

	Goal	Lower	Target	Upper	Weight	Import
Yield	Maximum	0.6	0.9	0.9	1	1
InhVisc	Maximum	0.6	1.6	1.6	1	1

the highest value of the experimental domain, "Cur" the current value resulting from optimization, and "Low" the lowest value of the experimental domain).

The individual desirability for each predicted response (yield and inherent viscosity) were calculated by MINITAB. The individual desirability values were then combined into the composite desirability. The desirability values can be of help for the understanding of how close the predicted responses are to the target requirements. Desirability is measured on a 0 to 1 scale. The optimal values for the parameters are presented in Table 6.

In the optimization process with the two functional requirements, Yield and InhVisc, data having quite good values, were obtained. The values of Global Solution are

ReacTime = 80
Temp = 50
Conc_NaOH = 2
Molar_Ratio = 2.5
Composite desirability = 0.922680

The calculated composite desirability value shows that the target values imposed to be reached for the reaction synthesis have been 92.27% obtained.

Conclusions

The simultaneous influence of various parameters (reaction time, temperature, NaOH concentration, and molar ratio PPD:BZ) on the yield and inherent viscosity in the synthesis of a new polyphosphonate obtained by a gas–liquid interfacial polycondensation of PPD with bisphenol Z was studied. DoE is an alternative way to the classical method for the optimization of the industrial processes. By this method, many parameters can be varied simultaneously and the experimentation time can be shortened. Also, the working time and the costs needed for synthesis optimization can be drastically reduced in the case of polyphosphonate synthesis by gas–liquid interfacial polycondensation. The DoE and statistical analyses performed for linear and nonlinear experiments led to a mathematical model with relations among objective functions, parameters, and interactions of the parameters of the process.

The DoE shows that in the redundant synthesis of polyphosphonate there are two parameters with significant effect on the yield and one with significant effect on the viscosity. An important conclusion is that these parameters have an insignificant effect on the yield and viscosity in the same time. The obtained results indicate that the synthesis is an uncoupled one and it can be optimized without difficulties. High values of reaction time and temperature, respectively, minimum values for NaOH concentration give maximum values of the quality characteristics of the synthesis.

References

1. Cortés MT, Sierra EV (2006) Effect of synthesis parameters in polyaniline: influence on yield and thermal behavior. Polym Bull 56:37–45
2. Ramos VD, da Costa HM, Pereira AO, Rocha MCG, Gomes AS (2005) Effect of peroxide concentration on the modification of the LLDPE: statistical experimental design and thermal properties. Polym Bull 54:117–122
3. da Costa HM, Ramos VD, Visconte LLY, Furtado CRG (2007) Design and analysis of single-factor experiments: analysis of variance of the effect of rice husk ash and commercial fillers in NR compounds. Polym Bull 58:597–610
4. Makoska M (2000) A general green methodology in organic synthesis. Pure Appl Chem 72:1399–1403
5. Millich F, Lambing LL (1980) Interfacial synthesis of polyphosphonate and polyphosphate esters. VII. Temperature effects and reaction loci in polycondensations of hydroquinone with phenylphosphonic dichloride and 4-methylthiophenil phosphorodichloridate. J Polym Sci Polym Chem Ed 18:2155–2162
6. Imai Y, Kamata H, Kakimoto M-A (1984) Preparation and properties of high transition temperature aromatic polyphosphonates by phase-transfer-catalyzed polycondensation of phenylphosphonic dichloride with bisphenols. J Polym Sci Polym Chem Ed 22:1259–1265
7. Richards M, Dahiyat BI, Arm DM, Lin S, Leong KW (1991) Interfacial polycondensation and characterization of polyphosphates and polyphosphonates. J Polym Sci A Polym Chem 29:1157–1165
8. Roy S, Maiti S (2001) Synthesis and characterization of unsaturated polyphosphonates. J Polym Mater 17:267–282
9. Senthil S, Kannan P (2002) Synthesis and characterization of liquid-liquid-crystalline polyphosphonates containing disubstituted ferrocene esters as mesogens. J Polym Sci A Poly Chem 40:2256–2263

10. Narendran N, Kishore K (2003) Studies on polyphosophate esters synthesis. J Appl Polym Sci 87:626–631
11. Huang X, Li B, Shi B, Li L (2008) Investigation on interfacial interaction of flame retarded and glass fiber reinforced PA66 composites by IGC/DSC/SEM. Polymer 49:1049–1055
12. Lyon RE, Takemori MT, Safronava N, Stoliarov SI, Walters RN (2009) A molecular basis for polymer flammability. Polymer 50:2608–2617
13. Iliescu S, Ilia G, Dehelean G, Popa A (2002) New polyphosphonates obtained by vapor-liquid interfacial polycondensation. Polym Bull 48:451–456
14. Iliescu S, Ilia G, Popa A, Dehelean G, Pascariu A, Macarie L, Plesu N (2004) Mixed quaternary ammonium and phosphonium salts bound to macromolecular supports for removal bacteria from water. Mol Cryst Liq Cryst 418:195–203
15. Iliescu S, Ilia G, Plesu N, Popa A, Pascariu A (2006) Solvent and catalyst-free synthesis of polyphosphates. Green Chem 8:727–730
16. Iliescu S, Ilia G, Pascariu A, Popa A, Plesu N (2007) Organic solvent-free synthesis of phosphorus containing polymers. Pure Appl Chem 79:1879–1884
17. Suh NP (2001) Axiomatic design advances and applications. Oxford University Press, New York
18. Miron M, Grozav I, Todea C (2004) Notiuni fundamentale de metodologia cercetarii stiintifice medicale (Fundamental notions on research methodology in medical science). Marineasa, Timisoara
19. Montgomery DC (1991) Design and analyses of experiments, 3rd edn. Wiley, New York
20. Jiju A (2003) Design of experiments for engineers and scientists. Elsevier, Burlington
21. Grozav I, Turc C, Banciu F (2007) The optimization of the soldering process through experiment design. In: Weiss Z (ed) Virtual design and automation. Publishing House of University of Technology, Poznan, pp 407–414
22. Hinkelmann K, Kemthorne O (2005) Design and analyses of experiments. Wiley, New York
23. MINITAB v. 15, Minitab Inc., USA. http://www.minitab.com/products/minitab/