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Optimization of Cationic Polymerization of Vinyl Ether Monomers

Hoang Trung Phong, Hoang Thi Kieu Nguyen*
Hanoi University of Science and Technology, Hanoi, Vietnam

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ABSTRACT

In this study, the optimization of the cationic polymerization of vinyl ether monomers was carried out. The aim is to maximize the conversion of the monomers. A factorial design was used to evaluate the effects and interactions of three factors: photoinitiator concentration, the weight ratio of monomer and oligomer and alcohol concentration on the conversion of monomers. The optimal conditions from the desirable response are initiator concentration 5%, monomer/oligomer 1/1, and alcohol concentration 1.45%. Under these conditions, the conversion of 86.5% is obtained. The polymerization prepared under the optimized conditions verified the statistical experimental strategies' validity

Keywords: Polymerization, UV Light Source, Cationic Initiator, Optimization, Experimental Design

I. INTRODUCTION

UV light-induced polymerization reactions have been continuously growing in interest in different fields, from protective coatings to printing inks, microelectronics, and smart materials for additive manufacturing [1- 3].

During a UV-curing process, radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of functional monomers. However, free radical polymerization has an inherent disadvantage: oxygen inhibits polymerization. An alternative curing mechanism [4, 5] has been developed to overcome this inhibition, cationic polymerization. In addition, the cationic polymerization has been effectively demonstrated for vinyl ethers (VEs) which are interested in sustainability demands [6]. The kinetics of the cationic polymerization of VEs has been drastically investigated in the past years to improve the rate of propagation as well as the conversion of photopolymerization.

To optimize the kinetics of the cationic polymerization of VEs, in this study, the 2k experimental design [7, 8] was applied to evaluate the individual contribution of selected variables to the conversion of this

polymerization. The investigated factors were photoinitiator concentration, the weight ratio of monomer and oligomer and alcohol concentration.

II. METHODS AND MATERIAL

A. Materials

Triethylene glycol divinyl ether (TEGDVE, from Sigma Aldrich) and 3,4-epoxy cyclohexyl methyl 3,4-epoxycyclohexanecarboxylate (CADE, Sigma Aldrich) were applied as model monomers. The photoinitiator Triarylsulfonium hexafluoro-phosphate salt (TAS-PF_6 50% in propylene carbonate) was supplied by Sigma-Aldrich. The chemical structures of the materials are shown in Fig. 1

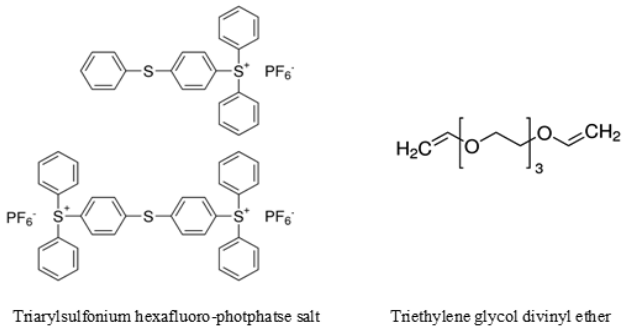

Figure 1: Chemical structures of the used compositions

B. Curing process

The compositions were mixed in such proportions as required. The solutions were prepared in glass vials made of dark glass and were applied immediately after preparation as follows.

The defined sample volume (according to layer thickness) was spread on the same area of a polyester film (white-back) by a handled roller. The thicknesses of the investigated films were about 20 g/m2 (equivalent to about 10 μm).

A UVB lamp (9 W) was arranged at a distance from the cured sample so that the light intensities used in all experiments were constant at 1 $mW.cm^{-2}$

C. Polymerization kinetics measurement

The curing process was evaluated by IR spectroscopy (Spectrophotometer IR Affinity – 1S of Shimadzu) based on the transmittance measurements.

The degree of conversion in the cured film was determined according to the amount of monomer double bond (twisting vibration at 810 cm^{-1}, stretching vibration at 1610 – 1640 cm^{-1}) by a baseline method [10]. The degree of conversion (X) and relative polymerization rate (R_p) were calculated from the well-known equation (1) [11]

$$X = 1 - \frac{A_{t(\lambda)}}{A_{0(\lambda)}} \quad (1)$$

where $A_{0(\lambda)}$ and $A_{t(\lambda)}$ is the absorbance of monomer's C=C bonds measured at the chosen wavelength (810 cm^{-1}) before and after the exposure to UV light for the time t, respectively

D. Experimental design and data analysis

In this work, a factorial design in which the influences of three experimental factors, e.g. photoinitiator concentration, the weight ratio of monomer and oligomer, and alcohol concentration, on the response, i.e. the conversion, was investigated. Two different levels were assigned to each factor. The factorial design is shown in Table I. The levels of the factors are given by – (minus) for low level and + (plus) for high level. A zero-level is also included, a centre, in which all variables are set at their mid-value. A sign table, or design matrix, used to calculate the main effects and the interaction effects from the factorial design is constructed in Table II.

TABLE I
FACTORIAL DESIGN

Exp. No	Variable			Response
	x_1	x_2	x_3	
1	-	-	-	y1

2	+	-	-	y2
3	-	+	-	y3
4	+	+	-	y4
5	-	-	+	y5
6	+	-	+	y6
7	-	+	+	y7
8	+	+	+	y8

TABLE III
MATRIX OF FACTORIAL DESIGN

Exp. No	X_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Response
1	+1	-1	-1	-1	+1	+1	+1	-1	y1
2	+1	+1	-1	-1	-1	-1	+1	+1	y2
3	+1	-1	+1	-1	-1	+1	-1	+1	y3
4	+1	+1	+1	-1	+1	-1	-1	-1	y4
5	+1	-1	-1	+1	+1	-1	-1	+1	y5
6	+1	+1	-1	+1	-1	+1	-1	-1	y6
7	+1	-1	+1	+1	-1	-1	+1	-1	y7
8	+1	+1	+1	+1	+1	+1	+1	+1	y8

The experiments were evaluated in order to fit a regression model

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

Where, y_j ($j = 1 \div N$, $N = 8$) is the response variable to be modeled; x_j ($i = 1 \div 3$) is the independent variable which influence y; b_0, bi ($i = 1 \div 3$), b_{iu} ($i = 1 \div 3$, $u = 1 \div 3$) are model terms, that are estimated by

$$b_i = \frac{1}{N}\sum_{j=1}^{N} x_{ij}\, y_j \quad (2)$$

$$b_i = \frac{1}{N}\sum_{j=1}^{N} x_{ij}\, x_{uj} y_j \quad (3)$$

Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The quality of the fitted model was expressed with the coefficient of determination, R^2, and its statistical significance was checked by the F-test. Model terms were selected or rejected based on the p value (probability) with 99% confidence level.

The regression model for real variables (z) describing the relationship between the investigated factors was determined from (1) by replacing variables x with z:

$$x_i = \frac{2(z_i^+ - z_i^0)}{\Delta z_i} \quad (5)$$

Where $\Delta z_i = z_i^+ - z_i^-$; z_i^+, z_i^0, z_i^- are values of the i^{th} variable at high, low and mid level, respectively.
The optimal values of selected variables were obtained by using MATLAB 6.0. The interactive effects of the independent variables on the dependent ones were illustrated by three dimensional plots.

III. RESULTS AND DISCUSSION

Two different levels were assigned to each factor. These levels were experimentally determined to assure that the polymerization has the conversion at least at 50%. The experimental domains of three investigated factors were determined (see Table III).

Eight experiments in the factorial design and three experiments at the centre point were simultaneously performed. The curing process kinetics was withdrawn from the IR spectrum of the composition irradiated with time (Fig.2) The conversion degree was calculated according to equation (1) basing on a decrease of the absorbance intensity of C=C band vibrations at 810 wavenumbers.

TABLE III

INVESTIGATED FACTORS: LEVELS AND CONDITIONS

Factor	Experimental domain		
	Level (-)	*Level (0)*	*Level (+)*
z_1:Initiator concentration (%)	0.2	2.6	5
z_2: Monomer/oligomer	1/4	5/8	1/1
z_3: Alcohol concentration (%)	1	5.5	10

All the experiment parameters are reported in Table IV and the model matrix is given in Table V.

Coefficient values and statistical parameters obtained for the model are given in Table VI. For assessing the statistical significance of the result, a t-test (t-Student) was carried to the 95% confidence level.

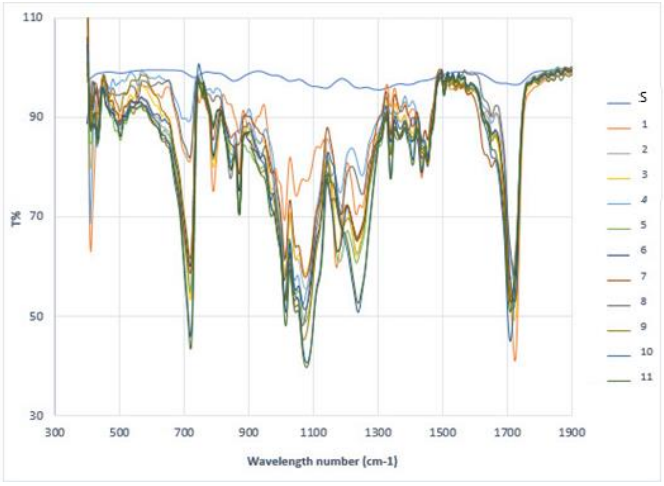

Figure 2: IR spectrum of reaction systems during irradiation

TABLE IV

EXPERIMENTAL PARAMETERS

Exp No	Initiator (% wt)	Monomer/ oligomer	Alcohol (% wt)	Conversion (%)
1	0.2	1/4	1	59.03
2	5	1/4	1	65.14
3	0.2	1/1	1	57.06
4	5	1/1	1	85.77
5	0.2	1/4	10	53.32
6	5	1/4	10	61.74
7	0.2	1/1	10	67.80
8	5	1/1	10	79.39
9	2.6	5/8	5.5	67.79
10	2.6	5/8	5.5	67.37
11	2.6	5/8	5.5	68.00

TABLE V

MODEL MATRIX AND RESPONSE

Exp. No	X_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Response
1	+1	-1	-1	-1	+1	+1	+1	-1	59.03
2	+1	+1	-1	-1	-1	-1	+1	+1	65.14
3	+1	-1	+1	-1	-1	+1	-1	+1	57.06
4	+1	+1	+1	-1	+1	-1	-1	-1	85.77
5	+1	-1	-1	+1	+1	-1	-1	+1	53.32
6	+1	+1	-1	+1	-1	+1	-1	-1	61.74
7	+1	-1	+1	+1	-1	-1	+1	-1	67.80
8	+1	+1	+1	+1	+1	+1	+1	+1	79.39
9									67.79
10									67.37
11									68.00

As the results shown in Table VI, with the confidence value > 99%, the coefficients, except b_3, are significant and the obtained equation is as follows.

$$\hat{y} = 66.16 + 6.85x_1 + 6.35x_2 + 3.22x_1x_2 - 1.85x_1x_3 + 1.68x_2x_3 - 2.43x_1x_2x_3 \quad (6)$$

This model was then analyzed by F- statistical test for analysis of variance (ANOVA) to assess the "goodness of fit". The analysis results are presented in Table VII. The value of F-statistic (the ratio of mean square due to regression to mean square to real error) of 272 is much larger than $F_{0.01,8,7}$ (6.87) so the model is significant at the chosen probability level and it is correct [6]. In addition, the lack of fit error was used to test whether the model can fit the data well. The ratio between lack of fit (SS_{lof}) and pure experimental error (SS_{pe}) is smaller the critical $F_{0.01,1,2}$ (98.50). This result confirms that the model adequately fits the data. The R^2 of 0.99 also indicates that only 1% of the total variation could not be explained by the empirical model [6]. Clearly, at that significance level, it is acceptable to use the obtained model that does not include the rejected terms.

TABLE VI

COEFFICIENT VALUES AND STATISTICAL PARAMETERS OBTAINED FOR THE MODEL

Coefficient	Coefficient value	Standard deviation	p-value
b_0	66.16	0.78	< 0.01
b_1	6.85	0.78	< 0.01
b_2	6.35	0.78	< 0.01
b_3	-0.59	0.78	< 0.01
b_{12}	3.22	0.78	< 0.01
b_{13}	-1.85	0.78	< 0.01
b_{23}	1.68	0.78	< 0.01
b_{123}	-2.43	0.78	< 0.01

TABLE VII

STATISTICAL PARAMETERS OBTAINED FROM THE ANOVA TEST PERFORMED FOR THE MODEL

Source of variation	Sum of square (SS)	Degree of freedom (ddl)	Average square	Fisher number	Signification	R^2
Regressio	878	8	109	272	6.87	0.99
Residues	2.82	7	0.40			
Lack of fit	2.61	1	2.61	26.1	98.50	
Pure error	0.21	2	0.10			

Replacing the x variables by the z factors, the model for real variables is obtained:

$$\hat{y} = 60.3 - 0.5Z_1 - 6.42Z_2 - 1.15Z_3 + 6.88Z_1Z_2 + 2.56Z_2Z_3 + 0.2Z_1Z_3 - 0.6Z_1Z_2Z_3 \quad (7)$$

The function above is now describing how the experimental variables and their interactions influence the conversion. A curvature in the surface of these factors indicates that they are interdependent (Fig.3). The response surface also implies that the optimal conditions were exactly located inside the design boundary (Fig.4).

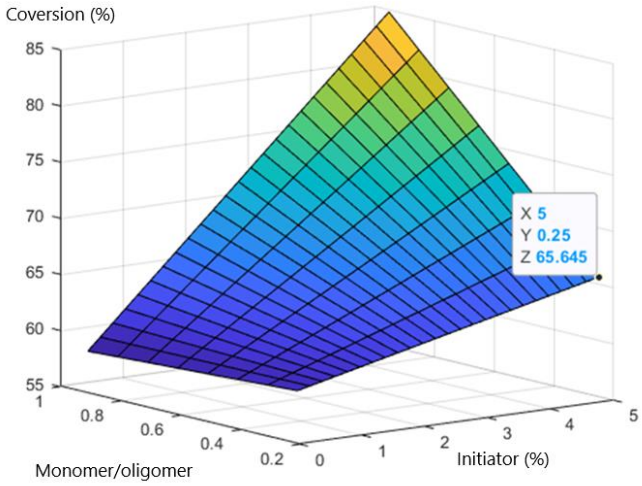

Figure 3: Surface graph of response y (conversion) showing the effect of initiator concentration and monomer/oligomer ratio (at alcohol concentration of 1.5 %)

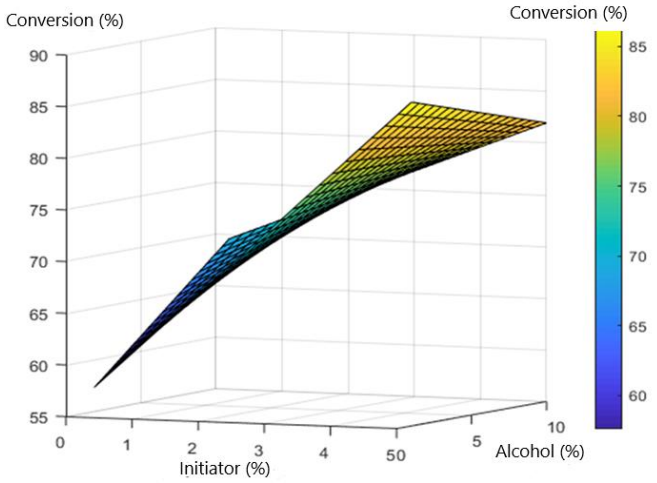

Figure 4 : Surface graph of response y (conversion) showing the optimal polymerization process

From (6), by using MATLAB software, the optimal conditions are calculated as follows. z1 = 5.0%; z2= 1/1; z3 = 1.45%. Under these conditions the maximal value of conversion is 86.16%. This result was confirmed by the experimental process under the optimal conditions. The IR spectrum of the system before and after UV expose is presented in Fig. 5. The obtained conversion is 86.5%

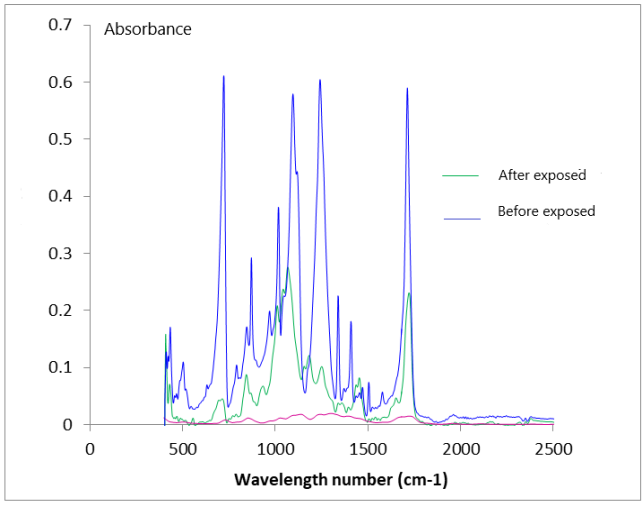

Figure 5: IR spectrum of the optimal reaction system during irradiation

IV. CONCLUSION

The results showed that the three factors considered in this study play an essential role in the polymerization process. The optimal conditions for initiator concentration, monomer/oligomer weight, and alcohol concentration are 5%, 1/1 and 1.45%, respectively. Under these conditions, about 86.5% of conversion is obtained. This result proves the effectiveness of the 2^k experimental design. The obtained conversion is higher than individual investigations. The accepted optimal model also allows for evaluation and control of the polymerization reaction.

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