

Influence of polymerization conditions on the molecular weight and polydispersity of polyepichlorohydrin

D. Guanaes^{a,*}, E. Bittencourt^b, M.N. Eberlin^c, A.A. Sabino^c

^a *Brazilian Army/IMBEL/Presidente Vargas Factory, Av. 15 de março sh, Piquete, SP 12620-000, Brazil*

^b *Department of Polymer Technology/Chemistry Engineering Faculty, State University of Campinas, Campinas, SP 13083-970, Brazil*

^c *Thomson Mass Spectrometry Laboratory/Institute of Chemistry, State University of Campinas, Campinas, SP 13083-970, Brazil*

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Abstract

The influence of the relevant reaction conditions on the molecular weight and polydispersity during the cationic ring-opening polymerization of epichlorohydrin has been studied using an experimental design. The polymerization was conducted in the presence of an alcohol (diol and triol), a Lewis acid at two temperatures (5 °C and 25 °C), and with two monomer addition rates. FT-IR spectra were used for the chemical characterization of the polymer, and MALDI-TOF mass spectrometry was used to determine the oligomeric composition and the masses of the initiator or transfer agent. The FT-IR showed the characteristic peaks of polyepichlorohydrin, and the mass spectra indicate that the alcohol was incorporated in the polymer structure. The MW and polydispersity were determined using gel permeation chromatography. We observed that the two most significant parameters that affected MW were the monomer addition rate and the reaction temperature, whereas polydispersity was most strongly affected by the monomer addition rate.

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1. Introduction

In the past years great efforts have been made to increase solid propellants output energy. One alternative has been to use energetic polymers as binders in the formulations, which are obtained by the introduction of energetic groups in the lateral chains or in the polymer backbone [1–4].

The glycidyl azide polymer (GAP) has been extensively investigated because it achieves the energetic polymer characteristics and is compatible with the other propellant ingredients [1]. GAP, when used as an energetic binder, must have the appropriate molecular weight ($1500 \leq MW \leq 3000$) and hydroxyl end groups to be later cured with isocyanates. GAP synthesis uses epichlorohydrin polymerization, followed by azidation, as seen in Fig. 1 [1–4].

The preparation of polymers with hydroxyl end groups from cyclic ethers in the presence of

* Corresponding author. Tel.: +55 12 3156 9078; fax: +55 12 3156 9099.

E-mail address: daniguanaes@yahoo.com.br (D. Guanaes).

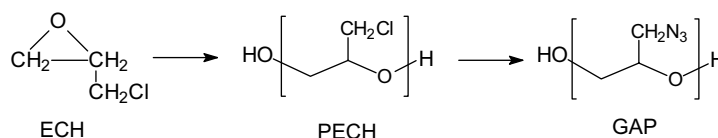


Fig. 1. Scheme of GAP synthesis.

hydroxyl-containing initiators has been studied by several groups [5–8]. In this reaction, two mechanisms compete (Fig. 2): (1) the active chain end (ACE) and (2) the activated monomer (AM). The first mechanism involves a tertiary oxonium propagation ion, and the generation of the hydroxyl group occurs by a chain transfer reaction by the hydroxyl-containing compound. In the second mechanism, the protonated monomer is attacked by the alcohol during the initiation step and by the neutral growing species in the propagation step, generating a polymer with the same number of hydroxyl groups as the initiator [5,7].

Cyclics are formed in the ACE mechanism by an intramolecular chain transfer reaction (Fig. 3), which reduces the MW of the end product and the yield of the reaction, but increases the polydispersity for the MW range studied [5,6]. Whereas the ACE mechanism can lead to undesirable cyclization reactions, the AM forms only linear polyols, which is advantageous in order to obtain higher MW products, as predicted by Eq. (1) [5,7]:

$$\overline{M}_n = \frac{n_{\text{monomer}}}{n_{\text{initiator}}} \times M_{\text{monomer}} + M_{\text{initiator}} \quad (1)$$

where n_{monomer} is the number of moles of the monomer consumed, M_{monomer} is the monomer molar mass, $n_{\text{initiator}}$ is the number of moles of the initiator, and $M_{\text{initiator}}$ is the initiator molar mass.

Recently, Kubisa and Penczek [7] showed that the AM mechanism is favored by maintaining a monomer's "starving" condition, i.e. the monomer should be slowly added to the reaction system, keeping its concentration as low as possible. The reac-

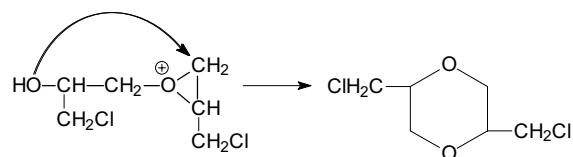


Fig. 3. Cyclization reaction.

tions in their study were conducted at a constant temperature of 25 °C.

Several authors studied other polymerization conditions that influence the characteristics of the end product in a ring-opening polymerization, but they were studied one for each time. Kubisa [5,9] and Biedron et al. [5] verified that the cyclic fraction in the final product depends on the nature of the initiator. Tokar and co-workers [10] verified that the MW of the polymer increases by decreasing the temperature in the cationic polymerization of glycidol.

Based on these studies, our aim was to determine how the polymerization conditions, such as the monomer addition rate, the initiator nature, temperature, and their interactions influence the MW and the polydispersity of the polyepichlorohydrin produced by the cationic ring-opening polymerization of epichlorohydrin in the presence of an alcohol using an experimental design.

2. Experimental design

To achieve our goal, the criteria of the factorial design was chosen, since it enables the simultaneous change of the reaction conditions, instead of one at

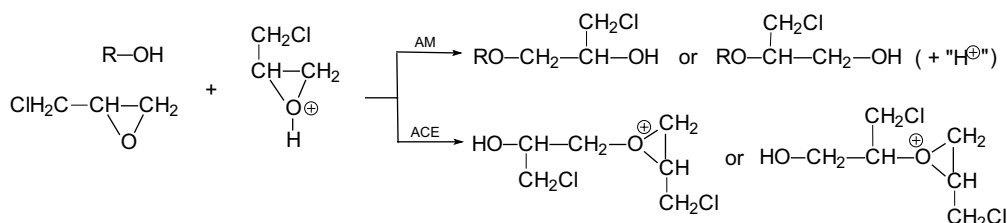


Fig. 2. Initiation mechanism for cyclic ethers in the presence of a hydroxyl-containing compound and a Lewis acid.

Table 1
Factor definitions

Factor	Definition	Levels	
		Low	High
<i>A</i>	Monomer addition rate	Fast	Slow
<i>B</i>	Initiator	EG	GLI
<i>C</i>	Temperature (°C)	5	25

a time, allowing the widest generation of information about the system, with the lowest number of experiments. The result of the experimental design is the selection of the most significant effects and the determination of the statistical model based on it.

In the present study, three factors (*A*, *B*, and *C*) were examined, each one at two different levels (low and high) in a single replicate design, resulting in a total of 2^3 experiments required (Table 1).

The effect of a factor in the system considered can be defined as the change in response produced by a change in the level of the factor. When the difference in response between the levels of one factor is not the same at all levels of the other factors, there are interactions between factors.

The effects can be estimated by multiplying each treatment combination by the signs in Table 2 and dividing its sum by the total of experiments. For example, the effect of the interaction *AB* can be estimated as

$$AB = \frac{1}{8}[ab - a - b + (1) + abc - bc - ac + c] \quad (2)$$

The statistical model for this study can be described by the equation:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 + \beta_{123}x_1x_2x_3 \quad (3)$$

where *y* is the predicted value, β_0 is the overall mean of the measured characteristic, β describes the effect of the main factors *A* (1), *B* (2), *C* (3) and their interactions, and the variables x_1 , x_2 and x_3 represent the values of *A*, *B*, and *C*, respectively.

The statistical analysis method used in this work is attributed to Daniel [15,16]. In this method the estimates of the effects are plotted on a normal probability plot. The effects that lie along a straight line are negligible, while the significant effects are far from the straight line. Only the significant effects are used in the statistical model.

To construct the normal probability plot, the data are arranged in an increasing order and the

Table 2
Estimation of the effects

Treatment combination	Factorial effect							
	I	<i>A</i>	<i>B</i>	<i>AB</i>	<i>C</i>	<i>AC</i>	<i>BC</i>	<i>ABC</i>
(1)	+	–	–	+				
<i>a</i>	+	+	–	–				
<i>b</i>	+	–	+	–				
<i>c</i>	+	+	+	+				
<i>ab</i>	+	–	–	+				
<i>ac</i>	+	+	–	–				
<i>bc</i>	+	–	+	–				
<i>abc</i>	+	+	+	+				

*k*th value of these ordered results are plotted versus the cumulative probability point given by

$$p_k = \frac{(k - 1/2)}{7} \quad (4)$$

The residuals are the difference between the value measured and the value predicted by the regression model approach, Eq. (3), for an experiment. In a normal probability plot of the residuals, the model accuracy is verified by the arrangement of the points close to a straight line.

3. Experimental procedure

3.1. Materials

Epichlorohydrin (ECH), 98% purity, purchased from Aldrich, was dried with calcium oxide, distilled, and stored in molecular sieves. Boron trifluoride diethyl ether ($\text{Et}_2\text{O} \cdot \text{BF}_3$) purified, from Aldrich, was distilled under an inert atmosphere and stored under refrigeration. Dichloromethane PA (DCM), purchased from Synth, was dried with calcium hydride, distilled and stored in molecular sieves. Ethylene glycol (EG) PA, purchased from Synth, and glycerol (GLI), kindly provided by Braswey, were used as received. Sodium bicarbonate was used as received.

3.2. Polymerization

The reaction was conducted under an inert atmosphere of nitrogen, with temperature and stirring control. The monomer (25 mL) was added to the reaction medium containing the alcohol (EG or GLI, 0.01225 mol), the Lewis acid ($\text{Et}_2\text{O} \cdot \text{BF}_3$), and the solvent (DCM, 25 mL). Two monomer addition rates were used: slow, where the addition proceeded for 24 h, and fast, where all the monomer

was added at one time. The number of catalyst moles used was based on the number of hydroxyl moles of the alcohol ($\text{OH}/\text{Et}_2\text{O} \cdot \text{BF}_3 = 31$). After the addition of the monomer was complete, the reaction continued for five additional hours. The reaction was then quenched by adding distilled water. The end product was washed with sodium bicarbonate solution (5% wt/vol), followed by several distilled water washings until it appeared neutral to pH paper. Afterwards, it was isolated by evaporation of the solvent at room temperature.

3.3. Characterization

3.3.1. FT-IR spectrometry

The chemical bonds of the polymerization end product were determined by the spectra recorded in pressed KBr pellets with a sample concentration of 1% wt/wt using a Perkin Elmer FT-IR spectrometer model Spectrum 2000.

3.3.2. MALDI-TOF mass spectrometry

The determination of the oligomeric composition, the repeating unit and the end group masses was performed by MALDI-TOF mass spectrometry. Analyses were done with a MALDI/TOF (Micro-mass/Waters) mass spectrometer. The samples were prepared by the mixing of 10 μL of the matrix solution (1% wt/vol dithranol in THF) with 1 μL of polymer solution (1% wt/vol in THF), and 1 μL of this resulting solution was added to spots on the MALDI target plate and left to dry in air before the analysis. The sample was ionized by a nitrogen UV laser (337 nm), and the ions formed were accelerated with 15 kV potential in the flight tube. The mass spectra were acquired using the TOF (time of flight) mass analyzer working in the reflectron mode.

3.3.3. Gel permeation chromatography (GPC)

The molecular weight and the polydispersity were measured by GPC using a Polymer Labs PL-GPC-210 chromatograph equipped with a refractive index detector and two columns PL-Gel (500 and 100 Å) in series. The mobile phase was THF, the flow rate was 1 mL min^{-1} , the experimental temperature was 30 °C, and the sample concentration was 0.20% wt/wt. The number average molecular weight (M_n) and the polydispersity (PD) were calculated by a calibration curve generated by polystyrene standards (580, 1300, 5460, and 10,850) with narrow MW distribution.

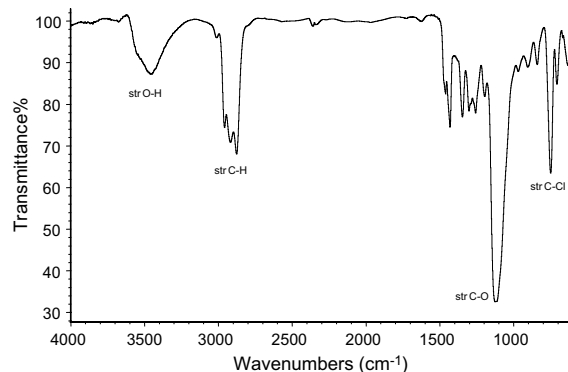


Fig. 4. FTIR spectrum of PECH.

4. Results and discussion

After the solvent evaporation, the end product obtained was a viscous liquid, which was then subjected to the analysis.

4.1. Chemical bonds by FT-IR

The FT-IR spectra for the viscous liquid obtained in all experiments showed typical bands of PECH, as assigned in Fig. 4.

4.2. Oligomeric composition and repeating unit

The mass of the repeating unit was calculated by the m/z difference between adjacent ions, as described before by other authors [12,13]. For all polymers, the MALDI-TOF mass spectra showed

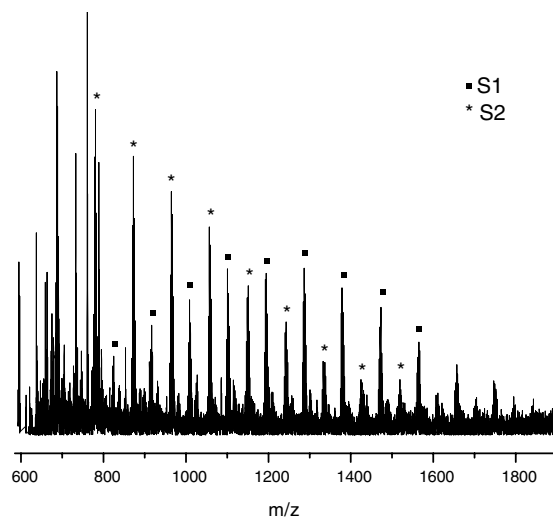


Fig. 5. MALDI-TOF mass spectrum for the PECH.

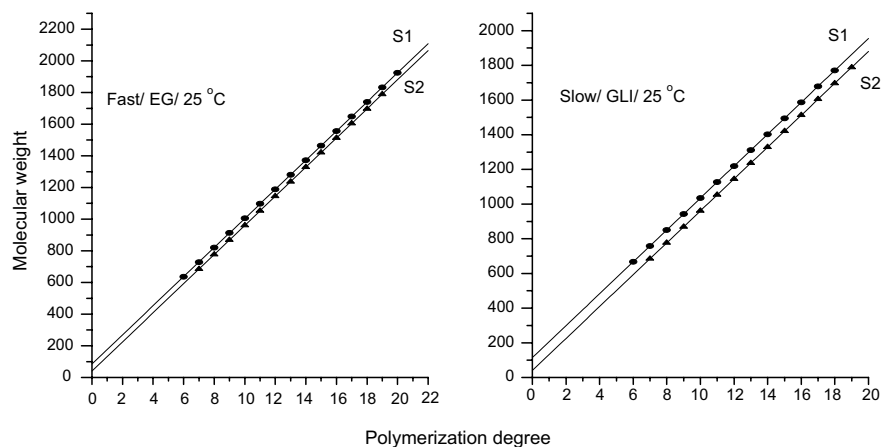


Fig. 6. Plots for the determination of the initiator or transfer agent mass.

two oligomeric series of ions (S1 and S2) (Fig. 5) each one separated by the same repeating unit corresponding to the mass of epichlorohydrin. These two oligomeric series suggest the presence of two different initiators or transfer groups, depending on the polymerization mechanism.

4.3. Transfer group or initiator

For the determination of the initiator or transfer group mass ($M_{in/ta}$) plus the cation mass (M_{cat}), the ion masses are plotted against the degree of polymerization (n), so that the intercept will represent their molar masses [9,11,12].

$$M_{peak} = n \times M_{monomer} + (M_{in/ta} + M_{cat}) \quad (5)$$

It was verified in all series that the cation mass corresponds to Na^+ . The first series revealed the presence of ethylene glycol or glycerol, depending on the alcohol used, while the second series revealed the presence of water in the structure of the polymer. It was presumed that water was away of the reaction medium, but it was present as a contaminant. An illustration of the process used to deter-

mine the mass of the initiator/transfer agent is shown in Fig. 6.

After the water identification, its presence in the reagents was quantified by the Karl Fisher method. The results found are shown in Table 3. According to these test results and the quantity of the reagents used in the polymerization, it can be concluded that the reagents that most contributed to the water contamination were epichlorohydrin and dichloromethane.

Table 3
Karl Fischer analysis results

Reagent	% wt/wt
ECH	0.135
DCM	0.106
EG	0.396
GLI	0.479

Table 4
Experimental results of the factorial design

Treatment	MW	PD
(1)	1027	1.356
<i>a</i>	1053	1.296
<i>b</i>	708	1.629
<i>c</i>	806	1.664
<i>ab</i>	647	1.224
<i>ac</i>	1265	1.207
<i>bc</i>	970	1.585
<i>abc</i>	1178	1.424

Table 5
Estimation of the factorial effects for the molecular weight

Order	M	PD				
		Effect	Estimate	$(k - 0.5)/7$		
1	<i>B</i>	-162.0	92.86	<i>A</i>	-0.271	92.86
2	<i>AB</i>	-84.5	78.57	<i>AC</i>	-0.0383	78.57
3	<i>ABC</i>	-41.0	64.29	<i>BC</i>	-0.0158	64.29
4	<i>A</i>	158.0	50.00	<i>AB</i>	-0.0122	50.00
5	<i>AC</i>	175.5	35.71	<i>B</i>	0.0848	35.71
6	<i>C</i>	196.0	21.43	<i>C</i>	0.0937	21.43
7	<i>BC</i>	200.5	7.14	<i>ABC</i>	0.16	7.14

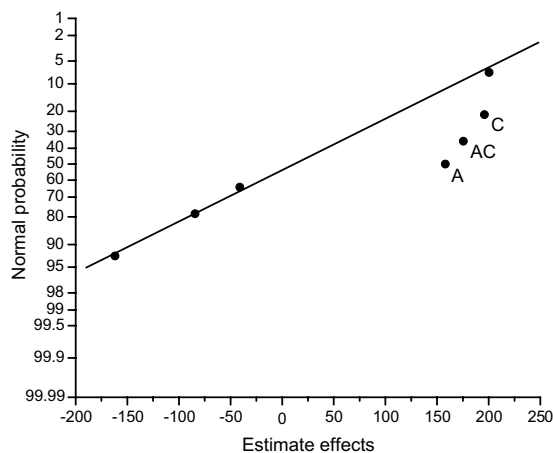


Fig. 7. Normal probability plot for the molecular weight.

4.4. Molecular weight

The molecular weight obtained (Table 4) was lower than desired due to the presence of water, as verified by the MALDI-TOF mass spectrometry data. Water initiates the polymerization or interferes with a premature transfer reaction with the propagation specie in the ACE mechanism. This

same water interference has been reported before [13,14].

From the results presented in Table 4, the factorial effects were estimated (Table 5) and the normal probability plot was constructed (Fig. 7). According to Fig. 7, we conclude that the more significant effects are *A*, *C* and the *AC* interaction. Fig. 8 shows that the main effects *A* and *C* are positive. The plot of the *AC* interaction indicates that the addition rate has little effect at low temperatures, but it has a large positive effect at a high temperature level. Then, in order to maximize the molecular weight, these factors should be run at high level (slow monomer addition rate, and 25 °C).

Based on the results of the significant effects, the fitted regression model can be represented by Eq. (6), where x_1 is the monomer addition rate and can assume the values of +1 or -1, according to the levels high or low, and x_3 is the temperature in °C.

$$M_n = 956.75 + (158/2) * x_1 + (196/2) * x_3 + (175.5/2)x_1 * x_3 \quad (6)$$

For the validation of the proposed model, a normal probability plot of the residues between the experi-

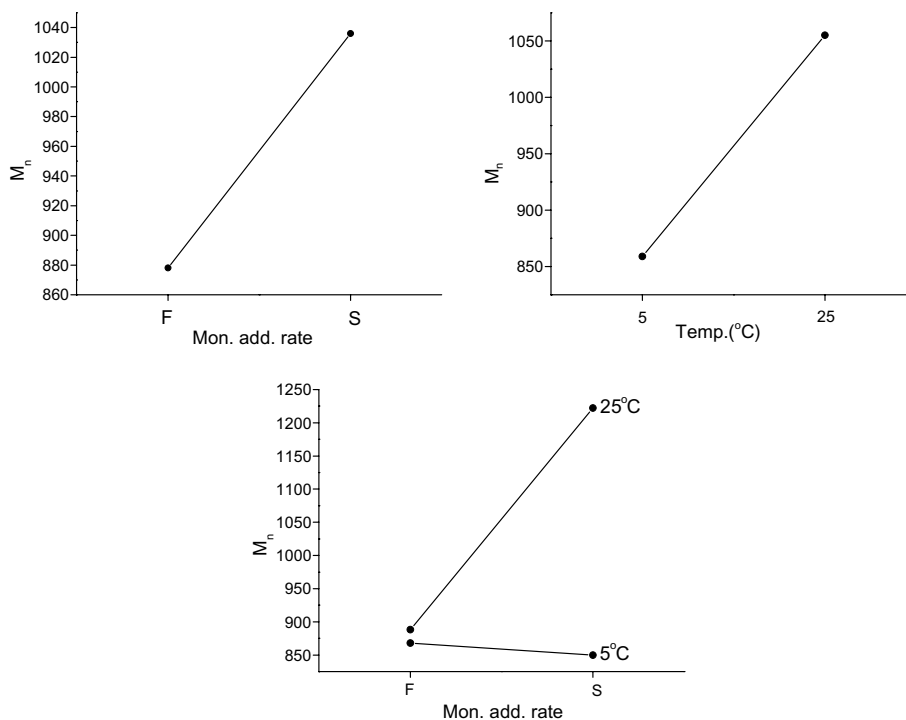


Fig. 8. Main effects and interaction plots for the molecular weight.

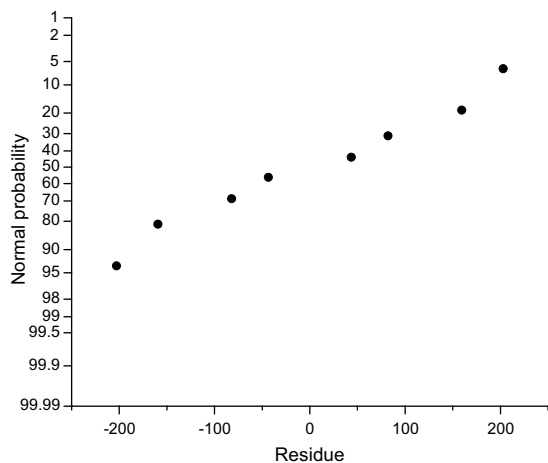


Fig. 9. Normal probability plot for the residue of the molecular weight.

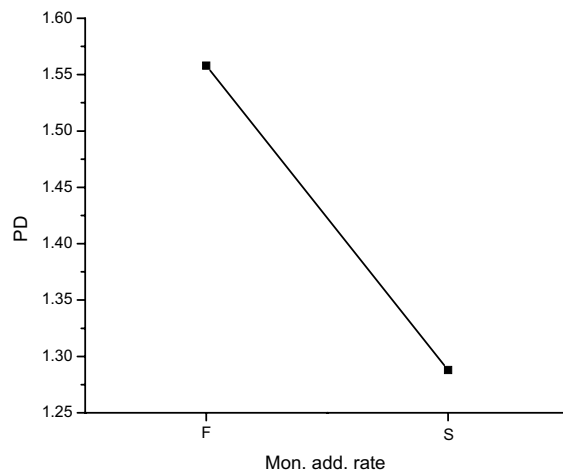


Fig. 11. Main effects and interaction plots for the polydispersity.

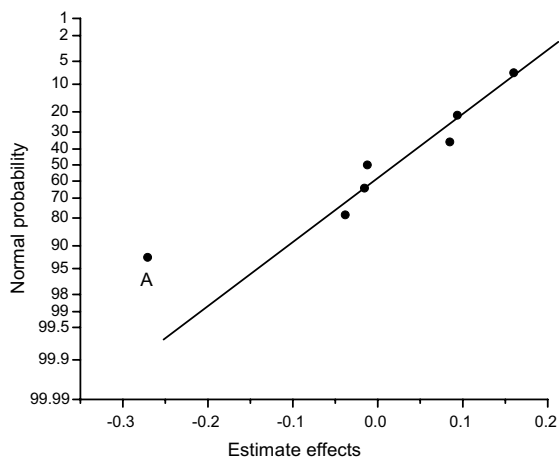


Fig. 10. Normal probability plot for the polydispersity.

mental and the calculated molecular weight is constructed. Fig. 9 shows that the points lie nearly along a straight line; hence we conclude that the proposed model is valid.

4.5. Polydispersity

Using the same procedure of the molecular weight, the normal probability plot of the polydispersity results (Tables 4 and 5) is shown in Fig. 10. According to Fig. 10, the most significant effect is the monomer addition rate. Fig. 11 then shows that this effect is negative, i.e. when the monomer addition rate is reduced the polydispersity is also reduced.

Using Eq. (7) of the fitted regression model, the normal probability plot of the residue was con-

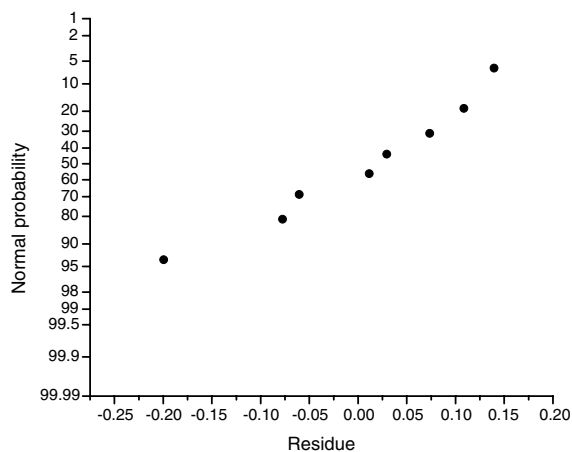


Fig. 12. Normal probability plot for the residue of the polydispersity.

structed (Fig. 12) indicating that the model proposed is acceptable.

$$PD = 1.42 + (-0,271/2 * x_1) \quad (7)$$

5. Conclusions

In this work we verified that the cationic ring-opening polymerization of epichlorohydrin in the presence of an alcohol is an appropriate method for obtaining polyepichlorohydrin. The end product was liquid, and the polyepichlorohydrin formation was confirmed by FT-IR, whereas the oligomeric composition, repeating unit and the initiator or transfer agent masses were determined by MALDI-TOF mass spectrometry.

According to the polymerization conditions studied, the most significant parameters for molecular weight control are the monomer addition rate, the temperature and its interaction, while for polydispersity, the monomer addition rate is far most important.

By the effects and interaction plots, we verified that, to achieve the highest molecular weight and lowest polydispersity, the polymerization must be run at the high level (slow monomer addition rate and 25 °C).

References

- [1] Frankel MB, Grant LR, Flanagan JE. *J Propul Power* 1992;8(3):560–3.
- [2] Ping W, Zhongjun X, Zhong W, Changqing L. *Int Ann Conf ICT*. In: 27th, 1996, Karlsruhe Proceedings, vol. 25, p. 1–10.
- [3] Stacer RO, Husband DM. *Prop Explos Pyrotec* 1991;16:167.
- [4] Vasudevan V, Sundararajan G. *Prop Explos Pyrotec* 1999;24:295.
- [5] Biedron T, Kubisa P, Penczek S. *J Pol Sci Part A* 1991;29:619.
- [6] Yu S. *Polym Prep* 1984;25:117.
- [7] Kubisa P, Penczek S. *Prog Polym Sci* 1999;24:1409.
- [8] Francis AU, Venkatachalam S, Kanakavel M, Ravindran PV, Ninan KN. *Eur Polym J* 2003;39:831.
- [9] Kubisa P. *Makromol Chem, Macromol Symp* 1988;13(14):203.
- [10] Tokar R, Kubisa P, Penczek S, Dworak A. *Macromolecules* 1994;27:320.
- [11] Chen H, He M, Pei J, Liu B. *Anal Chem* 2002;74(24):6252–8.
- [12] Ji H, Sato N, Nonidez W, Mays JW. *Polymer* 2002;43:7119.
- [13] Desai H, Cunliffe V, Stewart MJ, Amass AJ. *Polym Commun* 1993;34:642.
- [14] Qureshi MY, Ochel. *Eur Polym J* 1996;32:691.
- [15] Montgomery D. In: *Design and analysis of experiments*. Singapore: John Wiley & Sons; 1991. p. 197–310.
- [16] Hamada M, Balakrishanan N. *Statist Sin* 1998;8:1.