

PREPARATION OF HYDROPHILIC ESTER-BASED MONOMERS BY THE ADDITION REACTION OF EPOXIDES AND CARBOXYLIC ACIDS

Rahula Janiš
Pavína Vltavská
Jiří Krejčí
Věra Kašpárková
Lenka Navrátilová

Tomas Bata University in Zlin, Faculty of Technology
TGM 275, 762 72 Zlin, Czech Republic

Jana Bobálová
Tomas Bata University in Zlín, Innovation Centre
Mostní 5139, 760 01 Zlín, Czech Republic

ABSTRACT

The aim of this work is to verify procedure for preparation of acrylic acids esters with glycidol and epichlorhydrin, which could become the base for the producing of special hydrophilic polymers with polar groups. Reaction was carried out in a non-solvent system using the chromium (III) acetate hydroxide (CAH) as a catalyst. The influence of reaction temperature, time, ratio of reactants and the catalyst content on reaction conversion was studied. The purity of products was monitored by thin-layer chromatography and IR spectroscopy. In case of acrylic acid ester and epichlorhydrin, the highest conversion of 98,6% was reached in 1 hour at 90° C using 20% molar excess of epoxide and 0,4% (w/w) catalyst charge. When ester was prepared from glycidol, the conversion of 98% was reached at the same reaction conditions. The experimental results confirmed that preparation of esters by the epoxy ring opening using chromium complexes as catalysts is a suitable, simple and perspective method for the hydrophilic monomers preparation.

Keywords: glycidol, epichlorhydrin, esters, acrylic acid, hydrophilic monomers.

1. INTRODUCTION

Esterification is the most commonly used reaction for the preparation of esters. However, using this procedure, difficulties with the elimination of arising water and low reaction selectivity are in some cases observed. A perspective method, which can prevent these problems, is the addition of carboxylic acids to epoxides by the nucleophilic opening of epoxy ring. The advantages of this reaction especially include high conversions, regioselectivity, low catalyst charge and mild reaction conditions [1, 2].

2. MATERIALS AND METHODS

Acrylic acid, glycidol, epichlorhydrin, chromium(III) acetate hydroxide ($[\text{CH}_3\text{COO}]_7\text{Cr}_3[\text{OH}]_2$), 2,7-dichlorfluorescein, hydroquinone, were purchased from Sigma-Aldrich and were used without further purification.

The reaction was performed in a glass reactor equipped with a magnetic stirrer, reflux condenser and temperature-stabilized jacket enabling to control reaction temperature with an accuracy of 0.5°C. Catalyst and subsequently glycidol or epichlorhydrin were added to the acrylic acid (10g) in required quantity at a given temperature. Both epoxides were added to the acid at different molar ratio.

The used amount of CAH-catalyst was 0.3–0.5% (w/w) of the glycidol–acid reaction mixture weight. At 5-min intervals, samples of the reaction mixture were withdrawn, dissolved in xylene/ethanol (1:1, v/v) and titrated with 0,1 M ethanolic KOH to phenolphthalein end point. The conversions (%) of acid were calculated from arithmetic means of four acid-base determinations; the relative standard deviation was 2.85%.

Thin-layer chromatography (TLC) was carried out on silica gel plates Riedel-deHaen. Mixture of n-heptane : acetone (4:5, v/v) was used as an elution system. Detection was performed by 2,7-dichlorfluorescein. The structure analysis of the final reaction products purified by TLC was performed by IR analysis. The IR absorbance spectra (KBr pellet) were recorded using a Mattson 300 spectrometer over the wavenumber range of 400-4000cm⁻¹.

3. RESULTS

Optimization experiments aimed to reach the maximum reaction conversion at the lowest temperature, minimum catalyst charge, shortest time and the most advantageous molar ratio of reactants have proved that the highest conversion was obtained after 1 hour at 90° C, 0.4% (w/w) chromium catalyst and molar ratio of acrylic acid:glycidol 1:1.2. During the optimization process, just one reaction parameter was always changed, while the others were maintained on the constant level and the time dependence of reaction conversion was monitored.

The course of the reaction of acrylic acid with glycidol, added in one dose at optimum reaction parameters is shown in Table 1. From the table it is obvious that after the conversion of 78% was reached, the spontaneous polymerization occurred and the reaction system solidified in a reactor. Thus, it was decided to add glycidol into the reactor gradually. Results listed in Table 2 illustrate that this procedure had a positive effect in preventing the polymerization of mixture, since the final conversion was 98% at 20% molar excess of glycidol in the reaction system. Nevertheless, to get the high conversion, the reaction time has to be prolonged. The application of the polymerization inhibitor was another possibility how to ensure the ester stability during the reaction and following storage. Therefore, 1% (w/w) of hydroquinone related to acid weight was dosed at the beginning of reaction. This experiment proved that in the presence of hydroquinone, the hydroxyester of acrylic acid did not polymerize and the reaction conversion of 98.6% was reached after 1 hour. Identical results were obtained during the preparation of ester of acrylic acid with epichlorhydrin. Maximum conversion of 98.6% was achieved at optimum reaction parameters.

Table 1. Reaction conversion at molar ratio of acid: glycidol 1:1.2 (added in one dose): reaction temperature 90° C, 0.4% (w/w) CAH

	Time (min)	Conversion (%)
1	15	54.08
2	30	71.01
3	45	78.29
4	50	polymerization

Qualitative aspects of the reaction and the process selectivity in terms of presence of undesired isomers were monitored by TLC.

As an example, the TLC chromatogram of monomer prepared by the addition of acrylic acid to glycidol at the optimum reaction conditions is shown in Figure 1. It is apparent that almost pure 1-glycerylacrylate was obtained (see the sample no. 3, spot B, R_f = 0.21).

IR spectrum proved the anticipated structure of the purified ester showing the wide absorption band at about 3450 cm⁻¹ belonging to hydroxyl groups, absorption band at 1717 cm⁻¹ belonging to the group of atoms –COO– and bands at 1636 cm⁻¹ and 1619 cm⁻¹ assigned to vinyl group CH₂=CH–. The observed absorption bands 811 cm⁻¹, 984 cm⁻¹ and 1063 cm⁻¹ also corresponded to vinyl group.

Table 2. Reaction conversion after the gradual addition of glycidol: reaction temperature 90° C, 0.4% (w/w) CAH

Molar ratio Acid : Glycidol	Time (min)	Conversion (%)	Molar ratio Acid : Glycidol	Time (min)	Conversion (%)
1:0.5	10	32.45	1:0.9	130	72.22
	20	37.61		140	75.00
	30	39.27		150	77.34
	40	43.84		160	79.49
1:0.7	50	49.29	1:1	170	84.80
	60	60.08		180	85.77
	70	57.93		190	87.35
	80	59.58		200	88.89
1:0.8	90	64.00	1:1.2	210	92.53
	100	65.73		220	94.85
	110	68.25		230	97.58
	120	70.40		240	98.39

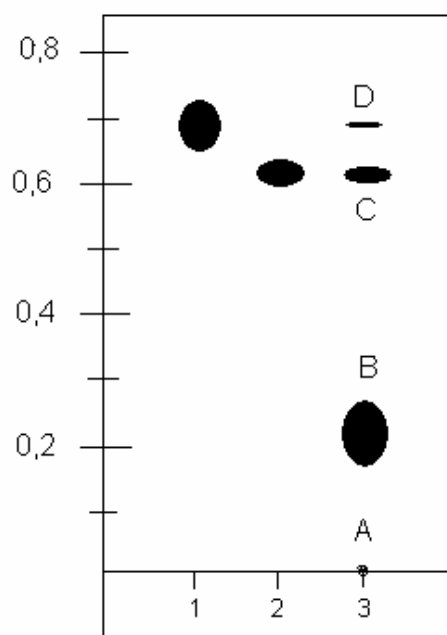


Figure 1. TLC of 1-glycerylacrylate. Sample 1: acrylic acid, sample 2: hydroquinone, sample 3 spot A: CAH, spot B: 1-glycerylacrylate, spot C: hydroquinone, spot D: acrylic acid

4. CONCLUSIONS

- Using CAH as a regioselective catalyst during the addition reaction of acrylic acid and glycidol, or epichlorhydrin resulted in the preparation of appropriate esters.
- Optimum reaction parameters are as follows: temperature 90° C, reaction time 1 hour, ratio of acid:epoxide 1:1.2 (mol/mol).
- Product structure was proved by IR spectrum.
- TLC analysis confirmed the reaction selectivity.

5. REFERENCES

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6. ACKNOWLEDGEMENT

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