

Synthesis and Characterization of the New Unsaturated Epoxyoligoester Suitable for Further Modification

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ABSTRACT: In this article, the synthesis and characterization of the new unsaturated epoxyoligoester suitable for further modification have been presented. The new unsaturated epoxyoligoester was prepared by the chemical modification of the structure of the unsaturated oligoester obtained in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and ethylene glycol. The chemical modification of the structure of initial oligoester by 38–40% peracetic acid in mild conditions allowed to introduce the oxirane groups into the oligoester backbone. The structure of the samples before and after epoxidation was characterized by FTIR, ^1H NMR, DSC, and elemental analyses. The FTIR and ^1H NMR analyses

confirmed that the oxidation reaction took place through the double bonds in cyclohexenyl rings, whereas the double bonds in the unsaturated chain remained unaltered. Moreover, the epoxidation reaction was performed at 20 and 40°C for 1–6 h to define the optimum temperature and time conditions of this process. The optimum temperature and time conditions were 40°C and 2.5 h, respectively. In this conditions, the maximum conversion of the double bonds (98.3%) and minimal epoxide degradation were observed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2973–2978, 2008

Key words: synthesis; structure; polyesters

INTRODUCTION

The use of peracids or *in situ* generated peracids as the oxidant agents for noncatalyzed reactions or hydrogen peroxide, iodosylbenzene, sodium hypochlorite, and *tert*-butylhydroperoxyde in catalytic reactions allows to introduce epoxy functionality into polymer backbone.^{1–5} Catalytic or noncatalytic epoxidation of polymers having a carbon–carbon double bonds allow to obtain the new epoxy materials suitable for many applications. In this way, the chemical structure of olefinic polydienes such as polybutadiene or polyisoprene or block copolymers which contains a polymer block of a diene, poly(vinyl chloride), rubber seed oil can be modified.^{6–8}

Cycloaliphatic epoxy resins can be prepared by epoxidation of unsaturated cycloaliphatic compounds with organic peracids. They have long been applied in a variety of industrial applications such as paints, coatings, reactive diluents, vacuum-pressure impregnation of coils, encapsulation of electronic circuit elements, and printed circuit-board coatings because of their good heat and chemical resistance, their high stiffness, high strength, good chemical resistance, and dimensional stability.^{9–15}

Epoxidation of polyesters obtained in polycondensation process of tetrahydrophthalic acid or anhydride, at least one cycloaliphatic polyol and at least one saturated polycarboxylic acid with peracetic or performic acid, the solid epoxidized polyesters useful for powder coating applications were obtained.^{16–18}

Some papers described the solid epoxypolyesters prepared by the condensation of glycols, 1,2,3,6-tetrahydrophthalic anhydride, and dicyclopentadiene followed by the epoxidation of the double bonds in the polyester useful for UV-curable powder coating.^{19,20}

In this article, the well-known conventional method of epoxidation was applied to obtain the new unsaturated epoxyoligoester suitable for further modification. The new unsaturated epoxyoligoester was prepared by epoxidation of the unsaturated oligoester obtained in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and ethylene glycol with 38–40% peracetic acid in mild conditions. The synthesis and characterization of the materials before and after epoxidation as well as the optimum temperature and time conditions of the oxidation process were presented.

EXPERIMENTAL

Materials

Tetrahydrophthalic anhydride (cyclohex-4-ene-1,2-dicarboxylic anhydride) and maleic anhydride were

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obtained from Merck-Schuchardt (Hohenbrunn, Germany). Ethylene glycol was obtained from Fluka (Buchs, Switzerland). Methylene chloride, tetrahydrofuran Lichrosolv (chromatographic grade) were purchased from Merck-Schuchardt (Hohenbrunn, Germany) and were used as the solvents. 38–40% solution of peracetic acid with 1% content of sulfuric acid was from Merck-Schuchardt (Hohenbrunn, Germany) and was used as the oxidation agent. Other reagents such as sodium carbonate, sodium hydroxide, sodium chloride, and magnesium sulfate were delivered by POCh (Gliwice, Poland). All reagents were used without further purification.

Characterization

Elemental analysis was performed with a Perkin-Elmer CHN 2400 analyzer in aluminum crucibles, the mass of the sample was about 2 mg.

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1725X FTIR spectrophotometer in the 400–4000 cm^{-1} wavenumber range using KBr pellets.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained by using a NMR Bruker-Avance 300 MSL (Germany) spectrometer at 300 MHz with deuterated chloroform (CDCl_3) as the solvent. ^1H NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Günzburg, Germany) operating in a dynamic mode. The nonisothermal scans were performed at a heating rate of 10 K/min from room temperature to a maximum of 500°C under nitrogen atmosphere (30 mL/min). As a reference, an empty aluminum crucible was used.

Synthesis of the unsaturated oligoester

In the three-necked flask equipped with a reflux condenser, a thermometer and a mechanic stirrer cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and ethylene glycol were placed and the reaction mixture was heated to 130°C. The reaction was carried out at 1 : 0.5 : 2.1M ratios of cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and ethylene glycol to obtain an unsaturated oligoester with hydroxyl end groups. For preliminary reaction of substrates the whole amount was heated at 130–150°C for 2 h. When the addition reaction was completed, 10 wt % xylene was added and subjected to the polycondensation. The process of polycondensation was carried out in the temperature range of 150–180°C with simultaneous azeotropic removal of condensation water from the reaction medium. The course of the process was controlled by determining

the acid number (defined as a number of mg KOH required for the titration of 1 g of a sample). The drop of an acid number of the reaction mixture from initial value 254 mg KOH/g to the final value not exceeding 2 mg KOH/g was taken as an indicator of the process completion. After that, the solvent-xylene was removed by distillation under reduced pressure at elevated temperature. The obtained oligoester containing cyclohexenyl rings and double bonds from maleic anhydride was analyzed and used for further chemical modification to produce the new epoxidized oligoester.

Epoxidation of the unsaturated oligoester

The obtained unsaturated oligoester was placed in the three-necked flask equipped with a water condenser, a thermometer, and a glass stirrer. The unsaturated oligoester was dissolved in the solvent (methylene chloride) and the resulting solution was heated to the reaction temperature (20 or 40°C). Then 38–40% solution of peracetic acid with 1 % wt content of sulfuric acid was added under vigorous stirring and then reacted at reaction temperature. With peracetic acid the reaction was almost immediately exothermic, so the reaction mixture had to be cooled down with an ice bath to attain the reaction temperature. The mixture was stirred for a predetermined time (1–6 h). After completion, the reaction mixture was cooled down and washed with the aqueous solution of sodium carbonate and sodium hydroxide saturated with sodium chloride to neutrality. Then, the mixture was placed in the separator and the organic phase was thoroughly washed two times with aqueous solution of sodium hydroxide and distilled water, dried over anhydrous MgSO_4 . The solvent was removed by vacuum distillation. The residue was diluted with tetrahydrofuran, dried and distilled off under reduced pressure. The theoretical chemical structure of the unsaturated oligoester and the new unsaturated epoxyoligoester is presented in Figure 1.

RESULTS AND DISCUSSION

Characterization of the unsaturated oligoester and the new unsaturated epoxyoligoester

The novel unsaturated epoxyoligoester was synthesized through a two-step procedure. First, the polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and ethylene glycol was performed to obtain oligoester containing cyclohexenyl rings and double bonds from maleic anhydride. Then, the obtained unsaturated oligoester was oxidized by 38–40% peracetic acid, in which the unsaturated cyclohexenyl rings were epoxidized

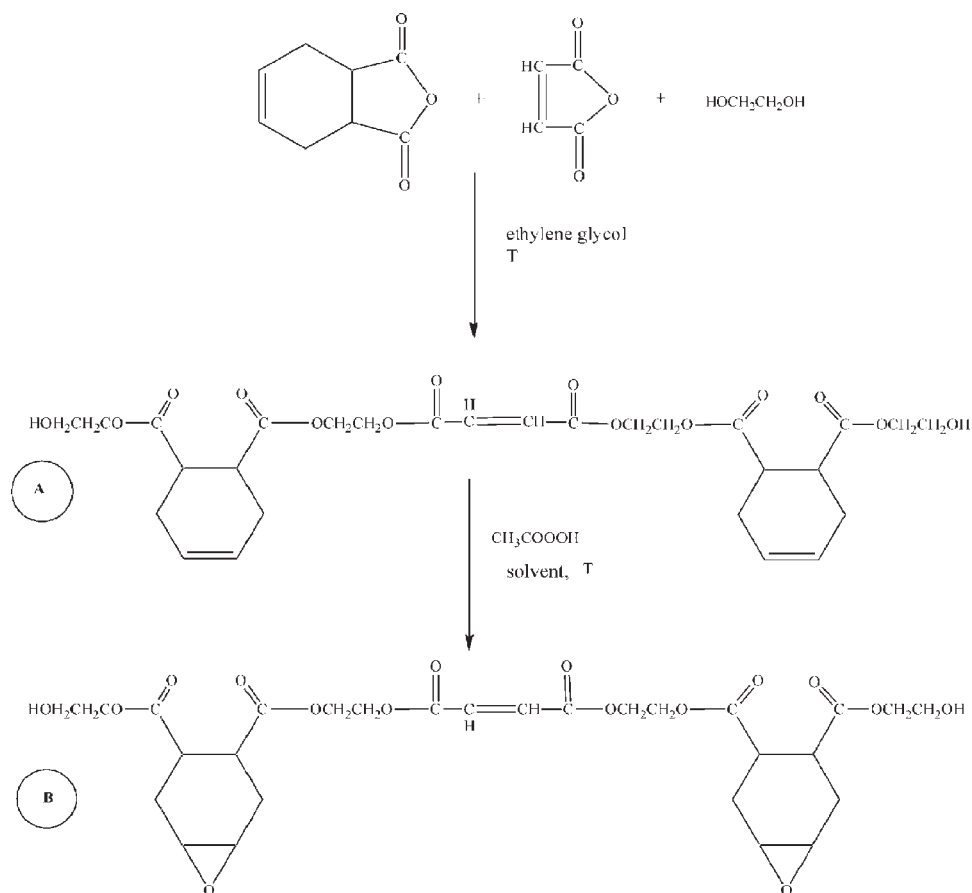


Figure 1 The scheme of synthesis of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B).

while the double bonds from maleic anhydride remained unaltered. The chemical structures of the unsaturated oligoester and the new unsaturated epoxyoligoester were confirmed by FTIR, ¹H NMR, and elemental analysis. Figure 2 shows the ¹H NMR spectra of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B). As can be seen from the ¹H NMR spectrum, all the signals corresponding to the proposed structures were observed. In the ¹H NMR spectrum of the unsaturated oligoester [Fig. 2(A)], the characteristic chemical shifts for the protons on the double bonds of cyclohexenyl rings (*H*₆) at $\delta = 5.67\text{--}5.7$ ppm and the other protons in the cyclohexenyl rings appeared in the range 2.15–2.6 ppm (*H*₅) and 2.90–3.13 ppm (*H*₄). Additionally, the characteristic chemical shifts for the protons on the double bond from maleic anhydride at $\delta = 6.29\text{--}6.35$ ppm (*H*₁, *cis*-form) and $\delta = 6.90\text{--}6.93$ ppm (*H*₁', *trans*-form) were observed.

Moreover, the isomerization of maleate to fumarate bonds was observed during the polycondensation process of the unsaturated oligoester. Maleate-fumarate isomerization takes place during the polycondensation process and can be affected by the reactive environment, the reactant (acid, glycol), and

the catalyst.^{21,22} The degree of isomerization (ISO %) can be written as the following equation:

$$\text{ISO \%} = (\text{trans}/(\text{trans} + \text{cis})) \times 100\%,$$

where *trans* and *cis* are the relative amount of the peak area for maleate and fumarate forms.

It is assumed that during the preparation of initial unsaturated oligoester *cis*–*trans* isomerization takes place and the degree of isomerization is 78%. It has some advantages, generally speaking it is easier to crosslink the prepolymer to form a network structure if the unsaturated acid exists in the *trans* form.²³

In the ¹H NMR spectrum of the new unsaturated epoxyoligoester [Fig. 2(B)], the resonance signals assigned to the olefinic protons of maleic anhydride (*H*₁ and *H*₁') showed no significant changes as compared with those of the unsaturated oligoester. However, the characteristic chemical shifts for the double-bond protons in the cyclohexenyl rings disappeared and the new proton signals at $\delta = 2.65\text{--}2.78$ ppm appeared, which can be attributed to protons attached to the epoxy groups and proved that the double bonds have been converted into epoxy groups. Moreover, in ¹H NMR spectra of the new

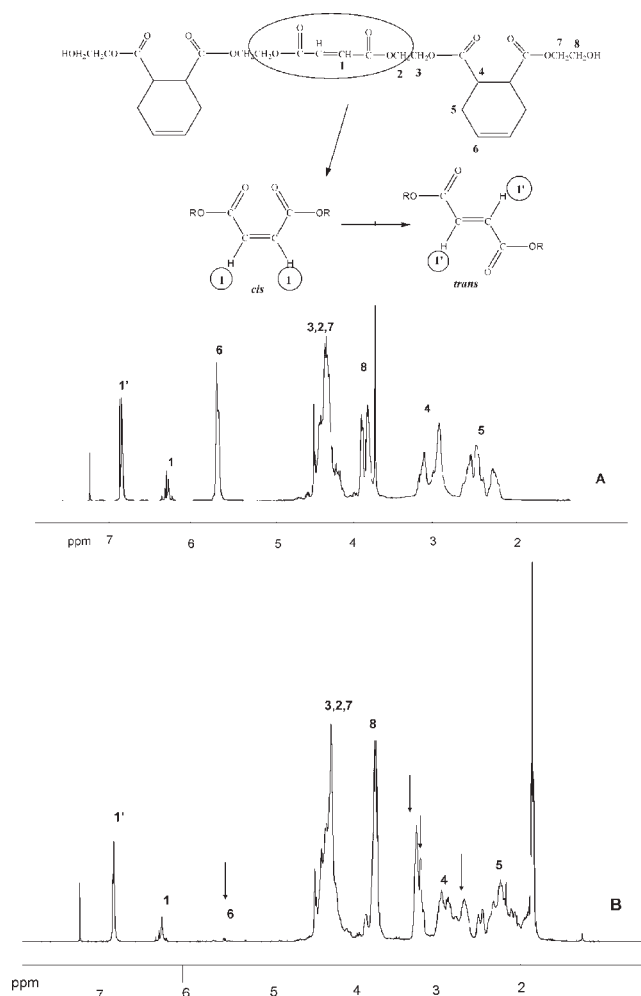


Figure 2 ^1H NMR spectra of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B).

unsaturated epoxyoligoester, the signals at $\delta = 3.17$ – 3.25 ppm were also observed. It is an indication that the secondary reactions of epoxy groups like hydrolysis or acidolysis can be occurred. Figure 3 shows

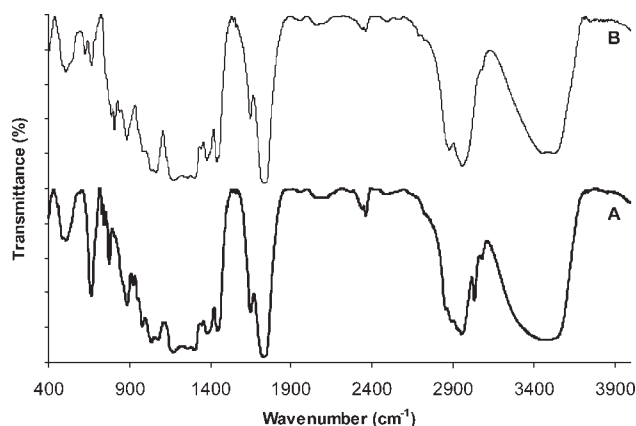


Figure 3 FTIR spectra of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B).

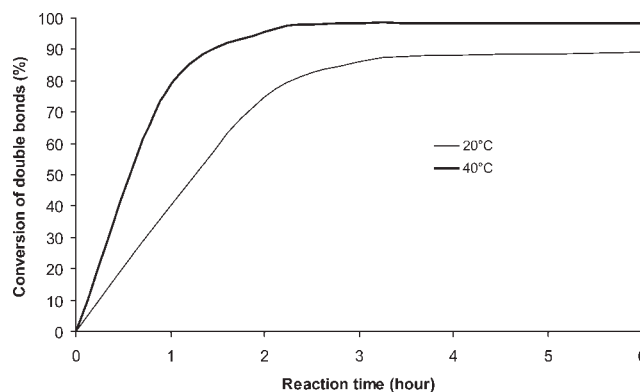


Figure 4 Dependence of the double bonds conversion at 20 and 40°C on epoxidation time.

the FTIR spectra of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B). The IR spectra of the unsaturated oligoester showed characteristic absorption bands in the range of 666 – 775 cm^{-1} related to the double bonds in the cyclohexenyl rings (m, C–H out-of-plane deformation vibration) and at 3031 cm^{-1} (m, =C–H stretching vibration). The characteristic absorption band at 1640 cm^{-1} was assigned to C=C stretching vibration for double bonds. After epoxidation reaction, the absorption band at 3031 cm^{-1} disappeared completely and the decrease of the characteristic bands at 666 – 775 cm^{-1} were observed. The new absorption bands after epoxidation in the range 789 – 836 cm^{-1} appeared in the spectrum, which are characteristic bands for oxirane ring vibration groups.

To understand the oxidation process of the unsaturated oligoester and to define the optimum conditions of this process, the reaction was carried out at temperatures 20 and 40°C for different times (1–6 h). It was found that with the increase in the reaction times from 1 to 4 h, significant reductions of the characteristic absorption band in the range 666 – 775 cm^{-1} in FTIR spectra and characteristic chemical shifts for the protons at $\delta = 5.67$ – 5.7 ppm in ^1H NMR spectra were observed. The conversion of the double bonds in the cycloaliphatic rings at different reaction times and temperatures was calculated by the integration of the double bonds resonance in the ^1H NMR spectrum. The results are shown in Figure 4. As can be seen from Figure 4, the conversion of the double bonds in cycloaliphatic rings increase rapidly during the 1–2 h at reaction temperatures, and then increases only slightly. Higher temperatures were needed to obtain higher conversion of the double bonds. The maximum conversion of the double bonds (98.3%) was achieved at 40°C after 2.5 h of synthesis. On the other hand, in epoxidation process several side reactions might occur. When the reaction time increased, the loss of epoxy groups (determined by epoxy number, Fig. 5) was observed. The

optimum level of epoxidation was attained at 40°C during 2.5–3.5 h of synthesis, the maximum of epoxy number was observed. Further increase of reaction time caused the decrease of the relative content of epoxy groups. It is an indication that another functionality was being introduced into the oligoester backbone probably due to the presence of high acidity of acetic acid. Additionally, proton signals at 3.17–3.25 ppm (signals assigned to OH—substituted carbons) in the ^1H NMR spectra and increase in the absorption bands at $1000\text{--}1100\text{cm}^{-1}$ in FTIR were reported. The presence of these groups suggests the formation of alcoholic groups bounded to the oligoester backbone caused by opening of the oxirane ring.^{24,25}

The carbon, hydrogen, and oxygen analysis data are consistent with the expected chemical structures. The oxygen content of the new unsaturated epoxyoligoester (41.12 wt %) was higher than that of initial unsaturated oligoester (37.84 wt %), but the carbon and hydrogen content of the new unsaturated epoxyoligoester (C: 53.13 wt %, H: 5.75 wt %) are lower than that of the initial unsaturated oligoester (C: 56.22 wt %, H: 5.94 wt %). Calculated C, H, O content of the new unsaturated epoxyoligoester is carbon 53.46 wt %, hydrogen 5.61 wt %, and oxygen 40.92 wt %, for the unsaturated oligoester 56.45, 5.92, and 37.63 wt %, respectively. FTIR, ^1H NMR spectra, and elemental analyses clearly confirmed the chemical structure of the new unsaturated epoxyoligoester.

DSC characterization

The thermal behavior of the initial unsaturated oligoester and the new unsaturated epoxyoligoester was investigated by DSC analysis. Figure 6 shows DSC thermograms for the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B) obtained at 40°C for 2 h. The DSC thermogram of the unsaturated oligoester showed two asymmetrical

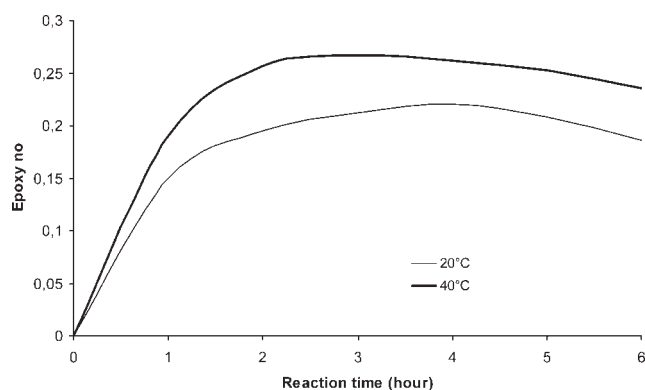


Figure 5 Variation of epoxy number of the new unsaturated epoxyoligoester obtained at 20 and 40°C as a function of epoxidation time.

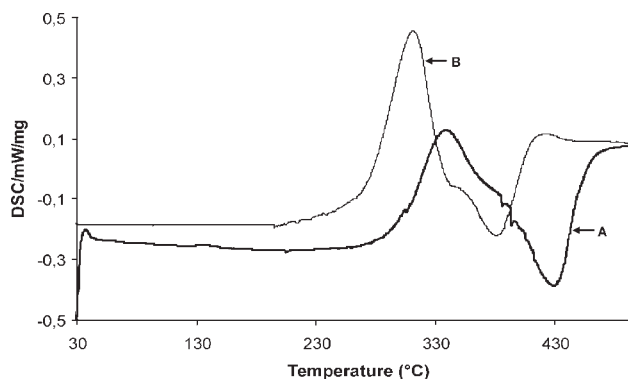


Figure 6 DSC curves of the unsaturated oligoester (A) and the new unsaturated epoxyoligoester (B).

peaks: the exothermic peak at 342.2°C, which can be due to copolymerization reactions of double bonds, and endothermic peak at 428.8°C, which resulted from their thermal degradation. The DSC thermogram of the new unsaturated epoxyoligoester showed two peaks as well. First, the exothermic peak at temperature 314.2°C can be ascribed to a thermal crosslinking reaction of epoxide groups with carboxylic acid groups, which are formed by the random chain scission at higher temperatures^{26,27} or to the addition reaction of epoxy groups to terminal hydroxyl end groups on oligoester at lower temperatures to form ether linkages. The decomposition endothermic peak at 384°C may result from the thermal degradation of the newly formed ester and ether bonds during the thermal crosslinking reaction.²⁶

CONCLUSIONS

In this article, the synthesis and characterization of the new unsaturated epoxyoligoester suitable for further modification have been presented. The obtained results confirmed that the new unsaturated epoxyoligoester can be prepared by chemical modification of the structure of the unsaturated oligoester containing cyclohexenyl rings and double bonds from maleic anhydride in oligoester backbone by well-known conventional method of epoxidation. It was proved that epoxidation reaction was successful and selective on basis of FTIR and ^1H NMR analyses. The double bonds in cyclohexenyl rings were converted into epoxy groups when the maleate-fumarate forms were not changed. It can be explained by the different reactivity of the double bonds in the unsaturated oligoester chain. It is well-known that the presence of carboxyl, carbonyl, or ester groups in the double bonds environment reduces the rate of the epoxidation, whereas the presence of other groups, e.g., alkyl groups near the double bonds increase the efficiency of epoxidation.²⁸

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