

Catalytic Activity of Schiff Base Cobalt(III) Complexes Immobilized on Terpolymers of Glycidyl Methacrylate in the Addition of Carboxylic Acids to Terminal Epoxides

Agnieszka Bukowska, Wiktor Bukowski, Jarosław Noworól

Faculty of Chemistry, Rzeszów University of Technology, al. Powstańców W-wy 6, Rzeszów 35-959, Poland

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ABSTRACT: Immobilization of Schiff base cobalt(III) complexes on a gel-type terpolymer obtained from glycidyl methacrylate (GMA, 20 mol %), styrene (S, 77 mol %) and diethyleneglycol dimethacrylate (DMDMG, 3 mol %) was carried out using a multi-step procedure. GMA resin was reacted first with an excess of diamine (ethylenediamine, *trans*-1,2-diaminocyclohexane or 1,3-diaminopropane) and then with salicylaldehyde (non-substituted or its 3,5-dichloro- and 3,5-di-*t*-butyl-substituted derivatives). Series of salicylaldehyde ligands immobilized on the polymer matrix obtained in this way were then applied to complex cobalt ions from solution of cobalt(II) acetate in the mixture of MeOH and CH₂Cl₂ (1/3 V/V). Obtained polymer bound cobalt salicylaldehyde complexes

were tested as catalysts of the addition of aliphatic carboxylic acids to terminal epoxides. It was found that the catalysts with 1,2-diamine moieties are clearly more active than the complexes with 1,3-diaminopropane one. Furthermore, the studies showed the highest activity of the complex with 3,5-di-*t*-butylsalicylaldehyde moiety and the least with 3,5-dinitrosalicylaldehyde one. The negative effect of methacrylic acid on the rate of the addition was also found. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 655–663, 2010

Key words: glycidyl methacrylate; a gel-type resin; Schiff base cobalt(III) complexes; polymer-supported catalysts; carboxylic acids; epichlorohydrin

INTRODUCTION

Catalysis with participation of metal complexes immobilized on reactive polymers is one of the most developing branches of modern organic chemistry.¹ Gel-type resins play an important role in this field. Because of these resins, it is possible to obtain supported metal complexes that provide a similar catalytic activity to their homogenous analogs. They are attractive both from the point of view of classic reactions catalyzed by metal complexes (e.g. hydrogenation, carbonylation, hydroformylation, isomerization, epoxidation, and others) and in asymmetric synthesis.

Styrenic polymers with reactive functional groups are the most common matrices for immobilization of metal complexes. However, polymeric materials obtained from easily available methacrylic monomers, such as glycidyl and hydroxyalkyl methacrylates can also be applied to immobilize suitable metal complexes for catalytic applications.^{2,3} From mentioned methacrylic monomers glycidyl methacrylate (GMA) which consists of epoxy group seems particularly useful to obtain reactive polymers for further chemical modification.

Epoxides are strained three-membered heterocycles due to that they can easily react with different nucleophiles. Ring-opening reactions of epoxides find many practical applications both on the industrial scale and in synthetic laboratories. Among them industrial synthesis of glycols, aminoalcohols, non-ionic detergents, vinyl and epoxy resins and hydroxyalkyl esters (mainly acrylates and methacrylates) can be listed.^{4,5} The synthesis of building-blocks for β -blockers is another example of utilizing of mentioned transformations.⁶ The addition of nucleophiles to epoxides can also play an important role in modification of polymers. Because of that many selective sorbents could be obtained previously from GMA polymers.^{7–13}

Selective ring opening reactions carried out in solution require, generally, using of catalysts to limit side-reaction of epoxides with products of the addition. To date, many substances have been tested as catalysts of the addition to epoxides. Among them, chromium(III) and cobalt(III) compounds turn out to be particularly useful. As an example, chromium(III) salen complex applied by Jacobsen in the reaction of TMSN₃ with *terminal* and *mezo* epoxides ensures an easy access to chiral aminoalcohols.^{14–17} Jacobsen chromium(III) complex proved to be active catalytically in the addition of thiols to epoxides as well.¹⁸ Jacobsen cobalt(III) complex is used in hydrolytic kinetic resolution (HKR) of terminal epoxides.^{19–23} It

Correspondence to: W. Bukowski (wbuk@prz.edu.pl).

also catalyzes the selective addition of phenols,^{24,25} alcohols,²⁶ and carboxylic acids²⁷ to epoxides. The HKR technology is already used on the industrial scale.

Our previous study²⁸ has shown that cobalt monosalicylalimine complex, consisted of ethylenediamine and 3,5-di-*t*-butylsalicylaldehyde moieties, supported on the polymer matrix is also capable to catalyze the addition carboxylic acids to epoxides. Hence, we decided to extend these studies on another monosalicylalimine systems. In this article, the catalytic activity of the series of monosalicylalimine cobalt(III) complexes immobilized on GMA resin in the addition of acetic, acrylic, and methacrylic acids to selected epoxides is discussed.

EXPERIMENTAL

Reagents

GMA resin was obtained by the suspension polymerization according to procedure described in our earlier work.²⁸ Initial composition of the mixture of monomers was 20 mol % glycidyl methacrylate, 3 mol % diethyleneglycol dimethacrylate, and 77 mol % styrene. The loading capacity of the resin was 1.43 mmol of epoxy groups per gram. The beads of the resin were sieved before using as a support for metal complex catalysts. The fraction in the range of diameters of 75–150 μm was applied in further modifications. Other reagents and solvents were purchased from POCh, Fluka or Aldrich.

Catalyst synthesis

A typical procedure of synthesis of catalysts was as follows:

GMA resin (1 eq.) was reacted with fivefold excess of diamine (ethylenediamine, *trans*-1,2-diaminocyclohexane or 1,3-diaminopropane) in *N,N*-dimethylformamide (10 mL/g of the resin). Reactions was carried out in thermostatic glass reactors placed on a horizontal shaker at 80°C for 24 h. The modified resins were filtered and they were washed several times, with DMF first, and then with methylene chloride and methanol, to remove the excess of diamine and the nonvolatile solvent used as a medium of the reaction. The resulted products were dried under reduced pressure at 40°C and their nitrogen and FTIR analysis were carried out.

The diamine-modified resins (1 eq.) was reacted with the solution of salicylaldehyde or its derivative (2 eq.) in methylene chloride. The reaction was carried out at room temperature for 24 h. Syringe-type reactors placed on a horizontal shaker were used for this step of modification. The products, as yellow beads, were filtered and washed several times with

methylene chloride and methanol to remove an excess of salicylaldehyde. After drying under reduced pressure at 40°C, FTIR and nitrogen analysis of modified resins were performed.

In the last step of catalyst synthesis, the polymer bound salicylaldimines were treated with the solution of cobalt(II) acetate (1 eq.) in the mixture of MeOH and CH₂Cl₂ (1/3 V/V). After 1 h of shaking of the mixtures at room temperature, the resins were filtered and rinsed sequentially with MeOH/CH₂Cl₂ (1/3 V/V), CH₂Cl₂, MeOH, CH₂Cl₂/AcOH (9/1), methanol, CH₂Cl₂ and then dried under reduced pressure. The products were yielded as dark brown beads. Their FTIR and elemental analysis were performed.

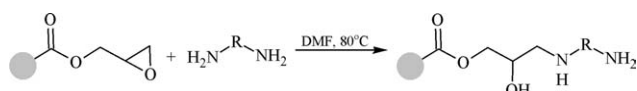
Catalytic tests

V-vials (5 mL) with screw-top caps were charged with polymer catalysts (1 mol % Co) and the equimolar mixture of carboxylic acids and epoxides (1 mL). Triangle magnetic stirring bars were put into the vials, which were then sealed and placed in a glycerin bath adjusted to the fixed temperature (25, 40, or 60°C). The mixtures were gently stirred using a magnetic stirrer. The progress of reactions was monitored by GC analysis (HP-FFAP capillary column was used). Catalysts were filtered, washed from reagents with methanol and methylene chloride and once again with methanol. The selected catalysts were recycled three times.

RESULTS

Catalyst synthesis

Glycidyl methacrylate, because of the presence of reactive epoxy groups, are often modified chemically with amines to obtain new materials.^{9,12,29–34} When polyamines are used, the transformation allows to build in NH₂ groups into a polymer matrix. The primary amine groups can be easily converted further, for instance, to imine ones in the reaction with salicylaldehydes. In addition, it is well known that salicylimines readily coordinate transition metal ions.³⁵ Using that route, in our previous study,²⁸ the polymer-bound ethylenediamine with the loading of ~ 1.1 mmol NH₂ groups per gram was obtained first from the highly swellable epoxy-functionalized GMA resin (~ 1.4 mmol/g). The diamine resin was then utilized to obtain polymer-bound cobalt(III) monosalicylalimine complex consisting of 3,5-di-*t*-butylsalicylaldehyde moiety. The complex showed the catalytic activity in the model reaction of addition of acetic acid to epichlorohydrin, that is way, in this work other monosalicylimine complexes were synthesized for more detailed catalytic studies.



Scheme 1 Synthesis of diamine resins.

Syntheses of new catalysts were performed in three stages. Samples of GMA resin (as beads in the range of diameters of 75–150 μm ; the loading capacity of ~ 1.4 mmol of epoxy group per gram) were first reacted with three easily available diamines: ethylenediamine, 1,3-diaminopropane or *trans*-1,2-diaminocyclohexane. Fivefold excess of each diamine was applied to reduce secondary cross-linking of GMA resin under influence of amine groups just introduced into the polymer matrix. The reactions were carried out at 80°C in DMF (Scheme 1). That solvent swells well both GMA and diamine resins, and it makes possible penetration of homogeneous reagent inside polymer network. Because of that high conversion degrees of epoxy groups can be achieved. The last was confirmed by results of nitrogen analysis (Table I). The results indicate that the reaction with diamines yields resins with about 2 mmol N atoms per gram.

Assuming that the process of the secondary cross-linking of polymers, as a result of side-reactions of immobilized amine groups with neighboring epoxy groups, could be neglected, the percentage of nitrogen could be used for assessment of the loadings of primary amine groups (NH_2 groups) in products. The loadings calculated in this way could amount to 0.97–1.06 mmol/g. The last corresponds to 81–85% conversion of epoxy groups in GMA resin.

TABLE I
Diamine Resin Characteristics

Diamine resin	Diamine, R	Nitrogen content, [%]	N atoms loading, [mmol/g]
1	$-\text{CH}_2-\text{CH}_2-$	2.87	2.04
2	C_6H_{10}	2.72	1.94
3	$-(\text{CH}_2)_3-$	2.96	2.12

The transformations of GMA resin under the influence of diamines were monitored by FTIR spectroscopy as well. Spectra of the initial polymer and products of its modification with selected diamine are presented in Figure 1. The comparison shows that a clear increase in absorption in the range of characteristic of OH, NH_2 , and NH groups is observed for products (Fig. 1). At the same time, a disappearance of bands characteristic of epoxy groups takes place. The residual absorption in the range of 910 and 840 cm^{-1} indicates, however, incomplete conversion of epoxy groups even though after 24 h.

In the second step of GMA resin modification, the polymer-bound diamines were reacted with salicylaldehyde and its some derivatives according to Scheme 2.

To maximize the conversion of NH_2 groups, two-fold excess of salicylaldehydes was applied. In addition, methylene chloride was selected as a reaction medium. This solvent, similarly to DMF in the first step of transformation of GMA resin, facilitated penetration of molecules of salicylaldehyde inside polymer beads. Although salicylaldehydes reacted with amine groups fast enough, the time of the reaction

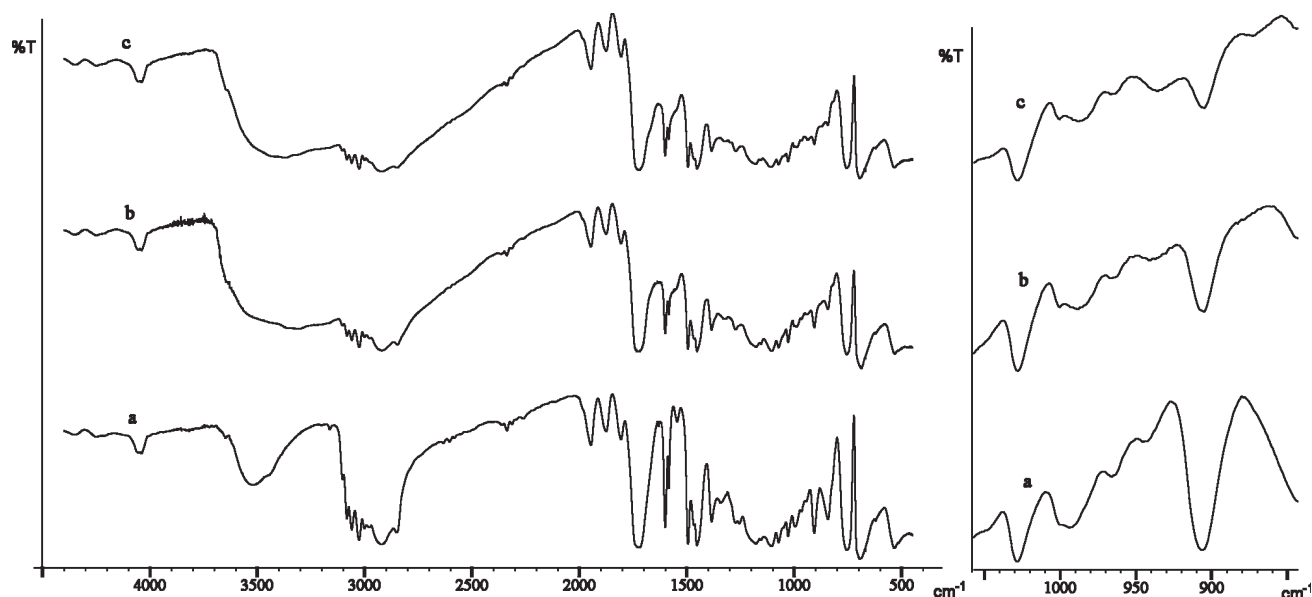
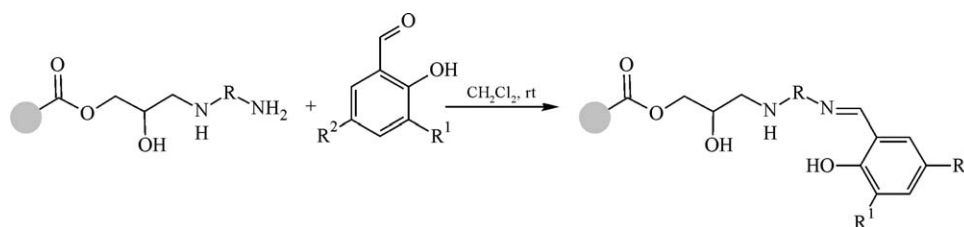


Figure 1 FTIR spectra of GMA-terpolymer (a) and product of its modification with ethylenediamine 1 (b) and (c), after 1 h and 24 h, respectively.



Scheme 2 Synthesis of diimine resins.

was prolonged up to 24 h. In this way a practically quantitative conversion of NH_2 groups could be achieved, what was concluded from the comparison of the results of nitrogen analysis of polymers before and after their transformation.

The reactions of polymer bound-diamines **1** with salicylaldehyde **1.1** results in changing of the picture of FTIR spectra of products (Fig. 2). Absorption in the range of $1600\text{--}1550\text{ cm}^{-1}$ and above 3200 cm^{-1} proves transformation of NH_2 group under the influence salicylaldehydes (Fig. 2). The new absorption band at around 1630 cm^{-1} , which appears in the spectra of products, is characterized by the intensity similar to ester $\text{C}=\text{O}$ band and can be ascribed to $\text{C}=\text{N}$ stretching.

In the final step of catalysts synthesis, light yellow beads of polymer-bound salicylaldimines resins were treated with a solution of cobalt(II) acetate in the mixture of methylene chloride/methanol (3/1 V/V) according to Scheme 3. Because of good swelling properties, the mixed solvent facilitated delivering of cobalt ions deeply inside beads of salicylaldehyde resins. High complexing ability of the resins

was achieved in this way. As a result, yellow beads changed color immediately to dark brown and polymer bound salicylaldehyde complexes with cobalt ion loadings of $0.76\text{--}0.88\text{ mmol/g}$ were delivered (Table II).

The complexing of cobalt ions resulted in further changing of FTIR spectra of polymers in the range characteristic of secondary amine and hydroxyl groups (Fig. 3). Moreover, one can notice that $\text{C}=\text{N}$ absorption band in the spectra of complexes is shifted toward higher frequency about 10 cm^{-1} . New bands at 1530 and 1360 cm^{-1} are also observed. The findings prove the interactions of NH , OH (phenolic), and $\text{C}=\text{N}$ groups with cobalt ions, on one hand, and the oxidation of Co(II) ions to Co(III) ones, on the other. The new bands can be assigned to acetate ions, which bond with cobalt(III) ions formed after treating of polymer-bound monosalicylaldehyde Co(II) complexes with the mixture of $\text{CH}_2\text{Cl}_2/\text{AcOH}$ of 9/1. The high ability Co(II) ions to oxidize to Co(III) ones after their complexing by salicylaldehydes is commonly known.

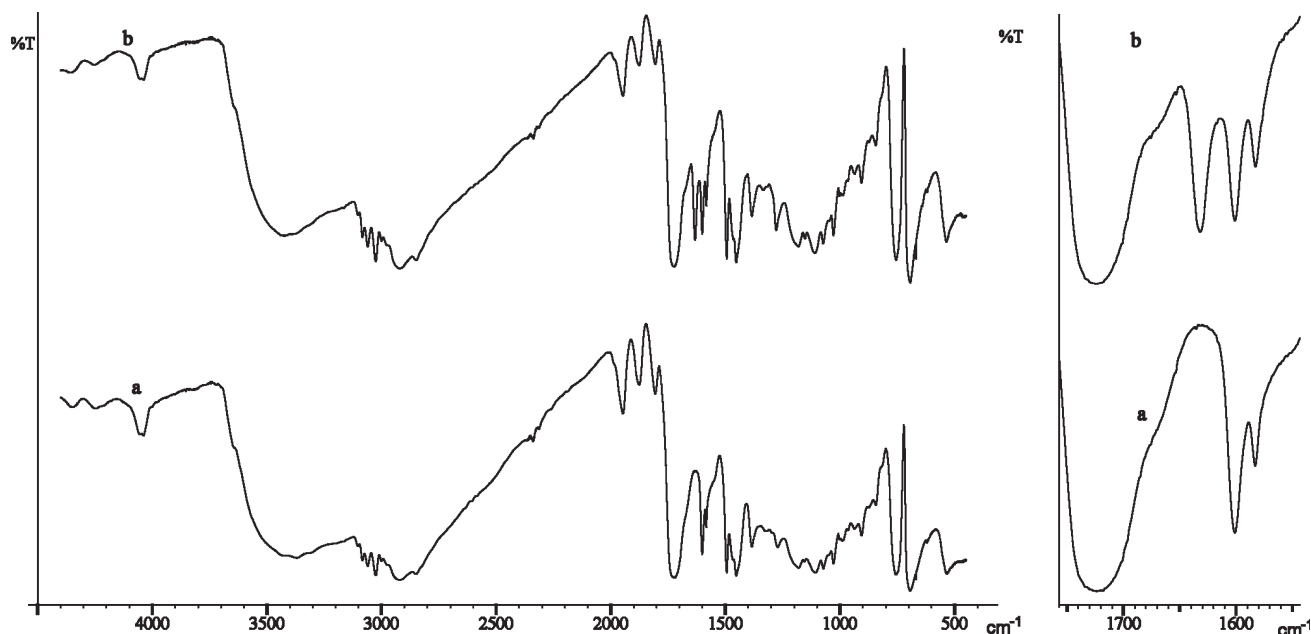
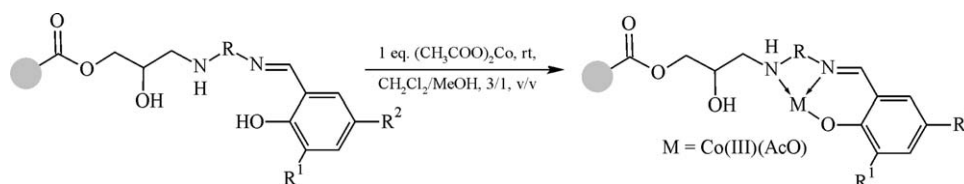


Figure 2 FTIR spectra of **1** (a) and product of its modification with salicylaldehyde **1.1** (b).



Scheme 3 Polymer-bound salicylaldimine Co(III) complexes.

From the chemical structures of polydentate ligands formed on the polymer after two stage modifications of epoxy groups in GMA resin with diamines and salicylaldehydes and from the changes in FTIR spectra in the range of hydroxyl group absorption one cannot also exclude the possibility of the additional interactions of alcoholic OH groups with cobalt ions, which are complexed by salicylimine-amine systems. Extra five-membered chelates can be delivered in this way.

Remains of unreacted epoxy groups in polymers after the stage of modification of GMA resins with diamines, theoretically amounted to 15–19%, can raise doubts whether the final polymer bound complexes can be used as catalysts of carboxylic acid addition to epoxides. As one can suspect the possibility of the side addition of carboxylic acids to the polymer matrix. To exclude that suspicion the additional experiments were carried out. First, polymer-bound salicylaldimine **1.1** was treated with the equimolar mixture of acetic acid and epichlorohydrin at 25°C. There was not observed any conversion of reagents during 48 h exposition. In the second experiment, the swelling abilities of the polymer-bound complex and the initial resins were assessed. It was found that the complex treated with the equimolar mixture of acetic acid and epichlorohydrin swelled around 1.8 ml/g. On the other hand, GMA and diamine resins, precursors of polymer-bound salicylaldimine **1.1**, treated with DMF swelled around 4.0 and 2.0 mL/g, respectively. The findings show clearly that DMF, which was used as a medium for transformation of GMA resins into diamine ones, should provide more favorable condition for conversion of epoxy groups inside beads of the resins than the mixture of reagents during catalytic tests.

Catalytic tests

Polymer-bound salicylaldimine cobalt(III) complexes were tested as catalysts in the addition of carboxylic acids to terminal epoxides (Scheme 4). The reaction has practical meaning in vinyl resins and hydroxyalkyl esters (mainly acrylates and methacrylates) synthesis. Cross-linking of epoxy resins by acid anhydrides is the other example of practical application of this transformation.⁵ In this work, acetic (AcOH), acrylic (AA), and methacrylic (MA) acids and epichlorohydrin (ECH), propylene oxide (PO) and phenylglycidyl ether (PGE) were used as model reagents.

The catalytic study was carried out in a parallel system of microreactors placed in a glycerin bath adjusted to 25, 40, or 60°C. Reagents (acids and epoxides) were used in stoichiometric quantities. The progress of the addition was monitored by GC analysis. The study was begun from the comparison of the catalytic activity of complexes, which differ in diamine moieties. It was found that the catalysts with 1,2-diamine moieties are clearly more active than the complexes with 1,3-diaminopropane one (Fig. 4). There were no sufficient differences in swelling of the catalysts in the reaction mixture (the complexes swelled around 1.7 ml/g), so the findings indicate that the differences in the catalytic activity of the complexes result mainly from the differences in their chemical constitution. Swelling properties of catalysts and suitable mixing of the reaction mixtures eliminate an influence of diffusion factors on the rate of catalyzed reactions.

Taking into account the constitution of ligands **1.3**, **2.1**, and **3.1** one can conclude that the main difference between three systems, important from

TABLE II
Characteristic of Polymer-Bound Salicylaldimine Co(III) Complexes

Polymer-bound Co(III) complexes	Diamine, R	Aldehyde		Co content, [%]	Co ion loading, [mmol/g]
		R ¹	R ²		
1.1.Co	—CH ₂ —CH ₂ —	H	H	5.19	0.88
1.2.Co	—CH ₂ —CH ₂ —	OCH ₃	H	5.01	0.85
1.3.Co	—CH ₂ —CH ₂ —	t-Bu	t-Bu	4.71	0.80
1.4.Co	—CH ₂ —CH ₂ —	NO ₂	NO ₂	4.71	0.80
1.5.Co	—CH ₂ —CH ₂ —	Cl	Cl	4.77	0.81
2.1.Co	C ₆ H ₁₀	t-Bu	t-Bu	4.48	0.76
3.1.Co	—(CH ₂) ₃ —	t-Bu	t-Bu	4.77	0.81

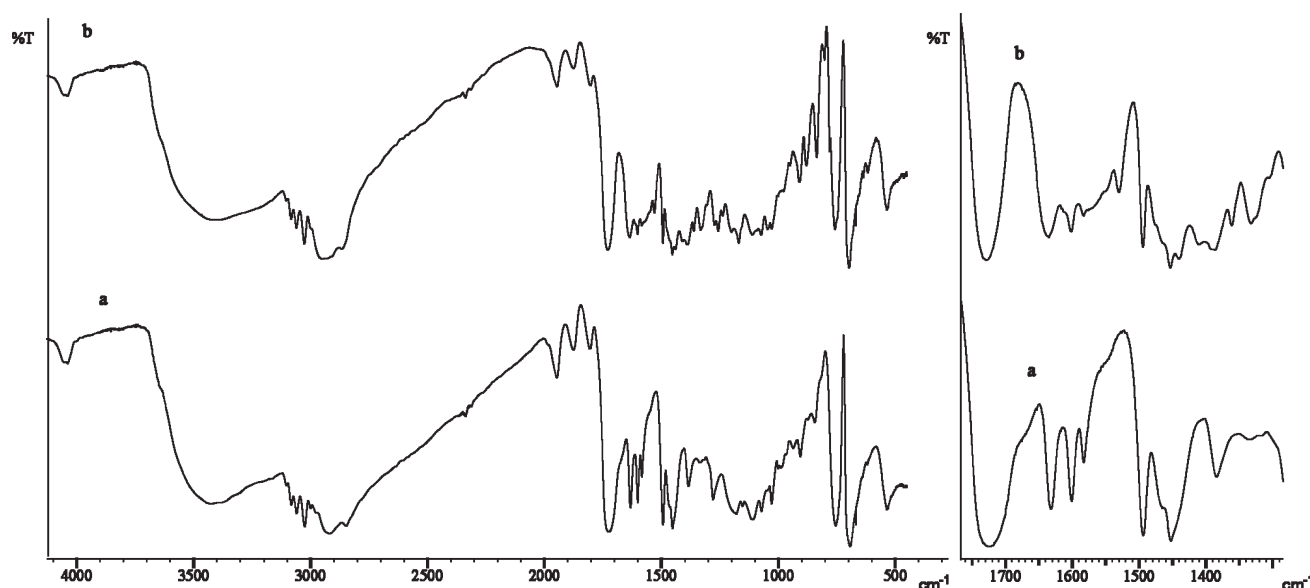


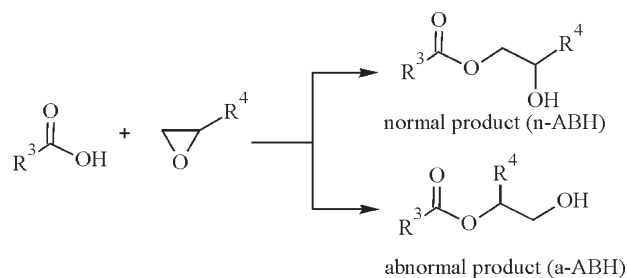
Figure 3 FTIR spectra of 1.1 (a) and product 1.3.Co obtained after sorption of stoichiometric cobalt ions (b).

complexing point of view, is a location of two nitrogen atoms. Ethylenediamine and *trans*-1,2-cyclohexyldiamine moieties in 1.3.Co and 2.1.Co respectively, generate the formation of five-membered *N,N*-chelates, whereas the moiety of 1,3-diaminopropane in 3.1.Co, is responsible for formation the second six-membered *N,N*-chelate next to six-membered *N,O*-one resulting from the presence of the salicylimine system. It is commonly known that stability of chelates decrease when larger rings are formed. Additionally, in the case of the possibility of forming more than one chelate ring, complexes which are composed of differ rings (e.g. 5 and 6-membered) are usually more stable.³⁶ Maybe, that fact should be associated with the improvement of the catalytic activity of complexes 1.3.Co and 2.1.Co in comparison with 3.1.Co.

The catalytic activity of the complexes proves that besides two (or three, if an additional interaction with hydroxyl group will be taken into account) chelate rings there are also a free (or labile) vacancy (or

vacancies) in polymer-bound cobalt(III) complexes (six is a standard coordination number of Co(III) ions) which is responsible for activation of substrates. From many examples of using salicylimine type cobalt(III) complexes as catalyst of ring opening reactions described earlier^{3,19–25} result that cobalt(III) ions activate epoxides which then react with nucleophiles. Nucleophiles are delivered to epoxy rings from the same complexes or neighbouring ones.

The activity of polymer-bound monosalicyaldimine Co(III) complexes turned out to be the function of salicylaldehydes (Fig. 5) as well. From tested complexes, complex 1.3.Co with 3,5-di-*t*-butylsalicylaldehyde moiety was the most active and 1.4.Co with 3,5-dinitrosalicylaldehyde one the least. The activity of nonsubstituted (1.1.Co) and 3-methoxy-



$\text{R}^3 = \text{CH}_3$ (AcOH), $\text{CH}_2 = \text{CH}$ (AA), $\text{CH}_2 = \text{C}(\text{CH}_3)$ (MA)

$\text{R}^4 = \text{CH}_2\text{Cl}$ (ECH), CH_2OPh (PGE), CH_3 (PO)

Scheme 4 The addition of carboxylic acids to terminal epoxides.

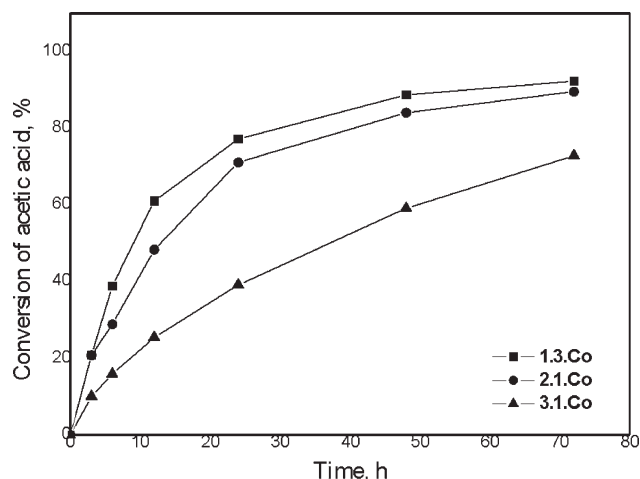


Figure 4 Conversion of acetic acid in the reaction with epichlorohydrin in the presence of polymer bound cobalt(III) complexes which differ in diamine moieties; $T = 25^\circ\text{C}$.

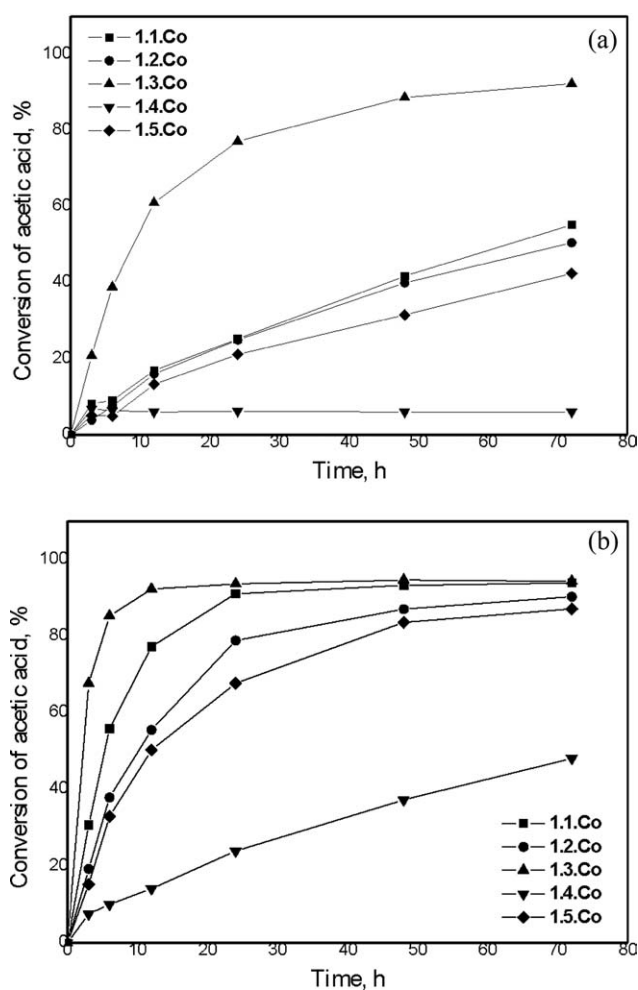


Figure 5 Conversion of acetic acid in the reaction with epichlorohydrin in the presence of polymer bound cobalt(III) complexes which differ in salicylaldehyde moieties; temperature: (a) 25°C, (b) 60°C.

substituted (**1.2.Co**) complexes were practically the same at 25°C. Complex **1.5.Co** based on 3,5-dichlorosalicylaldehyde proved to be the slightly less active than **1.1.Co** and **1.2.Co**. The findings can be ascribed to electronic factors as there were not distinct differences in swelling abilities of catalysts in the reaction mixtures. Hence, the advantageous effect of *t*-butyl groups as donors of electrons and the disadvantageous effect of NO₂ groups as strong acceptors of electrons on the catalytic activity of coordinated cobalt ions can be concluded. The differences in the activity of the complexes increased when the temperature of the reaction was risen (Fig. 5).

Complex **1.3.Co** was then tested in the addition of acrylic and methacrylic acids to epichlorohydrin, propylene oxide and phenylglycidyl ether. In the reaction with epichlorohydrin, it was found that the relative rate of the addition changes in order AcOH>AA>MA (Fig. 6). Similar findings were observed in our previous study for soluble salen complexes³⁷ and immobilized on HEMA resins salen

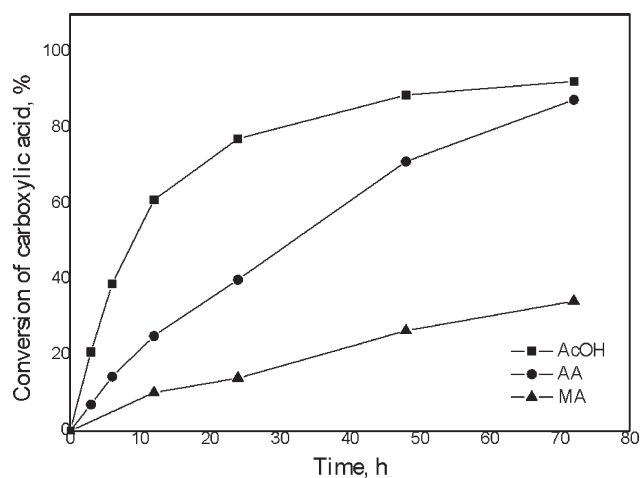


Figure 6 Conversion of carboxylic acids in the reaction with epichlorohydrin in the presence of complex **1.3.Co**; $T = 25^\circ\text{C}$.

complexes.³ It proves that also in the case of polymer-bound monosalicylaldehyde cobalt(III) complexes obtained in this work the steric factor resulted from the size of acid molecules (AcOH<AA<MA) is more important than the acidity of reagents (ionization constants in water, $K_a \cdot 10^5$, for AcOH, AA and MA amount to 1.75, 5.53 and 3.72, respectively).³⁸ It can be also concluded that monosalicylaldehyde ligands do not improve the access of more bulky reagents to coordinated cobalt ions in comparison with salen ligands, how it was expected. They are characterized by the less catalytic activity than immobilized cobalt salen complexes in the examined reactions of selected aliphatic carboxylic acid with terminal epoxides.³

The order of the relative reactivity of epoxides (ECH>PGE>PO) in the reaction with acetic acid presented in Figure 7 corresponds with commonly

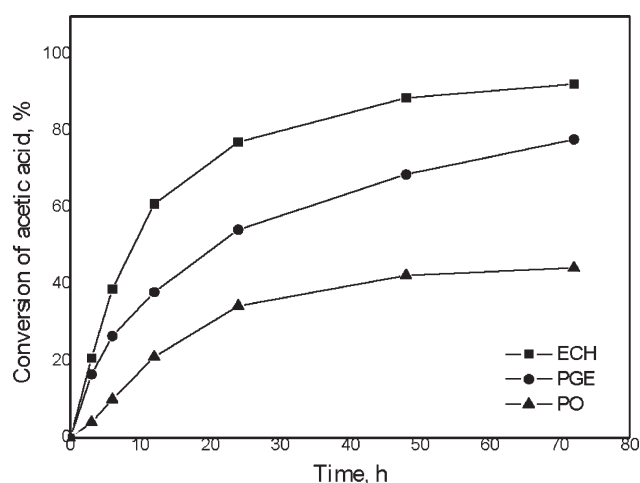


Figure 7 Conversion of acetic acid in the reaction with some epoxides in the presence of complex **1.3.Co**; $T = 25^\circ\text{C}$.

known relationships for kinetics of ring-opening reaction of epoxides under influence of nucleophiles.

Additional experiments carried out with complex **1.3.Co** showed that there was no a significant loss of its activity after three time recycling at 25°C (Fig. 8). However, the leaching of metal ions from the polymer catalyst is significant when the temperature is risen.

The ring opening of terminal epoxides under the influence of carboxylic acids always yields two isomeric hydroxyalkyl esters (Scheme 4). That is why, parallel to the study of the activity of the catalysts the regioselectivity of the addition was also explored. GC method was used to assess the ratios of regioisomers in the final reaction mixtures. It was found that the ratios (normal to abnormal product) practically do not depend on diamine and salicylaldehyde moieties (Table III). The ratio of isomers did not change with reusing of the catalyst (Table III). However, a disadvantageous effect of temperature on the regioselectivity was observed (Table III). Furthermore, the regioselectivity of the addition

TABLE III
Regioselectivity of the Addition of Carboxylic Acids to Terminal Epoxides

Catalyst	Temperature, °C	Carboxylic acid	Epoxide	Ratio of regioisomers n-ABH/a-ABH
1.1.Co	25	AcOH	ECH	93/7
1.2.Co	25	AcOH	ECH	93/7
1.3.Co	25	AcOH	ECH	93/7 (I run) 93/7 (II run) 93/7 (III run)
1.3.Co	40	AcOH	ECH	90/10
1.3.Co	60	AcOH	ECH	86/14
1.3.Co	25	AcOH	PGE	84/16
1.3.Co	25	AcOH	PO	81/19
1.3.Co	25	AA	ECH	95/5
1.3.Co	25	MA	ECH	95/5
1.4.Co	25	AcOH	ECH	93/7
1.5.Co	25	AcOH	ECH	93/7
2.1.Co	25	AcOH	ECH	95/5
3.1.Co	25	AcOH	ECH	94/6

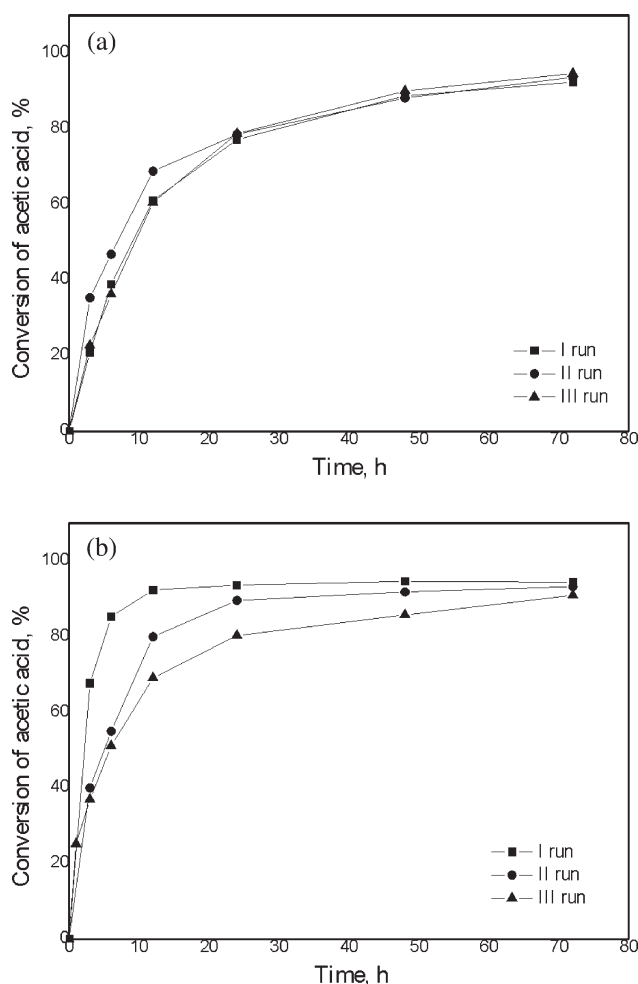


Figure 8 Recycling of complex **1.3.Co** in the reaction of acetic acid with epichlorohydrin; temperature: (a) 25°C, (b) 60°C.

depended mainly on the nature of epoxides. At 25°C it changed in order ECH>PGE>PO (Table III). The results obtained for different epoxides point to a disadvantageous effect of small donor substituent at epoxy ring such as CH₃ group. Steric limitations on the access of molecules acrylic and methacrylic acids to molecules of epichlorohydrin activated by cobalt salicylaldehyde complexes indicates only a slightly increase in regioselectivity. The regioselectivity of the addition in the presence of the polymer bound salicylaldehyde cobalt(III) complexes presented in this work is comparable to observed earlier for salenCo(III) complexes immobilized on HEMA resin.³

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