

Polyamine Functionalized Glycidyl Methacrylate Terpolymers as Scavengers for Metal Ions Uptake from Organic Solutions

Agnieszka Bukowska, Wiktor Bukowski

Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców W-woy 6, 35-959 Rzeszów, Poland

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ABSTRACT: Resins with amine functionalities were obtained as a result of chemical modification of low cross-linked terpolymers of glycidyl methacrylate with styrene and divinylbenzene or diethylene glycol dimethacrylate. The loading of amine groups, swelling in the selected organic solvents, and thermal properties of the resins were studied. FTIR, DSC, TGA, SEM, and stereomicroscopy methods were also applied for exploring of the resins. The amine functionalized resins were tested as sorbents for uptake of cobalt(II), copper(II), iron(III), and manganese(II) ions from methanol and its mixtures with methylene

chloride. The study show that all polyamine functionalized resins uptake quickly Cu(II) ions from methanol solutions. Their ability to remove cobalt(II), iron(III), and manganese(II) ions from solution depended on the mutual compatibility of solvents and resins. It increases clearly when the mixtures of methanol and methylene chloride are applied. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 904–914, 2012

Key words: glycidyl methacrylate resins; polyamine functionalized resins; metal ions uptake

INTRODUCTION

Ring-opening reactions of epoxides occurring under the influence of nucleophiles belong to very useful transformations in organic chemistry.¹ In industry, they found applications in synthesis of glycols, aminoalcohols, nonionic detergents, vinyl and epoxy resins, and hydroxyalkyl esters, mainly as acrylates and methacrylates which are important monomers.² Synthesis of β -blockers and the crosslinking of epoxy resins by polyamines can be mentioned as another important example of utilizing of the ring-opening of epoxides.³ The addition of nucleophiles to an epoxy ring plays also a significant role in the chemical modification of polymer materials. Many useful materials were obtained previously as a consequence of chemical transformations of epoxy group bearing polymers under the influence of amines, for instance, polymer supported enzymes,^{4,5} amino acids,⁶ proteins,⁷ and catalysts,^{8–11} sorbents for metal ions^{12–18} or surface-reactive acrylic copolymers for fabrication of microfluidic devices for chemical analysis.¹⁹

From among numerous applications of the functionalized polymers, their use as the reactive sorbents for metal ions deserves particular underlining.²⁰ The functionalized resins are commonly used in water softening and demineralization. They are applied for water desalination and removing heavy metal ions from industrial wastes. The polymeric sorbents bearing suitable functional groups are also very useful for recovering of precious metals from spent catalysts and electronic components. Furthermore, they play a sufficient role in purification of products of pharmaceutical synthesis where the transition metals and their compounds are very often applied as catalysts and the acceptable level of toxic metal ions impurities in drugs is below 1 ppm.

The introduction of epoxy functionalities into solids can be achieved by chemical transformations carried out on functional groups present in inorganic or organic matrices. The epoxidation of C=C bonds and the reactions of epichlorohydrin with proton bearing groups, e.g., NH₂, SH, OH, with the subsequent dehydrohalogenation of delivered chlorohydrines, on the one hand, and the grafting of epoxy functionalized polymers (e.g., poly(glycidyl methacrylate)) on solid matrices under the influence of radiation or chemical initiators, on the other, can be useful in these cases. However, the most common way of synthesis of epoxy functionalized polymers is the radical polymerization of glycidyl methacrylate (GMA) or its co- or terpolymerization with other unsaturated monomers.

Correspondence to: A. Bukowska (abuk@prz.edu.pl)

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Using this type of polymerization, a series of hydrophobic, easily modifiable epoxy groups bearing terpolymers have been obtained in our laboratory.²¹ It was found that these gel-type resins swell well in cyclic ethers (THF and 1,4-dioxane), chloromethanes (CH_2Cl_2 and CHCl_3), and aromatic (benzene, toluene) or amide (NMP, DMF, and DMA) solvents. The swelling ability of the resins with the nominal crosslinking degree equaling 3 mol % was even though comparable to one observed for classical styrenic resins with the nominal crosslinking equaling 1 mol %. The latter are used commonly in solid phase synthesis or as supports for specific reagents or catalysts in polymer assisted solution phase protocols.²² Hence, an idea of utilizing of these resins to synthesis of new functionalized polymers which could be useful as nucleophilic scavengers for purification protocols, on the one hand, and as sorbents for metal ions uptaking from organic solutions, on the other, came to our mind. In this work some peculiarities of the sorption of selected transition metal ions from organic solution by polyamine functionalized gels based on the GMA resins are presented.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA, 97%), styrene (S, 99%), diethylene glycol dimethacrylate (DEGDMA, 95%), and divinylbenzene (DVB, the mixture of isomers, ~ 80%) were purchased from Aldrich or Fluka. Before using, monomers were purified from inhibitors by extraction with 5 wt % NaOH in 20 wt % NaCl solution. Ethylenediamine (EDA, $\geq 99.5\%$, Fluka), diethylenetriamine (DETA, $\geq 99\%$ from Riedel-de-Haen), *tris*(2-aminoethyl)amine (TAEA, $\geq 98\%$, from Fluka), solvents and all analytical reagents were used as received from Aldrich, Fluka, or POCh. Cobalt(II) acetate tetrahydrate, cooper(II) acetate tetrahydrate, iron(III) chloride, and manganese(II) acetate tetrahydrate used as a source of metal ions were purchased from Aldrich.

Resin synthesis

The epoxy group bearing resins in the form of spherical microscopic beads were obtained by the suspension polymerization of the mixture of glycidyl methacrylate (20 mol %), styrene (77 mol %), and divinyl monomer (divinylbenzene or diethylene glycol dimethacrylate, 3 mol %) as has been described previously.²¹ The samples of glycidyl methacrylate resins **1** (3 g; a fraction of beads with diameters of 75–150 μm) were then reacted under the argon atmosphere with an excess of polyamine (10 eq.; eth-

ylenediamine, diethylenetriamine, or *tris*(2-aminoethyl)amine), in toluene (10 mL per gram of the resin). Modifications were carried out in 100-mL cylindrical glass reactors equipped with a heating coat connected to a thermostat and placed on a horizontal shaker. After 24 h shaking of mixtures at 80°C, the solid products were isolated using polypropylene syringes equipped with Luer valves and cellulose wadding filters. The final resins were then rinsed carefully by shaking with toluene (three times), and next with the mixture of CH_2Cl_2 — CH_3OH (1 : 1 V : V) (several times) to remove an excess of polyamine reactants. Finally, washing with CH_3OH was carried out to shrink swelled beads. Products were dried under reduced pressure at 40°C. Nitrogen percentages in amine modified resins as a key measure of the loading of amine groups was performed by the classic Kiehdahl method.

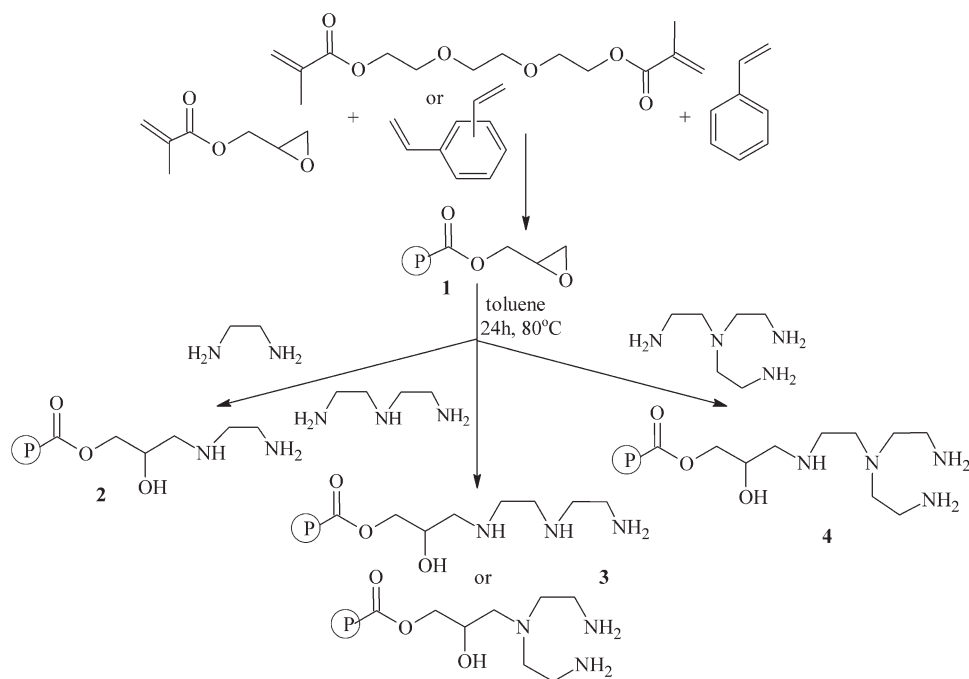
Resins characteristics

Loadings of epoxy groups in resins **1** were determined by Jay's method²³ modified as described previously.²¹ The percentage of nitrogen in polyamine functionalized resins was assessed by the Kiehdahl method. FTIR studies were carried out using Perkin-Elmer PARAGON 1000 FT-IR spectrometer and the standard technique of KBr pellets. Measurements of the glass transition temperature (T_g) were performed by the DSC method using Toledo 822^e calorimeter with Star^e System software. Samples of the resins (7–8 mg) were heated from 30 to 300°C and then cooled to 30°C. This procedure was repeated twice. The rate of heating and cooling was adjusted to 10°C/min.

Thermogravimetric analyses were performed using TGA/DSC Mettler Toledo system with Star SW 9.1 Software. Samples of the resins (~ 2 mg) were heated in nitrogen atmosphere from 25 to 500°C with heating rate adjusted to 10°C/min.

Morphology of the resins was estimated using JEOL JSM-5500LV scanning electron microscope and Motic SMZ-143 stereoscope microscope with digital camera.

Swelling ability was explored in the following way: 0.1 g samples of resins were placed in 2-mL graduated syringes equipped with filters and Luer valves and an excess of solvents (CH_2Cl_2 , CHCl_3 , CH_3OH , THF, H_2O , benzene, toluene, NMP, DMF, 1,4-dioxane, and mixtures of $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$) was then added to each sample. When the swelling equilibrium was settled, an excess of solvents was removed by means of a plunger. Volumes of absorbed solvents were calculated as $\Delta V_i = (m_s - m_d)/m_d \cdot d_i$, where m_d is the mass of dry resins, m_s , the mass of swelled resins, and d_i , the density of solvents.



Scheme 1 Synthesis and modification of the resins 1.

Uptake of metal ions

The uptake of metal ions (Co(II), Cu(II), Mn(II), and Fe(III)) from organic solutions on the polyamine resins 2-4 were carried out using a batch method. Samples of the resins (0.1 g) were placed into 5-mL glass vials equipped with screw tops and 2 mL of a solution of 0.02 mmol individual ions in methanol or in mixtures of methanol and methylene chloride (3 : 1, 1 : 1 or 1 : 3 V : V) were added. The vials were then sealed immediately and placed on a vibration shaker. The mixtures were shaken for a period of 5, 10, 20, 40, or 60 min. The resins were then filtered off and the residuals of metal ions in final solutions were analyzed by UV-Vis methods using specific metal ion complexones. Nitroso-*R*-salt, sodium diethyldithiocarbamate, 1,10-phenantroline and formaldoxime were used, respectively, to determine concentrations of cobalt(II) ($\lambda_{\max} = 415$ nm), copper(II) ($\lambda_{\max} = 460$ nm), iron(III) ($\lambda_{\max} = 508$ nm), and manganese(II) ($\lambda_{\max} = 450$ nm) ions in filtrates.²⁴⁻²⁷

RESULTS

Polyamine functionalized resins

Polyamine functionalized resins with high loadings of amine groups were obtained as a result of chemical modification of low crosslinked gel type glycidyl methacrylate terpolymers according to Scheme 1. The GMA resins 1 were synthesized by suspension terpolymerization of the mixture of glycidyl methacrylate (20 mol %), styrene (77 mol %), and divinylbenzene

or diethylene glycol dimethacrylate (3 mol %) according to the procedure described previously.²¹

As can be seen from the SEM microphotographs presented in Figure 1(a,b), spherical beads of resins 1A are characterized by nearly smooth outer surface. Furthermore, inside of the dried polymer beads one can also find the nonporous glassy nature without any fine structure [Fig. 1(c)]. However, when beads were crashed after their swelling in methylene chloride their solvent porosity could be revealed [Fig. 1(d)].

To obtain high amine group loadings, the resins 1 were treated with the 10-fold excess of polyamines in toluene at 80°C. The applied reaction conditions allowed to achieve very high efficiency of transformation of epoxy groups (94–98%, see Table I). The conversion of epoxy groups was concluded from the nitrogen percentage in the modified products, on the one hand, and from the comparison of FTIR spectra of the GMA resins and products of their modification, on the other (Fig. 2). Resins with lower loadings of amine group were obtained when a less excess of polyamines was applied.²⁸

Elemental analysis was limited to determining nitrogen content in amine modified resins because this parameter was recognized as a key measure of the loading of amine groups. The analysis was performed by the classic Kiehdahl method. The usefulness of this method was proved in our previous works comparing the results obtained by Kiehdahl method with the results of instrumental analysis. The values of modification degrees presented in Table I were calculated taking into account the

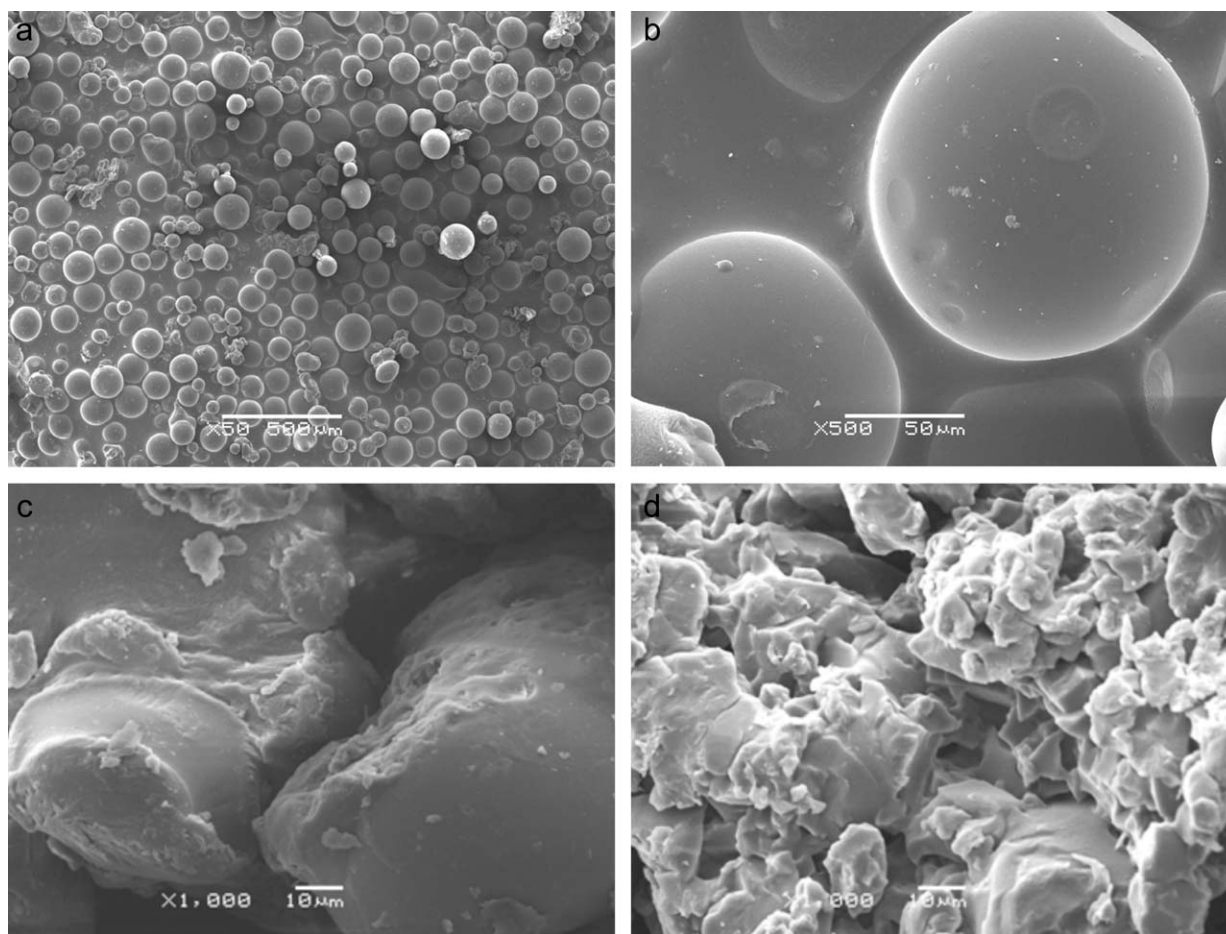


Figure 1 SEM micrographs of terpolymers 1A.

loadings of epoxy groups, the nitrogen percentages which could be obtained for quantitative addition of amines to epoxy groups (100% modification), and the nitrogen percentages found for the products of transformations of resins **1** under the influence of the individual polyamines.

From the comparison of the resin spectra taken before and after modification, one can find that the ring opening of epoxy groups is accompanied mainly with a decrease in intensity of the absorption bands at 1250, 910, and 840 cm^{-1} (epoxy ring vibrations²⁹) and with an appearance of new absorption

in the range of 3700–2200 cm^{-1} . The last can be ascribed to the stretching vibrations of OH, NH, and NH_2 groups which participate actively in hydrogen bond formation. Incomplete conversion of epoxy groups during modification is probably a consequence of the changes in the swelling ability of polymer beads which take place when polar polyamine moieties are immobilized onto resins **1**. Due to the incompatibility of amine groups with toluene, the shrinkage of modified beads occurs during modification. As a result, a part of epoxy groups is “closed” inside of the polymer network. In this way, they

TABLE I
Resin Characterization

GMA resins				Polyamine resins					
	Cross-linking agent	Loading of epoxy groups, mmol/g	T_{gr} , °C	Polyamine	%N	mmol N/g	Modification of 1 , %	T_{gr} , °C	
1A	DEGDMA	1.46	98	EDA	2A	3.76	2.68	96	142
				DETA	3A	5.23	3.73	98	128
				TAEA	4A	6.37	4.55	95	130
1B	DVB	1.40	108	EDA	2B	3.50	2.50	97	138
				DETA	3B	5.00	3.57	97	135
				TAEA	4B	6.13	4.38	94	126

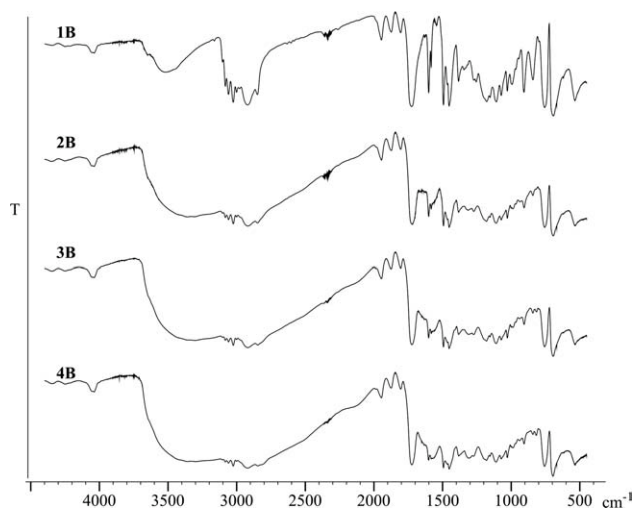


Figure 2 Comparison of FTIR spectra of terpolymer **1B** and products of its modification with a series of polyamines.

become inaccessible to polyamine reactants in toluene solution. In consequence the residual absorption bands at 910 and 840 cm^{-1} can be detected also in the spectra of products (Fig. 2). To better understand the nature of the gel type resins and the possibilities of their chemical modification, one should familiarize with the thorough review of Sherrington.³⁰

The chemical transformations of the resins **1** under the influence of EDA, DETA, or TAEA, respectively, to resins **2**, **3**, or **4** did not change the morphology of the polymer beads. However, noticeable changes in the glass temperature (T_g) of the products can be detected compared with the T_g of **1** (Table I). It was found that the T_g of **2** is about 40°C higher than the T_g of **1**. Glass temperatures determined for **2** were higher than the ones found for **3** and **4**. Probably, an increase in the concentration of flexible aminoethyl groups is responsible for these findings.

Figure 3(a–d) show the TGA and DTGA curves of GMA resins and their polyamine functionalized derivatives. Some differences in the thermal stability of the resins were found. From Figure 3(a,b) it is evident that the decomposition of the GMA resins intensified at around 350°C, whereas the amine modified resins started to decompose intensively at around 250°C [Fig. 3(a,b)]. The maxima of the decomposition rate of resins **1** were observed at 391°C and 398°C, respectively, for **1A** (crosslinked with DEGDMA) and **1B** (DVB) [Fig. 3(c,d)]. The modified resins decomposed most intensively at the temperature around 10°C higher, in ranges of 407–409°C and 409–411°C, respectively, for resins crosslinked with DEGDMA and DVB. Any dependence between the amine resin nature and the temperature

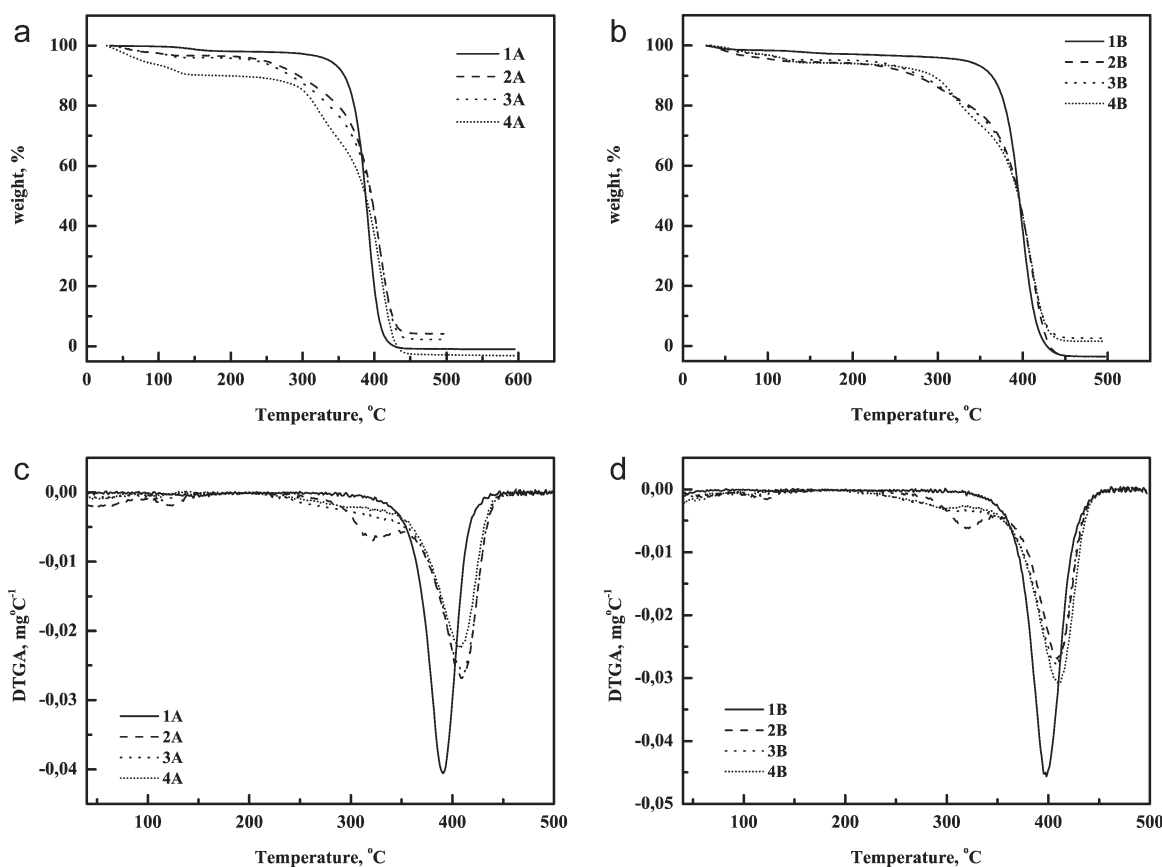


Figure 3 TGA and DTGA traces.

TABLE II
Swelling Ability of the GMA Resins and Polyamine Modified Resins

Solvent	ΔV							
	1A	1B	2A	2B	3A	3B	4A	4B
MeOH	0.5	0.4	0.6	0.7	0.5	0.6	1.0	0.8
MeOH:CH ₂ Cl ₂ (5 : 1 V:V)	0.4	0.4	0.7	0.5	1.2	0.9	1.3	0.8
MeOH:CH ₂ Cl ₂ (4 : 1 V:V)	0.3	0.4	0.7	0.6	1.6	0.9	1.6	1.1
MeOH:CH ₂ Cl ₂ (3 : 1 V:V)	0.5	0.4	1.5	1.1	1.9	1.2	1.9	1.2
MeOH:CH ₂ Cl ₂ (2 : 1 V:V)	0.6	0.8	1.6	1.2	1.8	1.2	2.0	1.1
MeOH:CH ₂ Cl ₂ (1 : 1 V:V)	1.6	1.3	2.6	1.8	2.8	1.7	2.6	1.8
MeOH:CH ₂ Cl ₂ (1 : 2 V:V)	3.8	2.4	3.5	2.1	2.8	2.0	3.0	1.9
MeOH:CH ₂ Cl ₂ (1 : 3 V:V)	3.9	2.5	3.6	2.3	3.5	2.0	3.8	2.2
CH ₂ Cl ₂	5.3	3.0	2.9	2.0	1.8	2.0	1.6	1.0
DMF	3.1	1.8	2.2	1.7	2.6	1.8	2.0	1.5
NMP	5.6	3.0	4.5	1.6	4.1	2.5	3.4	2.3
Toluene	3.0	2.0	1.4	1.2	2.0	0.9	2.1	0.8
1,4-Dioxane	3.6	2.3	1.9	1.5	2.7	1.6	2.0	1.4
THF	4.4	2.6	2.5	2.0	2.9	1.6	1.5	0.6
H ₂ O	0.5	0.6	0.7	0.7	0.7	0.7	0.7	0.6

of the maximum decomposition was not observed. TGA curves obtained for polyamine functionalized resins are generally similar for the same crosslinker. Only the one obtained for the resin **4A** was different from the ones obtained for **2A** and **3A**. Probably, the highest affinity of this resin to methanol is responsible for such a picture.

The higher values of T_g detected for polyamine functionalized resins are the proof of additional crosslinking taking place in resin beads as a consequence of hydrogen interactions between the functional groups present in modified polymers.

Swelling ability

As was mentioned above, the resins **1** with the nominal crosslinking degree equal of 3 mol % swell strongly in cyclic ethers (THF and 1,4-dioxane), chloromethanes (CH₂Cl₂ and CHCl₃), and aromatic (benzene, toluene) and amide solvents (NMP, DMF, and DMA). These features can be ascribed to their relatively low crosslinking degree, on the one hand, and nearly fourfold molar excess of styrene (as a hydrophobic monomer) in relation to methacrylic monomers which was used on the stage of resin synthesis. Dilution of monomers before their polymerization with the mixture of cyclohexanol-*n*-octanol²¹ is another reason of the unique swelling ability of **1**. On the other hand, the strongly hydrophobic aromatic nature of the resins causes that they do not swell in water, methanol, acetonitrile, and aliphatic hydrocarbons. Furthermore, it is worth mentioning that the resin crosslinked with DEGDMA swells clearly better than the one crosslinked with DVB.

The affinity of polymer beads to individual solvents changed however when EDA, DETA, or TAEA were immobilized onto the resins **1**. From the results

presented in Table II, one can easily conclude that resins **2**, **3**, and **4** delivered in this way swell clearly less in most of the solvents mentioned above, including toluene, used as a medium for immobilization of polyamines. The swelling decreases in the order of **2** > **3** > **4**, when the loading of the amine groups increases. A slight improvement in the swelling of the polyamine functionalized resins compared with the resins **1** was noted only in the case when methanol was used as a medium. However, the swelling ability of these resins can be increased when the mixed solvent systems are applied [Fig. 4(a,b)]. The last can be ascribed to a synergistic effect of individual solvents which affect both hydrophobic matrices (methylene chloride) and polar amine and hydroxyl groups (methanol) of **1**, **2**, or **3**.

Uptake of metal ions

It is well known that the gel-type resins obtained by radical polymerization are composed of an amorphous crosslinked infinite network of interpenetrating polymer chains without any fine structure. Such resins have very low surface area in the dry state because polymer chains are in molecular contact with each other. The diffusion of even small molecules through such polymeric glass is very slow. However, the gel type resins are capable of swelling when solvents thermodynamically compatible with them are applied as a medium. The swelling generates "solvent porosity" within resins. The last facilitates an access of small molecules to the polymer network. Hence, immobilization of metal complexes and metal particles on the gel type resins to obtain, for instance, polymer supported catalysts or other metal-containing polymers are commonly carried out using solvents compatible with starting

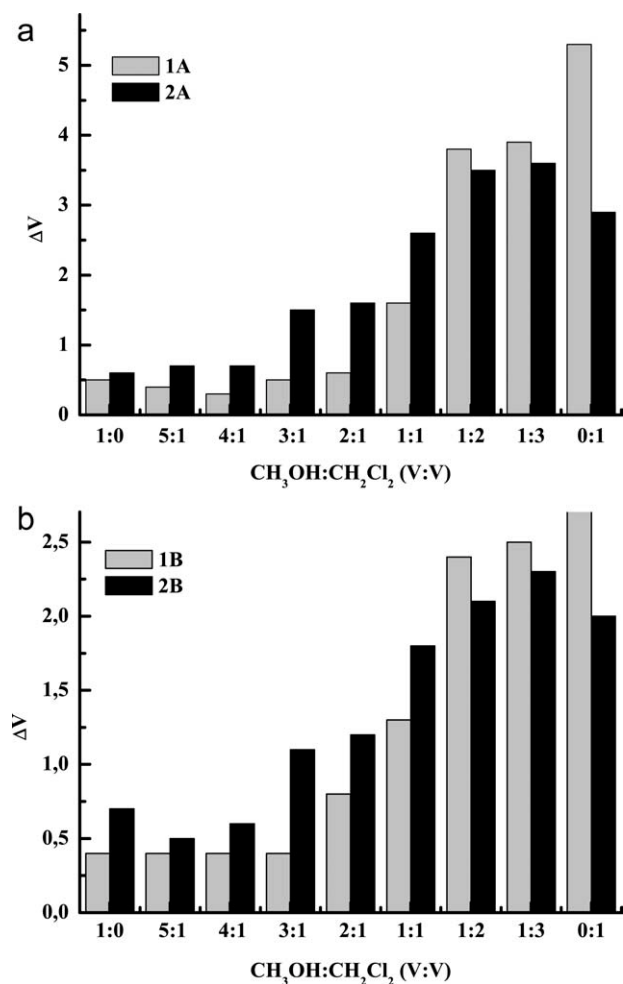


Figure 4 Swelling ability of the resins 1 and 2 in CH₃OH-CH₂Cl₂ systems.

polymeric reactants.³⁰ Similarly, the purification of organic compounds from traces of toxic metal ion impurities, which come from homogeneous catalysts, carried out using the reactive gel-type polymers is more effective when "good" solvents are applied. When however the solvents incompatible thermodynamically with the gel-type resins are used, the last can stay inactive in relation to potential reactants. It is due to the closing of functional groups inside the polymer network as a consequence of its shrinkage.

As was described above, resins 1, 2, and 3 showed noticeable affinity to methanol and their swelling in methylene chloride is still on the quite high level. Hence, it might be expected that these resins could be active in the uptake of transition metal ions from organic solutions due to the formation of metal ion complexes. The ability of the soluble polyamine ligands to complex many transition metal ions are well known.³¹

Cobalt(II), copper(II), and manganese(II) acetates and iron(III) chloride were used as a source of metal ions. Inorganic salts are generally poorly soluble in

organic solvents. However, some of them are soluble in methanol which by nature is very similar to water. The salts applied in this work belong just to this group. They have not only comparatively good solubility in methanol but are also sufficiently good in the mixtures of methanol-methylene chloride, even if these solvents are used in 1 : 5 V : V proportion. It was found in the separate experiments that the solutions which contained 0.4 mmol of Co(II), Cu(II), Mn(II), or Fe(III) ions in 1 mL of 1 : 5 V : V CH₃OH-CH₂Cl₂ mixture were stable for minimum 2 h at room temperature. The salts are insoluble in pure methylene chloride. That is why, methanol and its mixtures with methylene chloride were applied as a medium in the uptake of Co(II), Cu(II), Mn(II), and Fe(III) ions.

A series of experiments with resins 2 were carried out at first. It turned out that the rate and the efficiency of uptake of individual metal ions from organic solution by these resins strongly depended on their compatibility with a solvent. As a consequence, the differences in the affinity of 2 to individual metal ions were observed only in methanol [Fig. 5(a,b)]

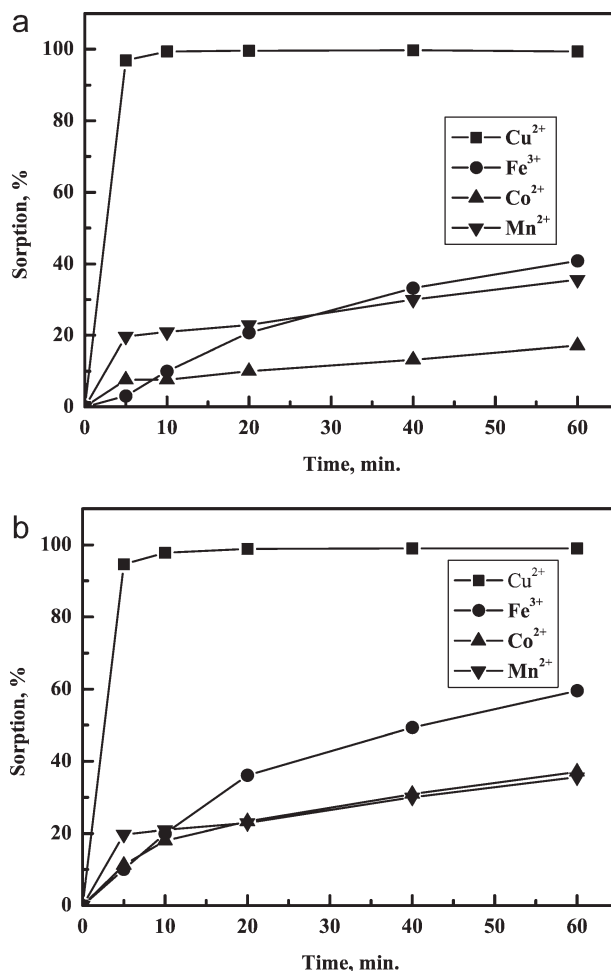


Figure 5 Metal ion uptake behavior of the resins 2 in methanol.

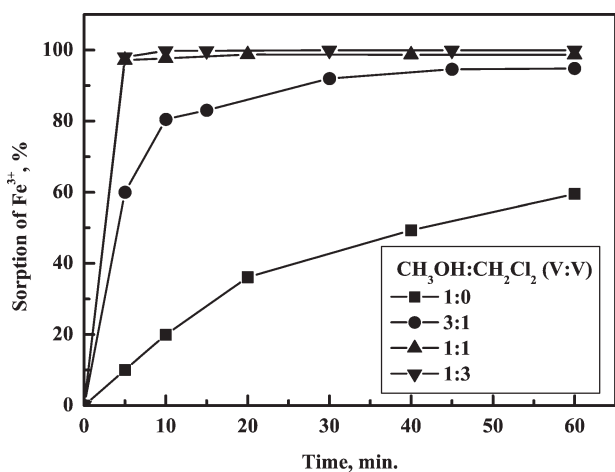


Figure 6 Uptake of Fe(III) ions by the resin **2B** in $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ systems.

which swelled these resins relatively weakly. Both of **2**, independently on the crosslinking agent, show the extremely high affinity in relation to Cu(II) ions in a medium of methanol. As a result, Cu(II) ions were removed from the solution practically completely within 10 min, whereas the yield of uptaking of Co(II), Mn(II), and Fe(III) ions by these resins after 60 min shaking of the mixtures come to 17, 36 and 41% for **2A** and 37, 35 and 60% for **2B**, respectively. Interestingly, the resin crosslinked with DVB turned out to be more active in relation to the metal ions than the one crosslinked with DEGDMA, although the last is characterized by better swelling abilities.

The swelling ability of the resins improves when methylene chloride is added to methanol (see Fig. 4). Hence, an increase in the rate of metal ion uptaking and an improvement in the efficiency of Co(II), Mn(II), and Fe(III) ions removed from the solutions might be expected when the mixed system of solvent is used. These expectations were confirmed by

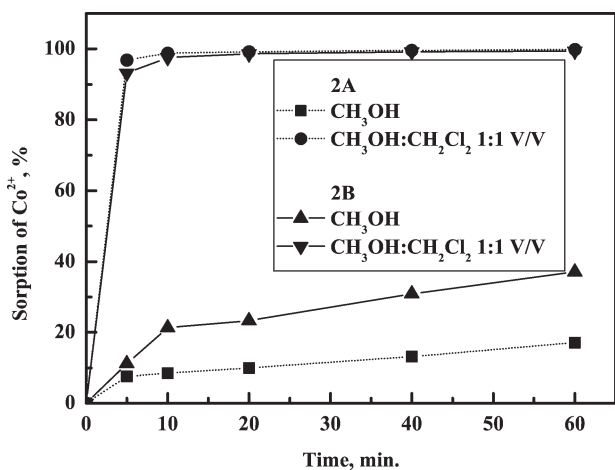


Figure 7 Uptake of Co(II) ions by the resins **2**.

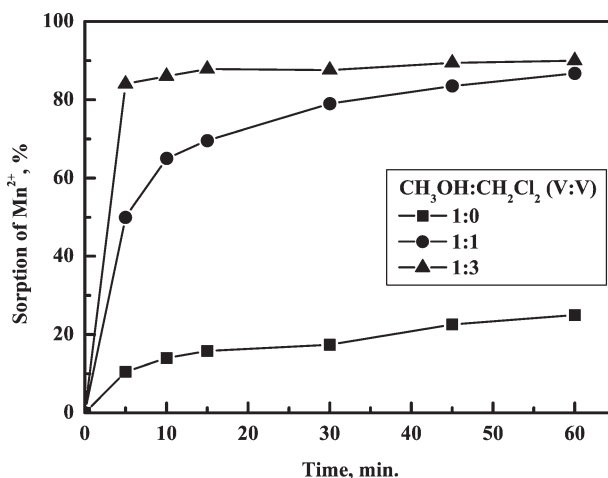


Figure 8 Uptake of Mn(II) ions by the resins **2B**.

experiments. Figure 6 presents the selected results obtained for Fe(III) ions using the resin **2B** and $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ mixtures. From these results one can conclude that the yield of Fe(III) ions uptaking

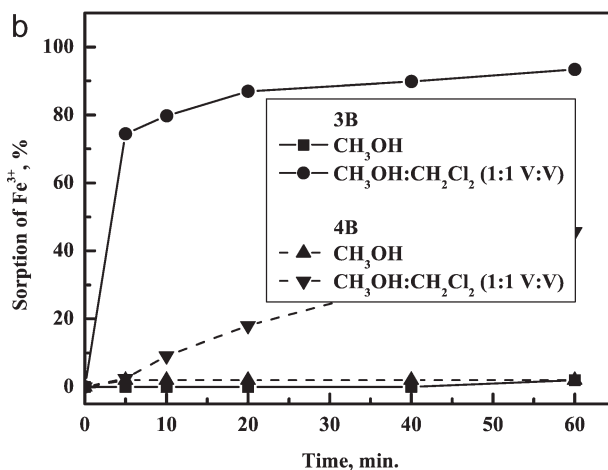
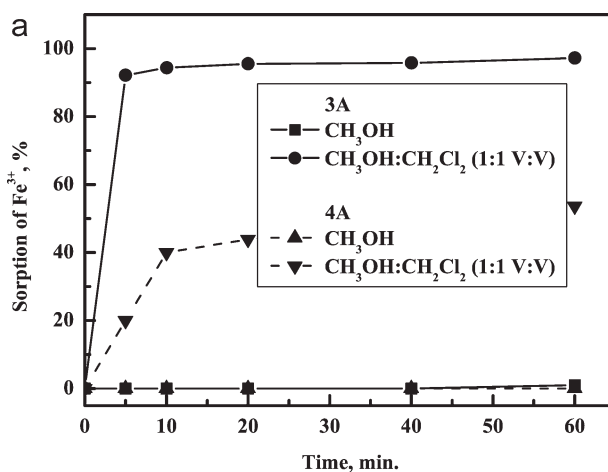


Figure 9 Uptake behavior of resins **3** and **4** in relation to Fe(III) ions in methanol and 1 : 1 V : V methanol-methylene chloride system.

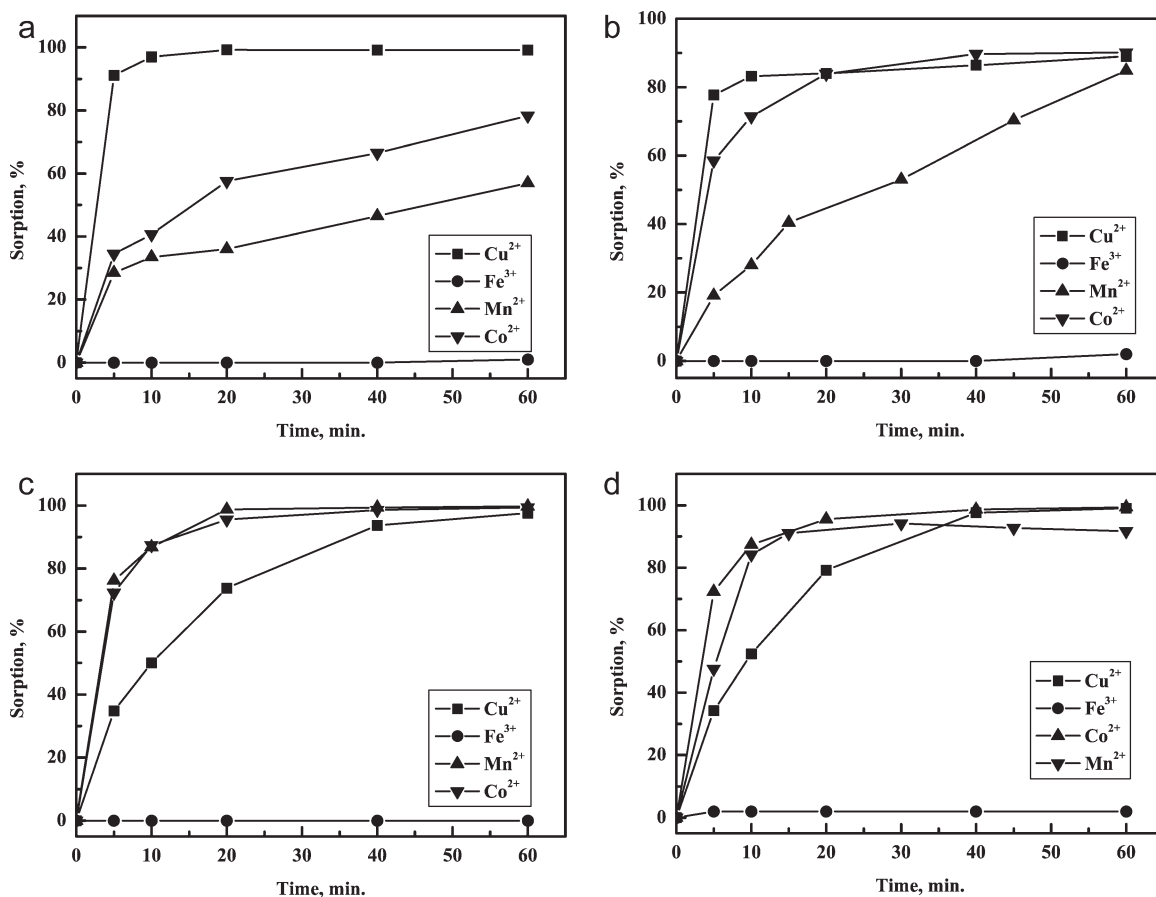


Figure 10 Metal ion uptake behavior of the resins 3 and 4 in methanol.

from 3 : 1 V : V methanol-methylene chloride solution after 60 min shaking increased to 95%. Furthermore, the quantitative uptake of these ions by **2B** could be achieved within 20 min when 1 : 1 V : V methanol-methylene chloride mixture was used as a medium.

When the uptake was carried out from the CH₃OH-CH₂Cl₂ systems, similar behavior of **2** was also observed in relation to Co(II) ions (Fig. 7). However, the uptake of Mn(II) ions was incomplete even though threefold excess of methylene chloride in relation to methanol was applied (Fig. 8). In this

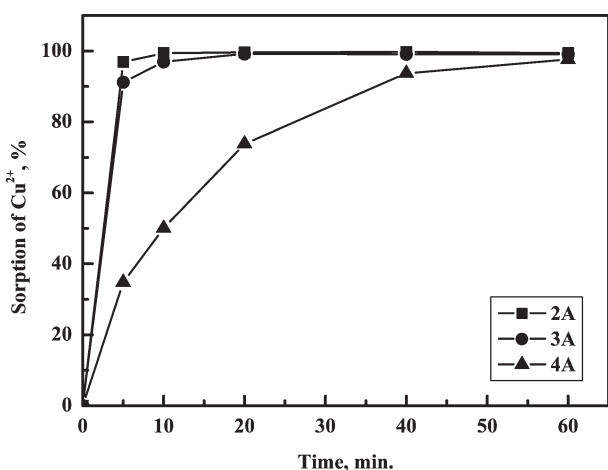


Figure 11 Comparison of the uptake ability of the polyamine resins in relation to Cu(II) ions in methanol.

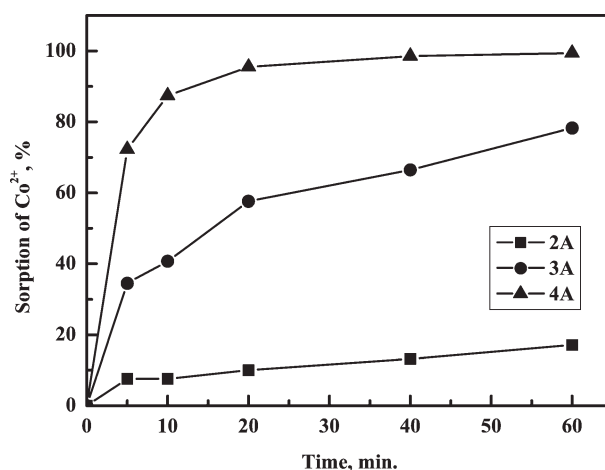


Figure 12 Comparison of the uptake ability of the polyamine resins in relation to Co(II) ions in methanol.

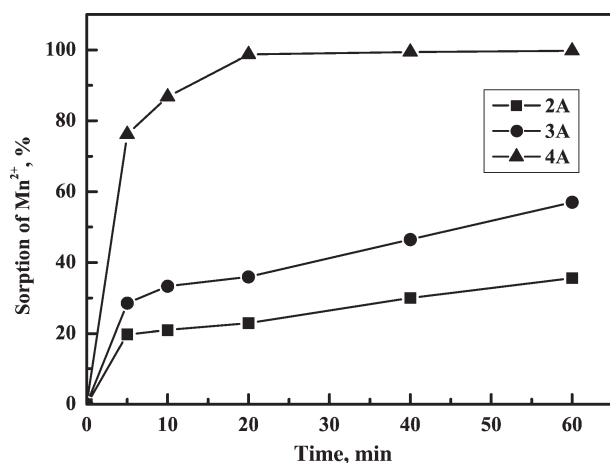


Figure 13 Comparison of the uptake ability of the polyamine resins in relation to Mn(II) ions in methanol.

case the efficiency of uptaking of the ions came to around 90%.

The analogous study to that carried out for resins **2** was performed for resins **3** and **4**. It turned out that those resins remained inactive in relation to iron(III) ions when methanol was applied as a medium [Fig. 9(a,b)]. Furthermore, their affinity with cobalt(II) and manganese(II) was higher than those found for **2** [Fig. 10(a–d)]. The relative reactivity of **3** to the individual ions changed in the order of Cu(II) > Co(II) > Mn(II) > Fe(III) and for **4** in the order of Co(II) \approx Mn(II) > Cu(II) > Fe(III).

A comparison of the affinity of the individual resins to the explored metal ions showed that resins **2** and **3** uptook Cu(II) ions comparably fast. They were clearly more reactive in relation to these ions than **4** (Fig. 11). The resins **4** turned out to be the most effective in uptaking of Co(II) and Mn(II) ions. The slowest rate of sorption of these ions was observed using **2** (Figs. 12 and 13).

The representative resins after their applying for the metal ion sorption were additionally characterized by DSC and FTIR as well. Microscopic observations were also carried out. Sufficient differences in SEM microphotographs taken for the beads before and after sorption were not found. However, the complexing of metal ions resulted in changes in FTIR spectra in the ranges characteristic of amine group absorption. Additionally, the new bands which were observed in the spectra of products at 1560 cm^{-1} pointed to the complexing of metal ions with acetate once. There were not sufficient changes in the spectra after sorption of Fe(III) ions. The complexing resulted in slight changes in T_g (an increase of $4\text{--}10^\circ\text{C}$).

Experiments with an excess of metal ions in relation to amine groups in the solution of 1 : 1 V : V methanol-methylene chloride mixture were also car-

ried out. They showed for instance that resins **2B** are capable of immobilizing in these conditions about 1.1 mmol metal ions per gram.

CONCLUSIONS

The study showed that polyamine functionalized gel type resins delivered from low cross-linked terpolymers of glycidyl methacrylate with styrene and divinylbenzene or diethyleneglycol dimethacrylate can be used as effective sorbents for removing of Co(II), Cu(II), Fe(III), and Mn(II) ions from organic solutions. However, the ability to uptake most of the ions, excluding Cu(II) ions, depends on the mutual compatibility of the solvents and resins. It is relatively low in methanol which swells the resins hardly and increases clearly when the mixtures of methanol and methylene chloride are applied. All polyamine functionalized resins turned out to be very reactive in relation to Cu(II) ions when methanol was used as a solvent.

The findings can make the polyamine functionalized resins interesting, for instance, from the point of view of their application for fast removal of residuals of metal complex catalysts from reaction mixtures.

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