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Improved synthesis of ion-exchange resins through copolymerization of ligand-modified monomers

P. M. van Berkel
Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

and D. C. Sherrington*
Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

The pyrazole-containing ligand 2-(3,5-dimethyl-1-pyrazolyl)ethanol (abbreviated NHed) has been coupled with the monomer glycidyl methacrylate. Subsequent copolymerization of this newly synthesized monomer with ethylene glycol dimethacrylate results in ion-exchange resins with a very high conversion of the epoxy groups, i.e. 76% (direct method), far better than the immobilization of NHed onto pre-formed poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (indirect method) which resulted in a conversion of only 6% of the epoxy groups. The newly obtained resins have been tested for their metal-ion binding capacities. Due to the non-chelating character of the immobilized ligand, the metal-ion uptake capacities are rather low. However, an unusual selectivity towards Ni^{2+} ions in the presence of other divalent transition metal ions was observed. At $pH < 2$ a very high and consistent Cd^{2+} uptake is observed under non-competitive and competitive conditions. It is anticipated that this improved polymerization route will not only provide resins with a high ligand concentration, but also with high uptake capacities if ligands with a better complexation ability are used. Copyright © 1996 Elsevier Science Ltd.

(Keywords: glycidyl methacrylate; immobilization; ligand concentration)

INTRODUCTION

Crosslinked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) resins (GMA/EDMA resins) containing epoxy groups have been studied extensively as a backbone material for ion-exchange resins. Facile ligand introduction via the ring-opening reaction of the epoxy groups with amines yields resins with favourable uptake kinetics, due to the hydrophilic character of the resultant resins[1-6]. The introduction of azole-containing amine ligands results in ion-exchange resins with a high selectivity for Cu^{2+} over a wide range of other divalent transition metal ions[7-9]. However, these resins have the important drawback that the ligand concentrations achieved are low. This has, consequently, a limiting effect on the maximum uptake capacity of these resins for metal ions.

In this paper a new route is reported for immobilizing azole-containing ligands yielding resins with an increased ligand concentration. Instead of anchoring the ligand after the polymer synthesis is completed (the so-called indirect method), the GMA monomer is first modified to bind the ligand before copolymerization with the EDMA crosslinker (the direct method). As a test case, the coupling of 2-(3,5-dimethyl-1-pyrazolyl)ethanol (abbreviated NHed) with the glycidyl methacrylate monomer is reported. The relatively small size of this ligand and the absence of a primary amine group, makes it very suitable for reaction with GMA and subsequent copolymerization with EDMA.

Using the direct method, resins abbreviated GMA6/4-Nd were prepared; for comparison purposes some resins were also prepared using the indirect method, viz. GMA6/4-Nid. Preliminary metal-binding studies are included in the present study.

EXPERIMENTAL

Analysis and spectroscopy

The surface area of the polymers in the dry state was determined by N_2 adsorption, using a Micromeritics Accusorb 2100E, the data being evaluated by the B.E.T. method[10]. The pore size distribution was determined by mercury intrusion, using a Micromeritics Autopure II 9220.

Elemental analysis (C, H, N, Cl) were performed by the Microanalytical Services in the Chemistry Department at the University of Strathclyde, UK and the Microanalytical Department of the University of Groningen, The Netherlands. Metal analyses were carried out on a Perkin-Elmer 3100 atomic absorption (AAS) and flame emission spectrometer connected to a Perkin-Elmer AS-90 autosampler using a linear calibration method.

Solid-state CP/MAS ^{13}C-n.m.r. spectra (cross polarization and magic angle spinning) were recorded on a Bruker

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* To whom correspondence should be addressed

MSL 400 spectrometer, operating at 400.1 and 100.6 MHz for ^1H and ^{13}C, respectively. Sample spinning rate was 7000 Hz. The cross-polarization contact time was 1.0 ms, with 3–4 s recycle delays between successive scans. Generally 6000 to 60 000 scans were employed. ^{13}C-n.m.r. spectra were recorded on a Jeol JNM-FX200 spectrometer employing a frequency of 199.50 MHz.

Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 580 spectrophotometer (4000–180 cm^{-1}).

Starting materials

All reagents and solvents were purchased from commercial sources and were used as received unless stated otherwise. Benzene and 1,4-dioxane were dried over molecular sieves (4 Å) and stored under dinitrogen. Azobisisobutyronitrile (AIBN) was freshly recrystallized from dichloromethane prior to use. The ligand NHed was synthesized according to literature procedures[11,12].

Synthesis of the monomer GMA-N

The monomer GMA-N was prepared according to *Scheme 1*. The ligand NHed was coupled with the GMA monomer by refluxing GMA (14.2 g, 0.1 mol) with NHed (21.0 g, 0.15 mol) in 100 ml dry benzene in the presence of a catalytic amount of hydroquinone (1 mmol) under a dry dinitrogen atmosphere for 24 h. The clear light brown reaction mixture was extracted with H_2O (4 × 30 ml). The collected benzene layers were dried over anhydrous $CaSO_4$ for 24 h. The reaction mixture was concentrated under reduced pressure and filtered over alumina (activated neutral Brockman I) with $CHCl_3$ as the eluent. The chloroform was removed under reduced pressure. The resulting product, the monomer GMA-N (11.9 g, 42%), appeared as a clear yellow oil. It was characterized by ^{13}C-n.m.r.

Synthesis of the polymers

Synthesis of the polymers GMA6/4 and GMA6/4-Nd. The suspension polymerization mixture consisted of the monomers GMA-N or GMA and EDMA (6/4 v/v), an equal volume of cyclohexanol/1-dodecanol (9/1 v/v) as the organic phase and an 8.5 times excess of aqueous phase. The aqueous phase consisted of a solution of boric acid (12.0 g) in water (500 ml), Cellosize stabilizer (81.6 mg) in water (40 ml), Biozan Gum R stabilizer (Xanthan gum, Hercules Powder) in water (200 ml, 0.3 w/w%) and NaCl (160 g).

The reactor vessel as described by Arshady and Kenner[13], was charged with the aqueous phase (272 ml) followed by a mixture of GMA-N or GMA (9.6 ml), EDMA (6.4 ml), cyclohexanol (14.3 ml), 1-dodecanol (1.7 ml) and AIBN (170 mg). The reactor vessel was placed in a water bath of 80°C. The stirrer speed was adjusted in such a way that good mixing of the two phases was obtained and no air was drawn into the reaction mixture. After 8 h the solution was allowed to cool down to room temperature and the beads were filtered off, washed thoroughly with water and ethanol and dried *in vacuo* at 60°C for 24 h. Typically the yield is qualitative with only very minor losses in adhesion to the stirrer and reactor walls. The beads were sieved and four fractions with different bead sizes (B_s) were obtained; fraction 1 ($B_s > 425\,\mu m$), fraction 2 ($212 < B_s < 425\,\mu m$), fraction 3 ($106 < B_s < 212\,\mu m$) and fraction 4 ($75 < B_s < 106\,\mu m$). Each fraction was checked under the microscope. Fraction 1 was discarded because this consisted mainly of large aggregated particles. Fractions 2–4 were mixed and purified by extraction in a Soxhlet using acetone for 16 h. For the polymer GMA6/4-Nd an additional extraction using ethanol for 5 h was performed. Finally the product was dried *in vacuo* at 60°C for 48 h. The beads synthesized using GMA were white and non-transparent under the microscope, the beads synthesized using the monomer GMA-N were pale yellow and transparent.

The polymers were characterized by elemental analysis (C, H, N), solid state CP/MAS ^{13}C-n.m.r. spectroscopy and infrared spectroscopy.

Synthesis of the polymer GMA6/4-Nid. The ligand NHed was also immobilized via the indirect route onto a GMA/EDMA polymer. The previously synthesized polymer GMA6/4 (15 g, 63.2 mmol of epoxy groups) and a 50% excess of NHed (13.3 g, 94.7 mmol) with regard to the amount of epoxy groups on the polymer, were added to dry 1,4-dioxane (150 ml) and refluxed for four days in a dinitrogen atmosphere. Another synthesis was carried out using the same reactants and conditions, but using dry benzene (300 ml) as the solvent. In both cases slightly yellow coloured beads were obtained. The beads were washed with ethanol and diethyl ether and purified in a Soxhlet apparatus for 17 h using ethanol. Finally the product was dried *in vacuo* at 60°C for 48 h.

The polymers were characterized by elemental analysis (C, H, N), solid state CP/MAS ^{13}C-n.m.r. spectroscopy and infrared spectroscopy.

Batch metal-uptake experiments

The batch metal-uptake experiments were performed using standard metal chloride solutions of 0.16 M and 0.6 M buffer solutions NaCl/HCl (pH 0.9–2.3) and NaOAc/HOAc (pH 2.5–6.0). All experiments were performed in polyethylene bottles mounted on a shaker at 25°C. The capacities for Cu^{2+}, Ni^{2+} Cd^{2+} and Co^{2+} under non-competitive conditions were determined as a function of pH. Batches of resin (0.2 g) were used, together with a mixture of metal solution (25 ml) and buffer (25 ml). After a shaking time of 48 h, the samples were filtered, washed subsequently with water, ethanol and ether, and dried *in vacuo* at 50°C. For the determination of the Cu^{2+} capacity at $pH > 5$ a lower Cu^{2+} concentration (10 ml of the standard Cu^{2+} solution and 40 ml of buffer) was used to prevent precipitation of Cu(II) hydroxides.

Batch metal-uptake experiments under competitive conditions were performed with standard metal chloride solutions of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} in a pH range from 0.9 to 6. Batches of 0.2 g resin were used together with a mixture of each metal solution (5 ml) and buffer (25 ml). After a shaking time of 48 h, the samples were further handled as described for the non-competitive experiments.

Samples for metal analysis were prepared by heating 0.1 g of the loaded samples with concentrated H_2SO_4 and subsequently with concentrated HNO_3 until clear solutions were obtained. The metal contents of these solutions were measured by AAS spectroscopy using a linear calibration curve.

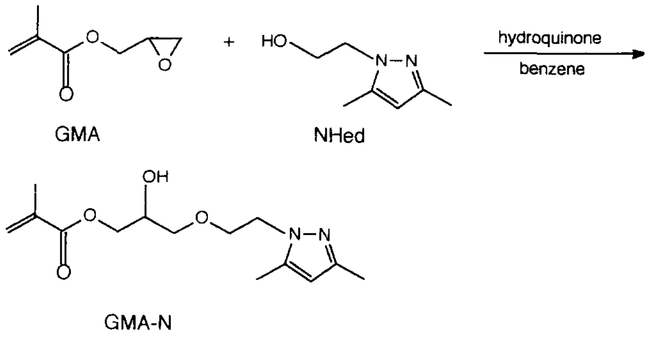
RESULTS AND DISCUSSION

Synthetic aspects

The GMA-N monomer was characterized by ^{13}C-n.m.r. spectroscopy giving the following chemical shifts δ (in ppm) in deuterated chloroform: 10.6 ($-CH_3$ on pyrazole-C5); 13.1 ($-CH_3$ on pyrazole-C3); 17.9 ($-CH_3$ GMA); 44.3 ($-\underline{C}H_2-O-CH_2-CH_2-N$); 47.0 ($-O-CH_2-\underline{C}H_2-N-$pyr); 49.1 ($-CH-OH$); 63.4 ($-O-\underline{C}H_2-\underline{C}H_2-N-$pyr); 64.9 ($-O-\underline{C}H_2-CH-OH$); 104.7 (pyrazole-C4); 125.8 ($-H_2\underline{C}=CH-$); 135.6 ($H_2C=CH-$); 139.1 (pyrazole-C5); 147.6 (pyrazole-C3); 166.7 ($C=O$)[14–16]. The downfield shift of one of the CH_2-groups of the ligand (from 61.6 to 63.4 ppm) and the upfield shift of the other CH_2-group (from 49.7 to 47.0 ppm) are both indicative of successful coupling according to *Scheme 1*.

Relevant structural and physical properties of the synthesized polymers are listed in *Table 1*. The nominal crosslink ratio for all polymers is 40%. The ligand concentrations of the synthesized resins, determined by elemental analysis, are listed in *Table 2*. Comparing the polymers GMA6/4-Nd and GMA6/4-Nid it can be seen that GMA6/4-Nd synthesized via the pre-modified GMA monomer has a 10 times higher ligand concentration than the GMA6/4-Nid polymers. The effective maximum conversion of epoxy groups in the synthesis of GMA6/4-Nd is 76%. This value is remarkably high. The maximum conversion for a GMA resin so far obtained in our group with an azole-containing ligand was 63%[17]. The conversion obtained with the amine analogue of NHed, 2-(3,5-dimethyl-1-pyrazolyl)ethylamine (abbreviated Naed), was 51%[9]. The coupling of NHed in the homogeneous phase, i.e. the coupling with GMA monomer, proceeds extremely efficiently although alcohols are generally not sufficiently nucleophilic to ring-open epoxy groups[2]. The formation of an intramolecular hydrogen bridge between the OH-group and the pyrazole nitrogen most probably increases the nucleophilicity of this ligand towards epoxides. The low conversion (i.e. 4 and 6%) obtained when immobilizing NHed onto a pre-formed GMA resin is ascribed to the fact that the coupling of NHed onto a GMA resin takes place in the heterogeneous phase where diffusion limitations play an important role.

The infrared spectrum of GMA6/4-Nd shows a characteristic pyrazole C–N stretch vibration at 1555 cm^{-1}(ref. 18). This absorption is present in the spectrum of GMA6/4-Nid, but as a weak peak due to the very low ligand concentration on this resin. The epoxy peaks, found in the spectrum of GMA6/4 at 850, 910 cm^{-1} (epoxy ring vibrations), 1260 cm^{-1} (epoxy ring breathing) and 1345 cm^{-1} (δ(CH) epoxy)[19], have disappeared completely from the spectrum of GMA6/4-Nd. In the



Scheme 1 Synthesis of the GMA-N monomer

Table 1 Structural and physical parameters of the synthesized polymers

Resin	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore diameter (nm)	Particle diameter (μm)
GMA6/4	63.0	1.61	40.2	75–425
GMA-Nd I + II	1.95	0.84	42.4	75–425
GMA Nd III	2.22	0.85	36.7	75–425
GMA-Nid I	90.8	[a]	[a]	75–425
GMA-Nid II	[a]	[a]	[a]	75–425

[a] Not determined

Table 2 Elemental analysis, epoxy-group conversion and ligand concentration of the synethesized resins. The values in parentheses were calculated

Resin	% C	% H	%N	Conversion of epoxy groups (%)	Ligand conc. ($mmol\,g^{-1}$)	% H_2O
GMA-Nd I + II	49.5	6.3	5.0	73	1.9	15
	(49.5)	(8.2)	(5.0)			
GMA-Nd III	57.5	7.3	5.9	76	2.1	7
	(57.5)	(8.1)	(5.9)			
GMA-Nid I[a]	56.3	7.1	0.7	6	0.24	6
	(56.3)	(7.4)	(0.7)			
GMA-Nid II[b]	57.8	7.2	0.4	4	0.14	1
	(57.8)	(7.3)	(0.4)			

[a] With 1,4-dioxane as the solvent
[b] With benzene as the solvent

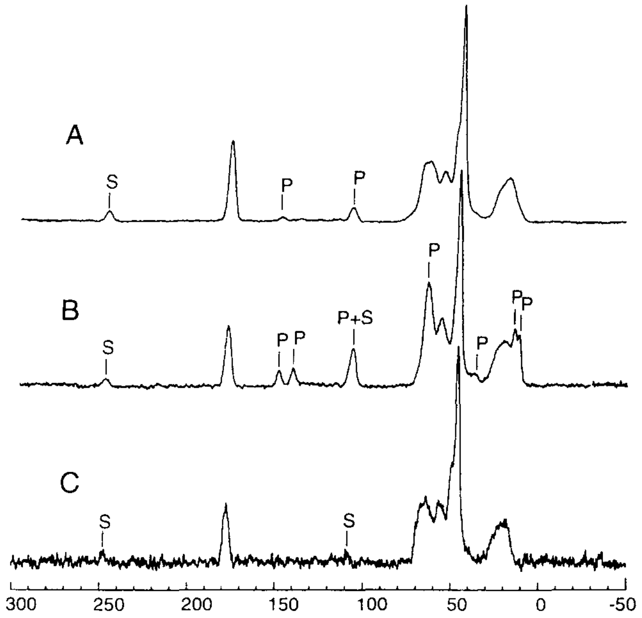


Figure 1 CP/MAS ^{13}C-n.m.r. spectra of the resins GMA6/4-Nid (A), GMA6/4-Nd (B) and GMA6/4 (C). Peaks originating from the pyrazole-containing ligand are marked P. Spinning side bands are marked S

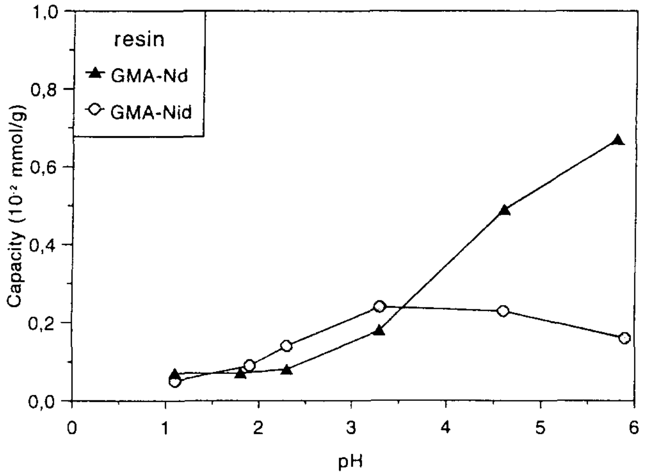


Figure 2 Capacity of GMA6/4-Nd and GMA6/4-Nid for Cu^{2+} under non-competitive conditions as a function of pH

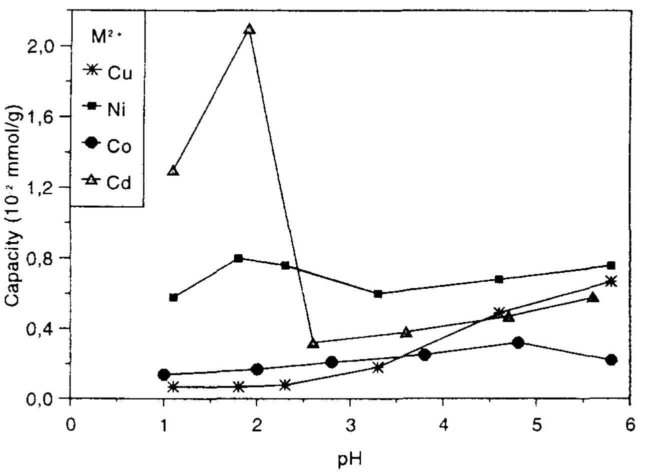


Figure 3 Capacity of GMA6/4-Nd for Cu^{2+}, Ni^{2+}, Cd^{2+}, and Co^{2+} under non-competitive conditions as a function of pH

spectrum of GMA6/4-Nid these peaks are still present, albeit very weak.

The solid-state CP/MAS ^{13}C-n.m.r. spectra of the resins GMA6/4-Nid (A), GMA6/4-Nd (B) and GMA6/4 (C) are presented in *Figure 1*. In addition to the peaks originating from GMA6/4, the spectrum of GMA6/4-Nd shows signals at 10.9 ppm (CH_3 on pyrazole-C5), 13.7 (CH_3 on pyrazole-C3), 36.1/63.2 ppm (ethylene group), 106 ppm (pyrazole-C4), 139 ppm (pyrazole-C5) and 147 ppm (pyrazole-C3)[14]. These peaks, originating from the ligand, are hardly visible in the spectrum of GMA6/4-Nid. The shoulder at 48 ppm in the spectrum of GMA6/4 (CH_2 epoxy)[15,16] is not detectable in the spectrum of GMA6/4-Nd. In the spectrum of GMA6/4-Nid this shoulder is still just visible. Comparison of the spectra of GMA6/4-Nd and GMA6/4-Nid shows that the ligand bands in the spectrum of GMA6/4-Nd are much more intense in agreement with the higher ligand concentration, i.e. 1.9 or 2.1 mmol g^{-1} in GMA6/4-Nd and 0.14 or 0.24 mmol g^{-1} in GMA6/4-Nid.

Batch metal-uptake experiments

The metal-ion capacities were determined under non-competitive conditions at several pH values of buffered solutions of a number of divalent metal chlorides. The results for the non-competitive Cu^{2+} uptake of GMA6/4-Nd and GMA6/4-Nid are given in *Figure 2*. The uptake curve of GMA6/4-Nd increases rapidly with increasing pH, whereas the uptake curve for GMA6/4-Nid shows a flat pattern in this pH range. However, less than 1% of the immobilized ligands in both resins are involved in complexation of the Cu^{2+} ions. The low maximum uptake capacity for both resins must be ascribed to the nature of the immobilized ligands and not to the properties of the polymer backbone. The resins, although having rather different surface areas, exhibit comparable uptake affinity for metal ions. This behaviour presumably arises because both resins are relatively well solvated by water. After immobilization of the originally didentate NHed ligand, this will most probably act as a monodentate species with only the pyrazole nitrogen as the coordinating atom. The hydroxyl group that is formed during the ring-opening reaction of the epoxide is not in the correct position to form a proper chelate structure with the pyrazole nitrogen[20]. The immobilization of the amine analogue of NHed, Naed, onto a GMA resin leaves the didentate character of this ligand intact. The uptake of this resin is therefore considerably higher[9].

Figure 3 shows the non-competitive uptake for Cu^{2+}, Ni^{2+} Cd^{2+} and Co^{2+} of GMA6/4-Nd as a function of pH. The uptake patterns show that the highest uptake over the whole pH range is obtained for Ni^{2+} followed by Cu^{2+} and Co^{2+}, when the Cd^{2+} uptake is excluded.

The metal-ion capacities of GMA6/4-Nd under competitive conditions as a function of pH for a number of divalent metal ions, are shown in *Figure 4*. At pH < 2 the resin shows a significant selectivity for Ni^{2+} over the other metal ions. This effect was anticipated as the capacity of Ni^{2+} ions is higher than that of the other

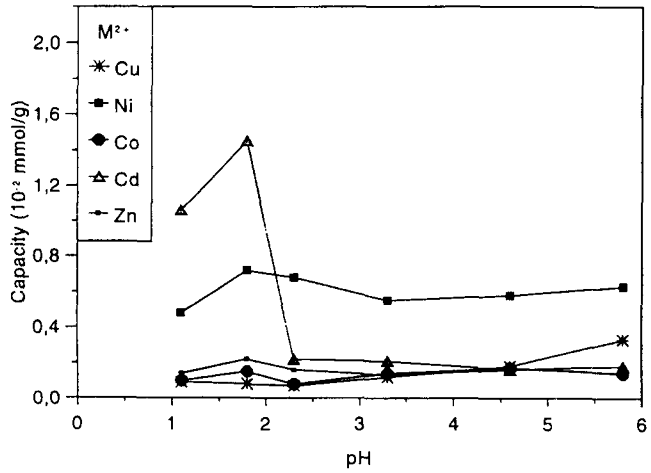


Figure 4 Capacity of GMA6/4-Nd for Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Co^{2+} under competitive conditions as a function of pH

metal ions under non-competitive conditions. The metal-uptake capacities decrease in the order $Ni^{2+} > Cd^{2+} \approx Zn^{2+} \approx Cu^{2+} \approx Co^{2+}$ at $pH > 2$; this sequence is not in accordance with the usually found Irving–Williams stability sequence[21].

At $pH < 2$, when only Cl^- counterions are present, a very high and consistent Cd^{2+} uptake is observed under both non-competitive and competitive conditions. From Cl analyses of the resins loaded with $CdCl_2$ at $pH < 2$, molar ratios of 1 : 2.3 (Cd^{2+} : Cl^-) could be calculated. This most probably implies that two mechanisms play a role in the uptake of Cd^{2+} by GMA6/4-Nd at $pH < 2$. The first mechanism involves chelation of Cd^{2+} ions by the immobilized NHed ligand, and the second mechanism involves protonation of the resin, followed by anion exchange between the chloride counterions and the anionic chloro-complexes of Cd^{2+}, i.e. $CdCl_3^-$ and $CdCl_4^{2-}$. The addition of 0.015 mmol of NaCl in the Cd^{2+}-uptake experiments under non-competitive conditions at $pH > 2$, resulted in a significantly increased uptake of Cd^{2+} by the ion exchanger GMA6/4-Nd.

Due to the low metal-uptake content of the loaded resins, no reasonable ligand field and e.p.r. spectra could be obtained, frustrating the description of the coordination geometry of the metal ions.

CONCLUDING REMARKS

This study has shown that glycidyl methacrylate can easily be modified with a pyrazole containing ligand, resulting in functional monomers. These monomers can be used in suspension-polymerization reactions resulting in resins with a very high ligand concentration, corresponding to a conversion of epoxy groups of 76%.

However, batch metal-uptake experiments showed that the metal-uptake affinity of these resins are rather low, which is most probably due to the low complex stability of the immobilized NHed ligand. Under competitive conditions the resin GMA6/4-Nd shows a significant and consistent selectivity for Ni^{2+} ions at $pH > 2$.

By using ligands with stronger chelating capability, it is anticipated that this polymerization route will not only provide resins with a high ligand concentration, but also with high uptake capacities for divalent transition-metal ions.

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