

# Dendritic Polychelatogens: Synthesis, Characterization, and Metal Ion Binding Properties

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**ABSTRACT:** In this article we demonstrate the synthesis of the dendritic polymers and their metal ion complexation. The concept of chemoremediation in liquid homogeneous phases using polymer reagents as a green technology is presented and outlined. First, as a hydrophilic ligand, AB<sub>3</sub> type of dendron and its corresponding dendrimer using Poly(ethyleneoxide)-Diacid (PEO-DA) have been synthesized; second, surface of the three branched Poly(propyleneoxide)-Triamine (PPO-TA) was modified with methylacrylate and subsequently deprotected to a carboxylic acid. The dendrimers with pendant carboxylic groups were shown to be hydrolytically and thermally stable. The metal complexing properties of the dendrimers were studied for Cr(III), Co(II), Ni(II), Cu(II),

Zn(II), Cd(II), Pb(II) and Ag(I) ions in aqueous solution using the Liquid-Phase Polymer-Based Retention (LPR) method. In addition, the complexing capacity of synthesized PEO and PPO based dendrimers towards to Cu(II) were determined by inductively-coupled plasma spectrometry (ICP) to be 260 and 142 mgg<sup>-1</sup>, respectively. According to the retention profiles determined as a function of filtration factor using LPR in conjunction with ICP, two and trivalent metal ions showed a strong interaction with these dendrimers © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2808–2814, 2008

**Key words:** poly(ethyleneoxide); poly(propyleneoxide); hyperbranched; metal-polymer complexes; microwave

## INTRODUCTION

Polymeric supports with complexing groups are widely investigated<sup>1–5</sup> and applied for the metal recovery from dilute solutions, such as industrial fluids and waste waters. The interest in the use on water soluble macromolecule (WSM) in conjunction with ultrafiltration membranes, to separate the metal ions from the aqueous solutions, has steadily grown in the last two decades.<sup>5–8</sup> The possibility of synthesizing derivatives of commercially available WSM to achieve selective metal ion complexation has been recognized from early on.<sup>9,10</sup> Recently carboxy-functional polyesters based on polyethylene glycol and oligofunctional carboxylic acids such as ethylenediaminetetra-acetic acid and ethylenetriaminepenta-acetic acid, which represent promising candidates for the preparation of environmentally degradable polycondensates, have been reported.<sup>11</sup> The separation and enrichment of hazardous metal ions in aqueous solutions play an important role for their municipal and industrial waste water. Among many

separation techniques membrane separation is an efficient and widely applied separation process that is comparable to other separation techniques in terms of technical and economical feasibility.<sup>12</sup> The general principle of this method, the Liquid-Phase Polymer-Based Retention (LPR), is to add water-soluble polymeric binding agents to a multicomponent solution, so that these agents will form macromolecular compounds with the target ions only. Thus, the size of the metal ion would be increased significantly whereas the size of the nontarget species would remain unchanged. If such a solution is then passed through an ultrafiltration membrane, the membrane would separate the target metal ions from the nontarget species.<sup>13,14</sup> This concentration method is designed to recover metal ions from dilute technological solutions and for absolute preconcentration of elements in analytical chemistry.

Therefore, the aim of this study is to synthesize a dendritic ligand with a partially green chemistry method, which allows us to avoid using large amount of solvents and chemicals, and naturally to test the efficiency of new polychelategon from the environmental perspectives. To enhance the liganding properties of the new polychelategon, a Newkome-type dendron,<sup>15</sup> as functional group has been synthesized via microwave irradiation technique with a better yield and in much shorter time, without using any solvent. After the reduction of nitrotriester **1** to an aminotriester **2**, the dendron **2** was

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successfully coupled with the freshly chlorinated PEO-DA **3**<sup>16</sup> to obtain esteric dendrimer **4**. To make the molecule water soluble, dendritic macromolecule **4** was converted to carboxylic acid **5**. As a second polychelatogen PPO-TA **6** was functionalized by the method reported by Twyman and coworkers.<sup>17</sup> Resulting three branched ester **7** was slightly soluble in water. Molecule **7** was also hydrolyzed to carboxylic acid to make it complete water soluble. After NMR, FT-IR, ESI-MS, and Elemental analysis characterization, LPR studies have been carried out and, the amount of complexed metal ions was determined by ICP measurements.

## EXPERIMENTAL

### Materials

All chemicals were analytical grade and obtained from Merck and Fluka. Solvents were dried and distilled according to literature.<sup>18</sup> Reactions were monitored by thin layer chromatography (TLC) on silica gel 60 F254, spots were detected either by UV-absorption or by charring with I<sub>2</sub> vapor. Dialyses were performed by Spectrum membrane filtration having molecular weight cut-off (MWCO) 1, 2, and 3 kiloDalton (kD) in water or in methanol. Some dendrons have been synthesized via Microwave (MW) irradiation technique (CEM, Discover labmade).

### Instruments and methods

NMR spectra were recorded on a NMR using an Inova 500 MHz Varian system spectrometer for solutions in CDCl<sub>3</sub>. FTIR spectra were recorded on Mattson Satellite spectrophotometer in the range of 400–4000 cm<sup>-1</sup> for neat compounds as films between NaCl or KBr plates or as disks with KBr. Elemental analysis were recorded with A Perkin-Elmer Model 2400 Series II for CHN/S. Mass spectral data were obtained using an Esquire electron ionization mass spectrometer (ESI-MS) and are reported as (assignment, relative intensity); ESI-MS samples were typically prepared in MeOH/H<sub>2</sub>O/TFA (70 : 30 : 1) for positive ion mode or Me<sub>2</sub>CHOH/H<sub>2</sub>O/NH<sub>3</sub> (70 : 30 : 1) for the negative ion mode. The concentrations of

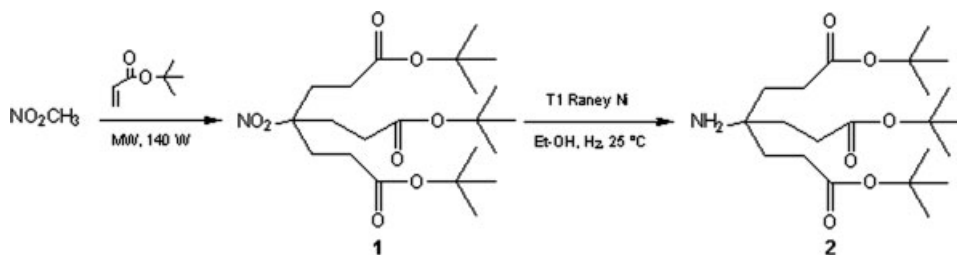
metal ions were determined by inductively-coupled plasma spectrometry (ICP, Thermo-Jarrell Ash IRIS/AP). Carboxyl groups were determined by using a titrator (Metrohm 702 SM Titrino). Autoclave and LPR systems were partially designed in our laboratory or purchased from Millipore.

### Synthesis of nitrotriester dendron, 1

The (Di-*tert*-butyl 4-(2-(*tert*-butoxycarbonyl)ethyl)-4-nitroheptanedioate): 0.61 g (10.0 mmol) of nitromethane and 3.84 g (30.0 mmol) of *tert*-butyl acrylate were weighed into A 50-mL flask, then 1–2 drops of triton-B soln. (10 mL, 40% in methanol soln.) was added. The flask was equipped with a reflux condenser and transferred into MW open vessel instrument, under N<sub>2</sub> atmosphere the Micheal-type reaction was initiated with a MW irradiation applying 140-Watt power for 5 min, then they system was cooled. The reaction mixture was treated first with 5-mL brine then washed with 10 mL of water three times, 4.30 g white crystals of nitrotriester **1** was obtained with yield of 97% without any further purification (Scheme 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.40 (s, 27H), 1.48–2.17 (m, *J* = 7.0 Hz, 6H and m, CH<sub>2</sub>CO, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 171.20 92.32), 81.26, 30.46, 29.80, 28.15); IR, (KBr), cm<sup>-1</sup>: 1748, 1160; MS (ESI) *m/z*: 468.1 (M+Na<sup>+</sup>), calcd. 468.5 (M+Na<sup>+</sup>).

### Synthesis of aminotriester dendron, 2

The (Di-*tert*-butyl 4-(2-(*tert*-butoxycarbonyl)ethyl)-4-aminoheptanedioate)<sup>19</sup>: Absolute Et-OH (25–30 mL) was added in to a 500 mL Parr hydrogenation bottle, followed by 3 g of freshly prepared T-1 Raney nickel catalyst, which should be covered by absolute ethanol during the entire transfer operation (required about 50–100 mL of ethanol). About 2.5 g (5.6 mmol) of previously synthesized **1** was added, followed by enough ethanol adding to fill about 50% of the volume of the 500 mL hydrogenation bottle. The Parr apparatus was charged and pressurized to 55–60 psi with H<sub>2</sub>. Generally 6 h were required until the hydrogen uptake ceased. The catalyst was removed by filtration through a glass sintered (celite pad which had been previously washed in ethanol) fun-



Scheme 1 MW preparation of dendron **1** and its amine **2**.

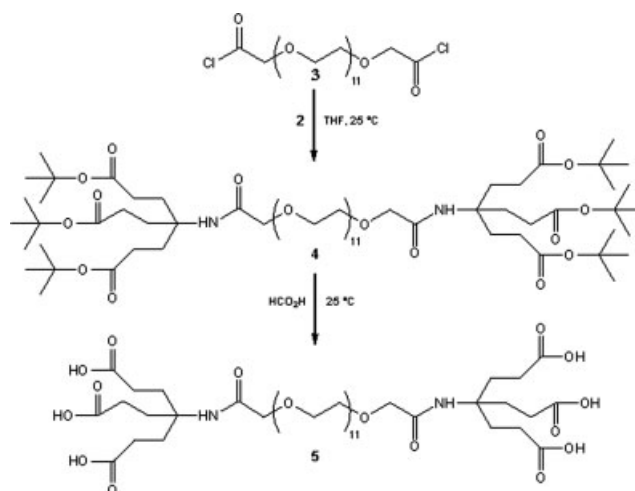
nel, and washed on the filter with ethanol (50–80 mL). Ethanol was removed in vacuum by rotary evaporator at a bath temperature of 45°C (the temperature have to be lower than 45°C otherwise cyclisation occurs) to get 2.32 g of dendron 2. The yield is 100% (Scheme 1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.44 (s, 27 H), 1.78–2.20 (m,  $J = 7.2$  Hz, 6H and m,  $J = 7.2$ , 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 173.17, 80.52, 52.75, 34.36, 30.10, 28.22; IR, (KBr),  $\text{cm}^{-1}$ : 3333, 1745, 1153; MS (ESI)  $m/z$ : 438.2 ( $\text{M}+\text{Na}^+$ ), calcd. 438.5 ( $\text{M}+\text{Na}^+$ ).

#### Synthesis of the PEO-hexa ester, 4

To a stirred solution of 1.74 g (4.2 mmol) amino-triester, 2 and 0.43 g (4.2 mmol)  $\text{Et}_3\text{N}$  in 10 mL of dry THF was added 1.34 g (2 mmol) of freshly chlorinated PEO-DA 3.<sup>16</sup> The mixture was stirred for 30 min at 0°C and then 6 h at 25°C. The mixture was first filtered to remove the  $\text{Et}_3\text{N}$  salt, and then the excess  $\text{Et}_3\text{N}$  and solvents were evaporated by reduced pressure apparatus. Finally product was dialysed (MWCO 1 kD) in methanol to afford 2.65 g of pure dendritic ester 4 (Yield: 95%), as light yellow viscous oil (Scheme 2).  $^1\text{H}$  NMR, ( $\text{CDCl}_3$ )  $\delta$ : 1.44 (s,  $\text{CMe}_3$  54 H), 1.90 (t,  $J = 7.2$  Hz, 12H) 2.25 (t,  $J = 7.2$  Hz, 12H), 3.30 (t,  $J = 4.8$  Hz, 2H), 3.42–3.60 (in PEO, m, 44H), 3.64 (q, 24H), 5.70 (s, 2H);  $^{13}\text{C}$  NMR, ( $\text{CDCl}_3$ )  $\delta$ : 177.13, 172.61, 81.05, 60.75, 34.91, 30.34, 28.25; IR, (KBr),  $\text{cm}^{-1}$ : 3339, 1676, 1625, 1145; EA, calculated %, C: 60.15, H: 9.23; N: 2.00, EA found, C: 58.34, H: 9.03; N: 1.98.

#### Synthesis of the PEO-hexa acid, 5

About 2.8 g (0.2 mmol) of polychelatogenic ester, 4 was hydrolyzed in 10 mL of formic acid in 12 h. After removing the external formic acid and resulted *tert*-butanol *in vacuo*, 2.12 g of product 5 was obtained as white viscous oil, (100%) (Scheme 2).  $^1\text{H}$  NMR, ( $\text{CDCl}_3$ )  $\delta$ : 2.19 (t,  $J = 7.2$  Hz, 12H), 3.46–3.64

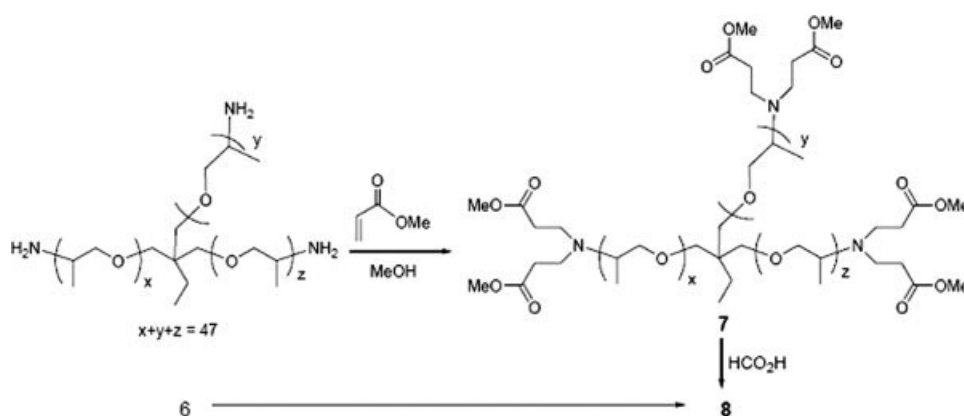


**Scheme 2** Synthesis of dendritic Polychelategon 4 and corresponding acid 5.

(in PEO, m, 44H), 3.66 (q, 24H), 5.70 (s, 2H), 8.02 (br, 6H);  $^{13}\text{C}$  NMR, ( $\text{CDCl}_3$ )  $\delta$ : 17.00, 170.00, 80.80, 34.00, 30.00; IR (KBr)  $\text{cm}^{-1}$ : 3430 (br), 1714, 1634; EA, calculated %, C: 52.07, H: 7.60, N: 2.64, EA found, C: 50.65, H: 7.41, N: 2.56.

#### Synthesis of PPO-hexa ester, 7

About 17 g (0.2 mol) methylacrylate was added to the 100 g (0.033 mol) methanolic solution of PPO-TA 6, and allowed to stir at room temperature for 48 h. The reaction was then heated to 50°C for 1 h. methanol and excess methylacrylate were removed by rotary evaporator. After the dialysis using membrane filter with a MWCO of 3 kD in methanol, 6 g of product 7 was obtained as yellow viscous oil. (yield 98%) (Scheme 3).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.96 (t,  $J = 7.0$  Hz 3H), 1.16 (d, 141H), 2.39 (t,  $J = 7.2$  Hz, 12H), 3.37 (m(br), 47H), 3.48 (t, 12H), 3.37–3.49 (d(br), 94H)  $^{13}\text{C}$



**Scheme 3** Surface modification of PPO with methylacrylate 7 and corresponding acid 8.

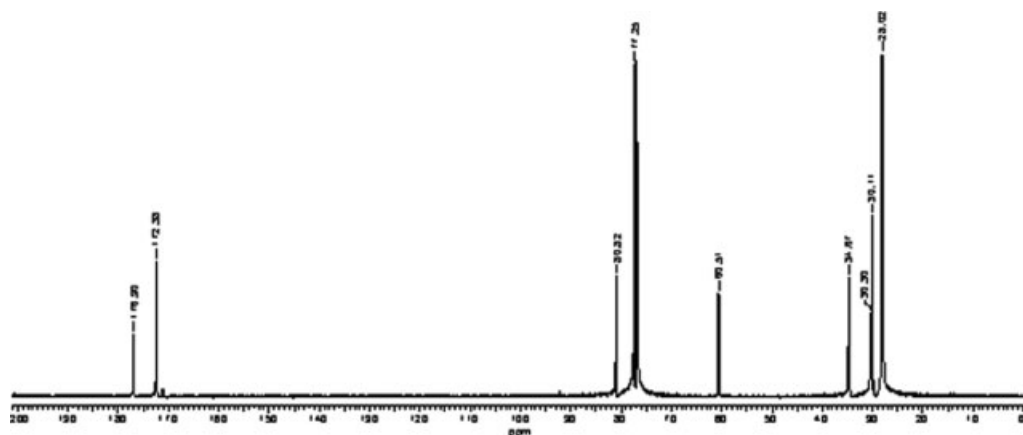


Figure 1  $^{13}\text{C}$  NMR of PEO-Hexa ester 4.

NMR ( $\text{CDCl}_3$ )  $\delta$ : 173.06, 75.47, 75.26, 73.32, 72.75, 55.19, 51.35, 46.38, 34.46; IR, (neat),  $\text{cm}^{-1}$ : 1774, 1107; EA, calculated %; C: 62.18, H: 10.23, N: 1.20. EA, found; C: 59.42, H: 9.01, N: 1.18.

#### Synthesis of PPO-hexa acid, 8

About 3.5 g (0.1 mmol) of 7 was added into 5 mL of Formic acid, and allowed to stir at room temperature for 12 h. The formic acid and hydrolyzed esteric groups were removed by rotary evaporator. The aqueous solution of 8 was dialyzed (MWCO, 3 kD) in water. About 3.45 g of oily product was obtained (yield 99%) (Scheme 3).  $^1\text{H}$  NMR, ( $\text{CDCl}_3$ ,  $\delta$ ): 1.14 (t,  $J = 7.0$ , 3H), 1.15 (d, 141H), 2.63(t,  $J = 7.2$ , 12H), 3.38(m(br) 47H), 3.49(d(br), 94H), 3.58 (t,  $J = 7.2$ , 12H), 3.69 (s, 6H), 8.08–8.13 (s, 6H); IR (neat)  $\text{cm}^{-1}$ : 3500 (br, OH), 1736, 1674, 1109; EA, Calculated %: C: 61.60, H: 10.13, N: 1.22, EA found: C: 59.72, H: 9.65; N, 1.21.

#### Metal ion binding capacity procedure

To determine the complexing binding ability of dendritic polychelatoxens 5 and 8, an aqueous solution of WSM (20 mg) was prepared and adjusted the desired pH, by adding 0.1N of  $\text{HNO}_3$  or  $\text{NaOH}$ . Separate solutions of 5 and 8 with metal nitrate (0.08 mM) were placed in a filtration cell. The total volume of the cell was kept constant at 20 mL. To accelerate the filtration, the system was pressurized by 300 kPa nitrogen gas. A Teflon membrane with an exclusion rate of  $1 \text{ d mol}^{-1}$  was used for the 5 and  $\text{d mol}^{-1}$  for the 8. The filtration fractions ( $Z = 1$ –10) were collected, and the concentration of metal ions in the filtrate and were determined by ICP.

## RESULTS AND DISCUSSION

To functionalize the PEO-DA and PPO-TA, first a dendritic monomer was synthesized via microwave irradiation technique; this was first attempt to make a Newkome type of dendrons via Microwave irradiation technique. Synthesized nitrotriester 1 was quantitatively reduced to aminotriester 2 (Scheme 1).

Dendritic amine 2 was successfully coupled with freshly chlorinated PEO-DA 3 via nucleophilic substitution reactions. This was confirmed by the new amide peak at 177.13 ppm (CONH), and esteric C=O at 172.61 ppm in the  $^{13}\text{C}$  NMR (Fig. 1). It was also confirmed in the IR spectra by assigning the esteric carbonyl groups at  $1625 \text{ cm}^{-1}$  and amide carbonyls as a shoulder at  $1676 \text{ cm}^{-1}$ . Hydrolysis of terminal esters was also confirmed by the appearance of acidic broad OH peak at  $3430 \text{ cm}^{-1}$  (Fig. 2). Similarly, formation of PPO-Hexa ester was proved by

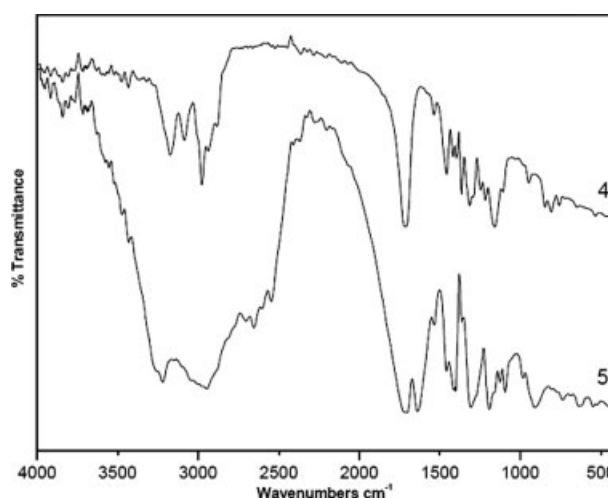
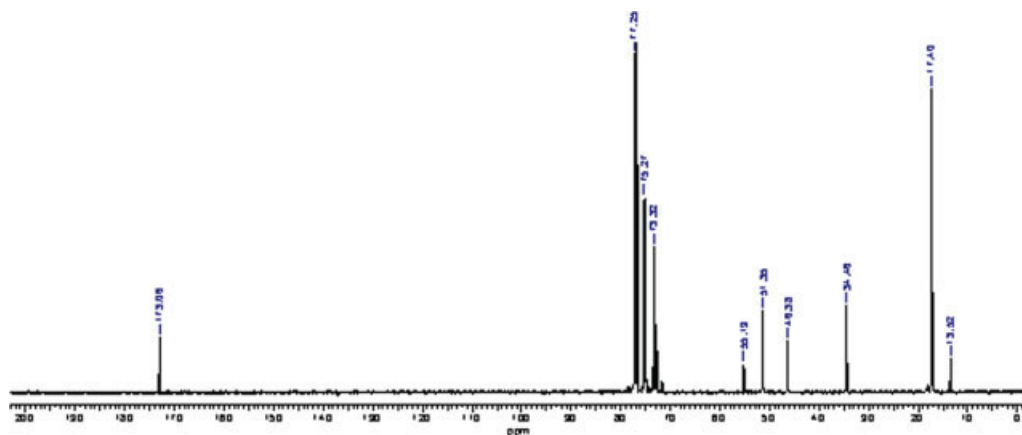


Figure 2 FTIR spectra of 4 and 5.



**Figure 3**  $^{13}\text{C}$  NMR of PPO-Hexa ester 7. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the appearance of CO at 173.06 ppm in the  $^{13}\text{C}$  NMR spectrum (Fig. 3) and formation of broad acidic peak starting at  $3400\text{--}3300\text{ cm}^{-1}$  in the FTIR (Fig. 4). All of synthesized macromolecules contain many methylene and free methyl groups, so their proton spectra were interpreted in the experimental part, but not included as spectral picture. Resulted polyamido esters were soluble in many organic solvents but not in water (only the product 7 was slightly soluble in water), so the ester groups, on periphery of macromolecules were converted to carboxylic acids (Schemes 2 and 3). The pendant carboxylic groups of both polychelatogens were determined by titration to be 260 and  $142\text{ mg g}^{-1}$ , respectively. Although, structural number of carboxy functional groups in the PPO-Hexa acid is equal to that of PEO-Hexa acid, its acidity is less than that of PEO-Hexa acid, since the number of acidic groups per gram of polychelator is more limited.

The dendrons and WSM were characterized by spectroscopy and its structures were confirmed. All the data are included in the experimental part (Figs. 1 and 2).

The metal ion retention ability of the polychelator was studied by the LPR technique, using the washing method. Its retention profiles were also determined (see Figs. 5 and 6). The retention of metal ions by membranes is influenced by many parameters, depending on reactions. Their type, solution composition, pH, temperature, membrane material, pore size, hydrodynamics, etc. However, mostly the size of a dissolved species (hydrated ions, hydrated molecules, colloidal particles, etc.) is essential for the retention by membranes. The interaction pattern of polymeric ligands with metal ions are documented<sup>20</sup> in LPR profiles, which are plots of the retention  $R$  versus the filtration factor  $Z$ .

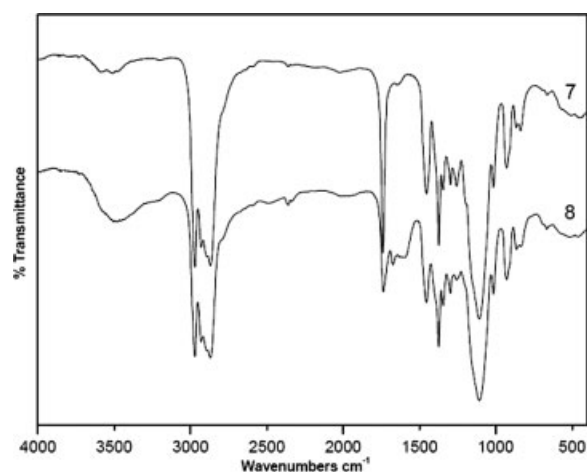
The retention of metal ions in solution by polymeric reagents can be calculated as follows

$$R(\%) = c_r \cdot c_o^{-1} \cdot 100 \quad (1)$$

where  $c_r$  is the metal concentration in the retentate after a filtrate volume of  $V_f$  has been passed, and  $c_o$  is the initial metal concentration. The filtration factor  $Z$  is defined as the ratio of the volume of filtrate  $V_f$  and the volume of cellsolution  $V_o$ :

$$Z = V_f \cdot V_o^{-1} \quad (2)$$

It was found that dendritic polychelator forms stable complexes through the freely branched carboxylic acids combining with the lone pair of amide bond. In our previous study we have showed that this dendritic acid had also strong polyelectrolyte property, so coordination of metals can also be attributed to this property. Since we assume that, at



**Figure 4** FTIR spectra of 7 and 8.

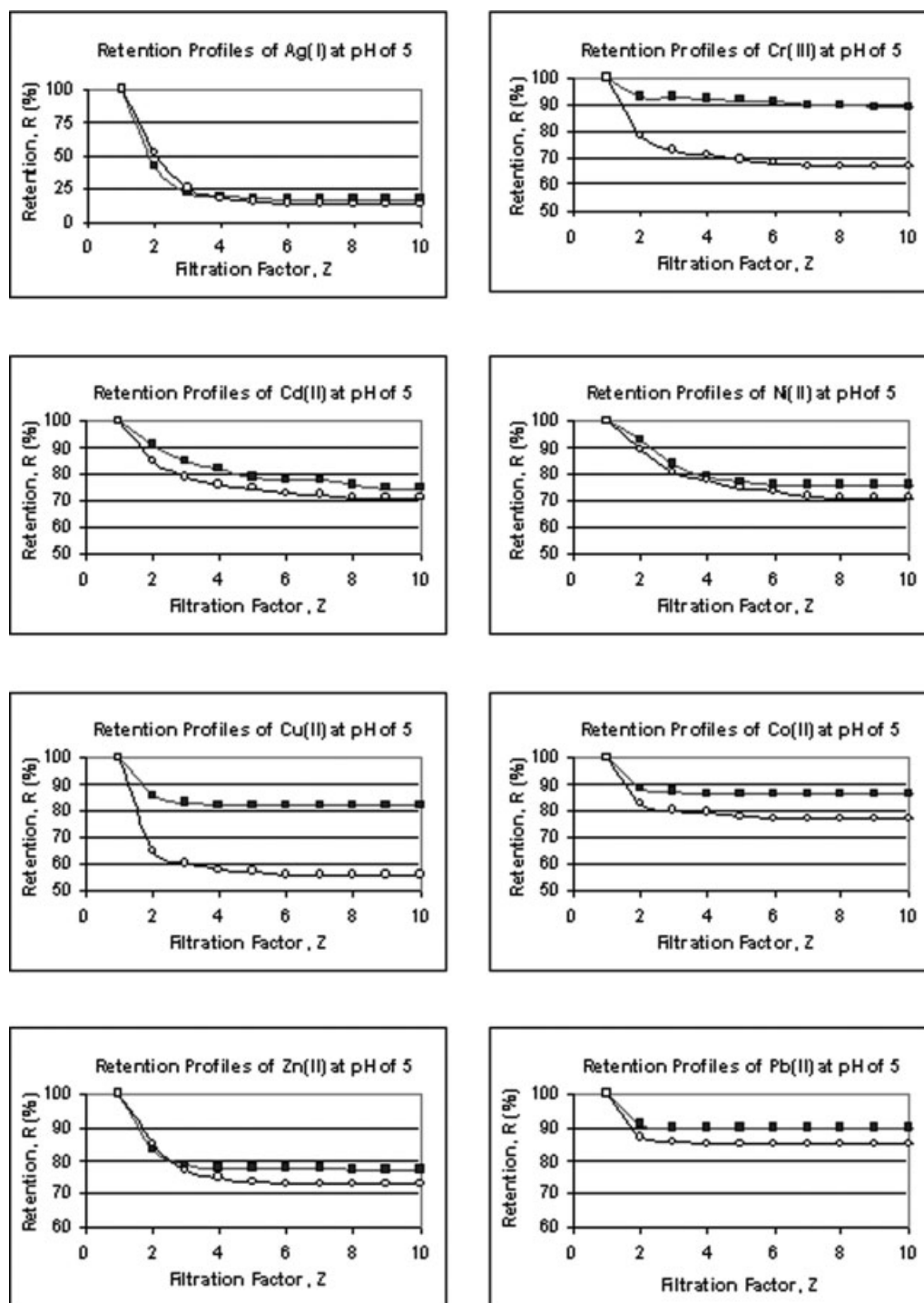


Figure 5 Retention Profiles of the polychelotogens, 5 (■) and 8 (○) with the standard metal ions at the pH value of 5.

pH of 1, 3, even 5 the acidic groups deprotonates and resulting carboxylates become strong nucleophile towards to the metal ions. At  $\text{pH} \leq 1$ , all the metal ions released the ligand and could be totally regenerated and only Cr(III) showed a retention more than 30% at  $Z = 10$ . At pH 3, the retentions

were higher than 50% for Cd(II), Cu(II), Ni(II), Co(II), and Zn(II) and 100% for Cr(III). Best complexations were performed at pH value of 5 for the divalent cations Co(II), Ni(II), Zn(II), Cd(II), and Pb(II), with retention values of close to 85% (see Fig. 5). Their retentions were very close to 90%. Only Ag(I)

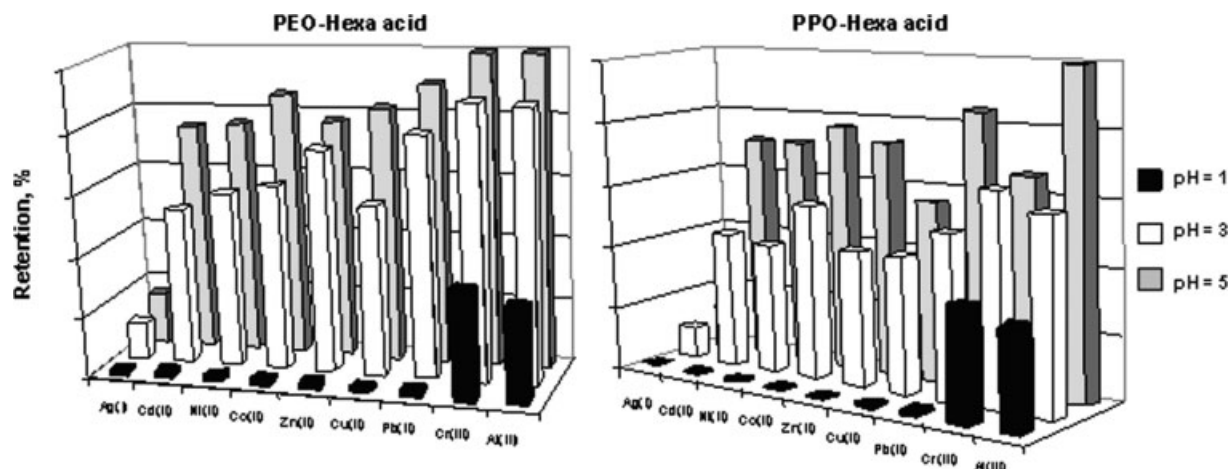


Figure 6 Retention Profiles of the Polychelators 5 and 8 at  $Z = 10$  and at the pH of 1, 3, and 5.

showed a weak interaction at this pH, (30% at  $Z = 10$ ), this was attributed to the monovalency of that metal ion. The retention curves versus pH values shown in Figures 5 and 6 reflect selectivity of the polymer against Co(II), Cu(II), Ni(II), Pb(II), Cu(II), and Zn(II). This is a large extend in accordance with the known chelating properties of carboxylated PEO and PPO.

## CONCLUSIONS

Novel metal chelating dendritic molecules have been synthesized by the surface reaction of PEO-DA 3 with dendritic aminotriester 2 and PPO-TA 6 with methylmetacrylate, and later both dendritic ester have been converted to carboxylic acid 5 and 8. The products have been characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, EA, and ESI-MS for the dendrons. Synthesized dendritic polychelators have been purified by dialysis depending on the solubilities either in water or methanol-water mixture. The metal binding properties of the polychelators were studied by LPR technique. The products were stable enough in acidic media. The regeneration of the metal loaded dendritic polychelator can easily be achieved by decreasing the pH of aqueous solution. In the case of copper, the metal ions bounded to the ligand can be released by applying sulfuric acid ( $\text{cH}_2\text{SO}_4 = 4 \text{ mol L}^{-1}$ ). Increasing the functional groups of dendrimers caused to increase in the ability in metal binding properties, but no linearity has been observed due to cumulative increases of carboxylic groups.

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