# Synthesis, Characterization, and Chelating Properties of the Polymacromonomer: Poly[(Ethyleneglycol) Methyl Ether Methacrylate]

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**ABSTRACT:** The radical polymerization of the macromonomer poly(ethyleneglycol) methyl ether methacrylate with ammonium persulfate at 60°C was carried out. The polymer was completely soluble in water. Yield was 75%. The polymacromonomer was characterized by Fourier transform infrared, proton nuclear magnetic resonance (NMR), and $^{13}$C NMR spectroscopy. $M_n$, $M_w$, and the polydispersity were determined by gel permeation chromatography. The polymacromonomer showed a high thermal stability with a TDT$_{50\%}$ of 420°C. The metal ion binding capacity of this polychelatogen with respect to different metal ions was investigated through the liquid-phase polymer-based retention (LPR) technique. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2929–2934, 2002

**Key words:** polymacromonomer; chelating properties; metal ions.

## INTRODUCTION

Recent progress in macromonomer synthesis, macromonomers polymerization, and characterization of branched polymers obtained and their applications appears to ensure continuing interest in designing and characterizing a variety of branched polymers and in their unique applications.[1–4]

A macromonomer is defined as a polymeric or oligomeric monomer with a polymerizable or copolymerizable functional group at one end. They afford a comb-shaped polymer with regularly and densely attached branches resulting from homopolymerization, as illustrated in Scheme 1. A formerly comb-shaped polymacromonomer may actually be forced to take a conformation that looks like a star as in Scheme 2, or a brush, as in Scheme 3, depending on the relative lengths of the macromonomer branch and the polymacromonomer backbone.

As macromonomers are already polymers with $\bar{M}_w$ between $10^3$ and $10^4$, their polymerization and copolymerization involve polymer–polymer reaction. Thus, a question of continuing concern has been how and why a macromonomer is different in its reactivity than a corresponding conventional monomer of low $\bar{M}_w$.

The aim of this article is to synthesize a polymacromonomer containing potential metal ion coordinating groups. Accordingly, the following metal ions; Ag(I), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Cr(III), are studied through liquid-phase polymer-based retention (LPR)[5–15] varying the pH and the filtration factor.

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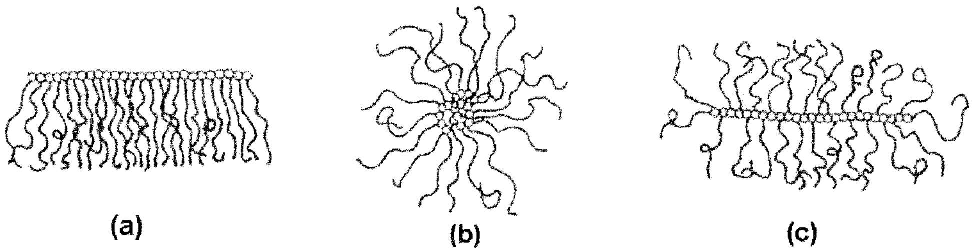


Scheme 1

## EXPERIMENTAL

### Reagents

Poly(ethyleneglycol) methyl ether methacrylate $\bar{M}_w$ 2080 (Aldrich) and ammonium persulfate (Merck) were used without further purification. The metal salts as nitrates (Merck, analytical grade) were used as received.

### Polymerization

The homopolymer was prepared by radical polymerization in water by using ammonium persulfate (APS) (0.2 mol%) as initiator reagent. The reaction mixture was kept at 60°C for 48 hours. The polymer was purified by ultrafiltration membranes with a cutoff 10,000 and 100,000 D and isolated by lyophilization. Yield was 75%. $TDT_{50\%}$ 420°C.

$(C_{95}H_{188}O_{47})_n$ $(2080)_n$ Calc. C 54.80 H 9.04 O 36.16

Found C 54.47 H 9.36 O 36.17

### Characterization

The Fourier transform infrared (FTIR), (KBr pellets), proton nuclear magnetic resonance ($^1H$ NMR) and $^{13}C$ NMR (250 MHz, $D_20$, 29°C) spectra were recorded on a Magna Nicolet 550 spectrophotometer and Bruker AC 250 P Multinucleous spectrometer, respectively. The polymer was purified by ultrafiltration (Amicon, membranes YM100, XM50 and PM10). The molecular weights were determined by gel permeation chromatography (GPC) in water with a Perkin Elmer Chromatograph with a refraction index detector. The thermal stability was studied under nitrogen with a Polymer Laboratories STA 625 Thermoanalyzer. For the LPR technique, a membrane filtration system was employed to investigate the coordinating properties of the polychelatogen. A Unicam Solaar M5 Atomic Absorption Spectrometer was used for the determination of the metal ions in the filtrate.

### Procedure

The aqueous solution of polymacromonomer (0.2 m*M*) and metal salt (nitrates) (0.05 m*M*) was placed into the cell. The total volume in the cell was kept constant at 20 mL. A membrane with a molecular mass cutoff of 5,000 D (Filtron) was used. The system was pressurized (300 Kpa), and the cell solution was stirred and then washed in reservoir fluid at the same pH. The filtration fractions ($Z$ = 1–10) were collected, and the concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy.

**Table I Molecular Weight Distribution and Polydispersity of the Different Fractions of Polymacromonomer (Solvent: Water, temperature 20°C, Amount of Sample: 50.0 mg)**

| Molecular Mass Cutoff | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| > 100,000 D | 288.597 | 52.259 | 5.522 |
| < 100,000 > 50,000 D | 251.097 | 51.920 | 4.836 |
| < 50,000 > 100.00 D | 223.598 | 59.368 | 3.749 |

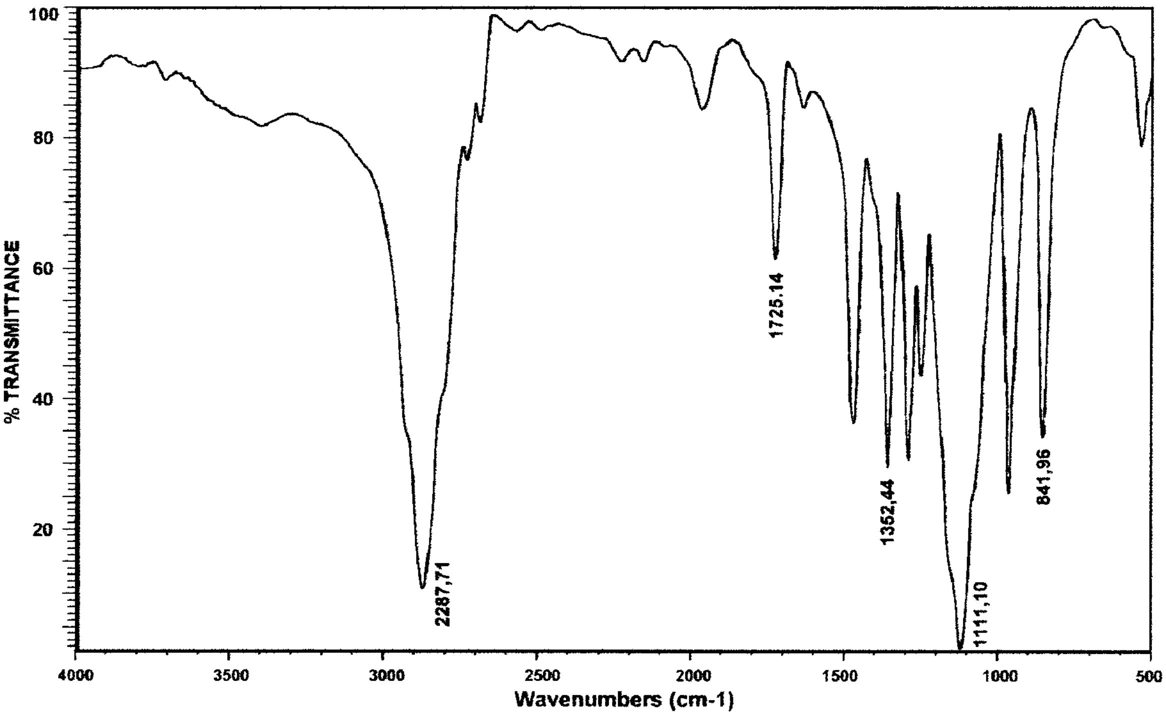
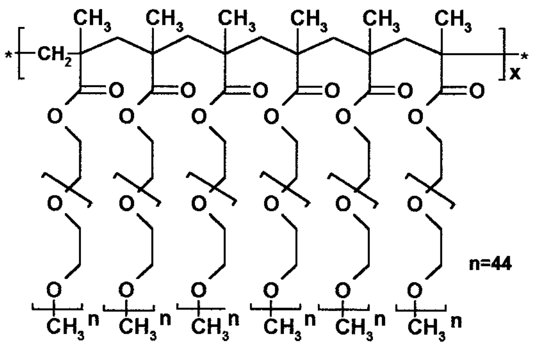


**Figure 1** Fourier transform infrared (KBr pellets) spectrum of the polymacromonomer.

## RESULTS AND DISCUSSION

The polymacromonomer was synthesized by radical solution polymerization, using ammnium persulfate as the initiator.



The polymerization yield was 75%. The polymacromonomer was fractionated by LPR technique by using ultrafiltration membranes with different molecular mass cutoff (see Table I). The $\bar{M}_n$ and $\bar{M}_w$ for the different molecular mass cutoff (MMCO) of the membranes were determined by GPC (tetrahydrofurane, 20°C). Increases in the MMCO increases the molecular weight and the polydispersity (see Table I). The polymacromonomer shows a high polydispersity, $\bar{M}_w/\bar{M}_n$, which ranged between 5.52 and 3.75. The smallest value corresponds to the fraction with MMCO $< 50{,}000 > 10{,}000$ D.

The FTIR spectrum (KBr pellets) demonstrated that the polymerization occurred as result of the decrease in the intensity of the double-bond absorption signal. Among the most characteristic absorption bands are at (in $\text{cm}^{-1}$) 2,888 (s C–H), 1,720 (s O–C=O), 1,111 (s $CH_2$–O–$CH_2$) (see Fig. 1). All the expected signals for the polymacromonomer are present in the $^1$H NMR and $^{13}$C NMR spectra; $^1$H NMR ($D_2O$, TMS as reference, in ppm) shows the most important absorption signals at $\delta$ = 4.22 (C=O–O–C**H₂**), 3.82 (C=O–O–$CH_2$–C$\mathbf{H_2}$), 3.66 (O–C$\mathbf{H_2}$–C$\mathbf{H_2}$–O), 3.34 (O–C$\mathbf{H_3}$), 1.82 (C–C$\mathbf{H_2}$), and 1.46 (C–$CH_3$). $^1$H NMR spectrum shows a strong decrease in the vinyl protons (see Fig. 2). $^{13}$C NMR spectrum ($D_2O$, TMS as reference, 29°C, in ppm) shows all the expected carbon signals at $\delta$ = 170 (**C**=O, ester), 71 (O–**C**$H_2$–$CH_2$–O), 66 (C=O–O–**C**$H_2$), 59 (O–**C**$H_3$), and 19 ($CH_3$).

The polymacromonomer shows a high thermal stability that is slightly higher in respect to the

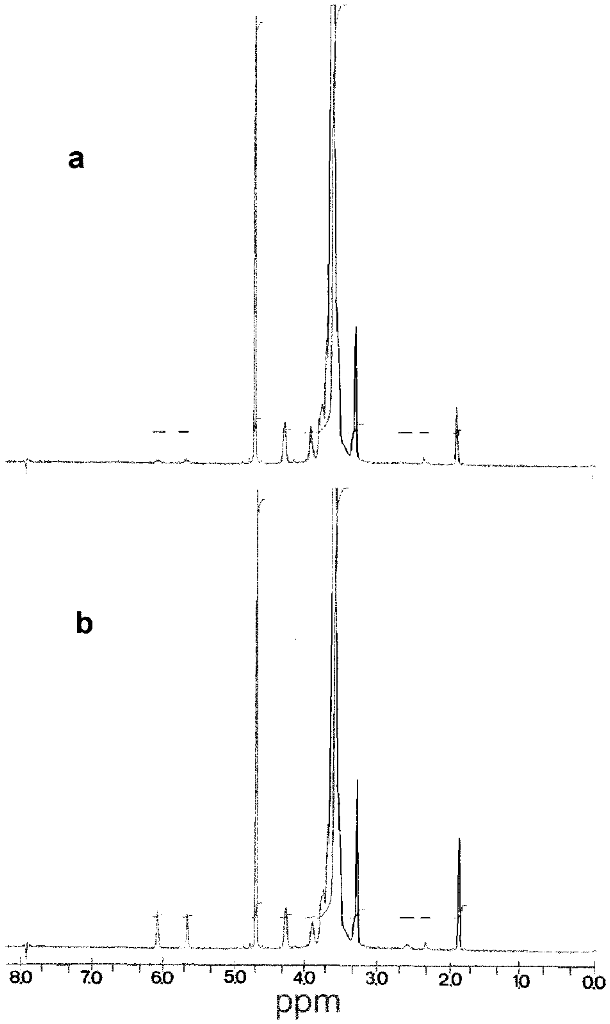


**Figure 2** Proton nuclear magnetic resonance spectra of the (a) macromonomer and (b) polymacromonomer ($D_2O$, 29°C, internal standard).

macromonomer. Up to 300°C the weight lost is lower than 10% of the total. The $TDT_{50\%}$ (temperature at which loss is 50% of the weight) is 420°C, which is higher than that of the macromonomer $TDT_{50\%}$ at 395°C (see Table II).

The polymacromonomer shows also a high chemical stability in an acid medium. Hydrolysis of the ester function up to pH 7 was not observed.

To investigate the metal ion binding capability of the polymacromonomer for different di- and trivalent metal cations, the MMCO $< 100{,}000$ $> 50{,}000$ D which corresponds to $\bar{M}_n = 51{,}920$, $\bar{M}_w = 251{,}097$, and polydispersity $= 4.8$.

The ability of the polymer to interact with the metal ions shows a strong dependence on the pH and filtration factor $Z$. $Z$ is defined as the ratio between the volume in the filtrate ($V_i$) and the volume in the cell ($V_o$). It is reported that the polyethers form “wrapped” complexes with mono- and divalent metal cations. At pH = 1, the retention is lower than 10%, but as the pH increases, the metal ion retention increases. A pH ranging between 3 and 5 should be the most appropriate for the formation of metal complexes for the majority of metal ions. The highest retention value (c.a. 60%) was observed at pH = 5 for all the metal ions investigated except for Cr(III), which precipitates at this pH (see Table III).

The retention behavior at pH = 3 is very relevant. Only Ni(II) is significantly retained, at 60%, respective to all other metal ions (lower than 10%) for all the filtration factor values (see Fig. 3). The polymacromomomer was not reused as polychelatogen.

The interaction with the metal ions occurs through the oxygen atom. The most important

**Table II Thermal Behavior of the Macromonomer and the Polymacromonomer at Different Temperatures (°C)**

| | Weight loss (%) | |
|---|---|---|
| Temperature (°C) | Polymacromonomer | Macromonomer |
| 22 | 0.0 | 0.0 |
| 100 | 0.0 | 0.0 |
| 200 | 0.0 | 0.0 |
| 300 | 0.0 | 0.0 |
| 400 | 29.5 | 50.3 |
| 500 | 96.3 | 94.5 |
| 550 | 96.8 | 95.7 |

**Table III Metal ion retention (%) at different pH and filtration factor (*Z*)**

| Metal Ion | Ag(I) | | Cd(II) | | Co(II) | | Cu(II) | | Ni(II) | | Zn(II) | | Pb(II) | | Cr(III) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Z/pH | 3 | 5 | 3 | 5 | 3 | 5 | 3 | 5 | 3 | 5 | 3 | 5 | 3 | 5 | 3 | 5[a] |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | — |
| 1 | 51.3 | 77.6 | 50.4 | 76.2 | 47.6 | 77.5 | 47.7 | 76.5 | 72.0 | 77.1 | 51.2 | 80.0 | 48.5 | 76.0 | 58.6 | — |
| 2 | 31.0 | 70.7 | 19.9 | 67.3 | 18.7 | 67.8 | 19.4 | 67.2 | 61.9 | 67.6 | 21.3 | 63.0 | 19.0 | 65.6 | 31.9 | — |
| 3 | 26.1 | 66.6 | 9.1 | 62.4 | 8.5 | 62.2 | 8.9 | 62.3 | 57.1 | 62.1 | 10.5 | 58.2 | 8.8 | 59.7 | 20.1 | — |
| 4 | 22.7 | 64.5 | 4.5 | 59.9 | 3.8 | 58.9 | 3.8 | 59.6 | 54.7 | 58.6 | 5.9 | 55.5 | 3.5 | 56.2 | 13.3 | — |
| 5 | 20.0 | 63.6 | 2.3 | 58.3 | 1.4 | 56.9 | 1.5 | 58.0 | 53.2 | 56.5 | 3.4 | 54.0 | 1.5 | 54.2 | 8.1 | — |
| 6 | 17.6 | 63.2 | 1.0 | 57.0 | 0.0 | 55.3 | 0.0 | 56.8 | 53.2 | 54.9 | 1.7 | 52.9 | 0.0 | 52.6 | 4.1 | — |
| 7 | 14.4 | 62.9 | 0.4 | 56.3 | 0.0 | 54.4 | 0.0 | 55.9 | 53.2 | 53.9 | 1.0 | 52.2 | 0.0 | 51.2 | 1.7 | — |
| 8 | 11.7 | 62.5 | 0.1 | 55.8 | 0.0 | 53.5 | 0.0 | 55.1 | 53.2 | 52.9 | 0.5 | 52.0 | 0.0 | 50.2 | 0.0 | — |
| 9 | 9.2 | 62.2 | 0.0 | 55.5 | 0.0 | 52.5 | 0.0 | 54.2 | 53.2 | 51.9 | 0.2 | 51.7 | 0.0 | 49.3 | 0.0 | — |
| 10 | 6.9 | 61.9 | 0.0 | 54.8 | 00 | 51.6 | 0.0 | 53.4 | 53.2 | 50.9 | 0.0 | 51.4 | 0.0 | 48.3 | 0.0 | — |

[a] Not determined as Cr(III) precipitates at this pH.

specie of nickel at pH = 3 is $Ni^{2+}$ and a very low content of NiOH, which increases at pH = 5. In addition, Ni(II) forms stable complexes with coordination index 4, which is difficult to oxidize.

## CONCLUSIONS

The macromonomer poly[(ethyleneglycol) methyl ether methacrylate)] (Mn 2080) was polymerized by radical polymerization using ammonium persulfate. This compound was completely water soluble and showed a broad molecular weight distribution. It showed a high thermal stability with a $TDT_{50\%}$ of 420°C. The metal ion retention properties studied by LPR technique showed a high pH dependency, with the pH range of 3–5 being the most appropriate. This polymeric material showed a high selectivity to Ni(II) ions at pH = 3 with respect to other divalent metal ions, such as Cu(II), Co(II), Cd(II), Zn(II), and Pb(II). The polychelatogen–Ni(II) interaction was stable during all the filtration factors *Z*, studied.

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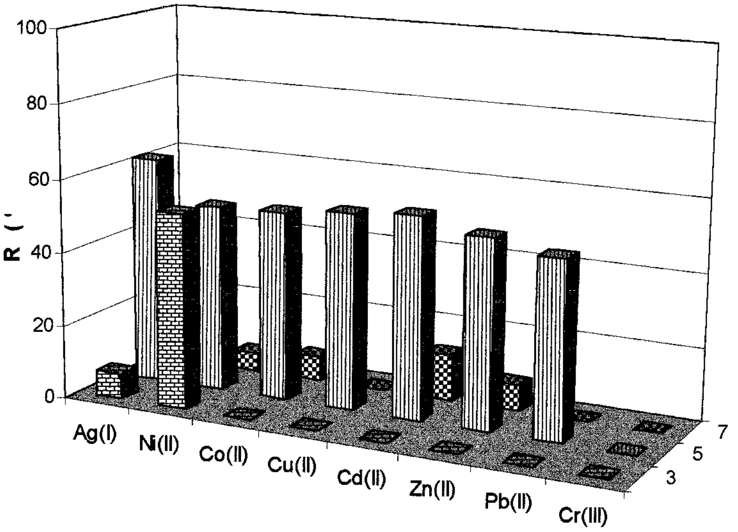

**Figure 3** Retention (%) of polymacromonomer for the metal ions at different pH and filtration factor *Z* = 10.

## REFERENCES

1. Ito, K.; Kawaguchi, S. Adv Polym Sci 1999, 142, 129.
2. Ito, K. Progr Polym Sci 1998, 23, 581.
3. Gnanou, Y.; Lutz, P. Macromol Chem Phys 1989, 190, 577.
4. Rempp, P. F.; Franta, E. Adv Polym Sci 1984, 58, 1.
5. Rivas, B. L.; Geckeler, K. E. Adv Polym Sci 1992, 102, 171.
6. Beauvais, R. A.; Alexandratos, S. D. Reactive Polym. 1998, 36, 113.
7. Geckeler, K. E.; Zhou, R.; Fink, A.; Rivas, B. L. J Appl Polym Sci 1996, 60, 2191.
8. Geckeler, K. E.; Bayer, E.; Spivakov, B. Ya.; Shkinev, V. M.; Vorobeva, G. A. Anal Chim Acta 1986, 189, 285.
9. Geckeler, K. E.; Zhou, R. Naturwissenschaften 1993, 75, 198.
10. Spivakov, B. Ya.; Geckeler, K. E.; Bayer, E. Nature 1985, 315, 313.
11. Bayer, E.; Eberhardt, H.; Grathwohl, P. A.; Geckeler, K. E. Israel J Chem 1985, 26, 40.
12. Rivas, B. L.; Pooley, S. A.; Soto, M.; Maturana, H. A.; Geckeler, K. E. J Appl Polym Sci 1998, 67, 93.
13. Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. J Polym Sci Part A Polym Chem 1997, 35, 2461.
14. Rivas, B. L.; Moreno-Villoslada, I. J Phys Chem 1998, 102, 6994.
15. Rivas, B. L.; Moreno-Villoslada, I. Macromol Chem Phys 1998, 199, 1153.
16. Rivas, B. L.; Pereira, E. Bol Soc Chil Quim 2000, 45, 259.