

Synthesis of *N*-Polyetheral Polypyrroles and Their Application for the Preconcentration of Rare Earth Ions

Bahar Köksel,¹ Atilla Cihaner,² Murat Kaya,¹ Mürvet Volkan,¹ Ahmet M. Önal¹

¹Department of Chemistry, Middle East Technical University, İnönü Bulvarı, 06531 Ankara, Turkey

²Chemistry Group, Faculty of Engineering, Atılım University, Incek, 06836 Ankara, Turkey

Received 17 August 2007; accepted 12 November 2007

DOI 10.1002/app.27781

Published online 21 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Conducting polymers containing polyether pseudocages (PI, PII, PIII) have been synthesized via chemical oxidation of 1,5-bis(1,1-pyrrole)-3-oxabutane (MI), 1,8-bis(1,1-pyrrole)-3,6-dioxahexane (MII), and 1,11-bis(1,1-pyrrole)-3,6,9-trioxaundecane (MIII) using anhydrous FeCl₃ in CHCl₃. Because as obtained polymer resins did not give any response toward any cations, they were reduced (undoped) using chemical reducing agents. Tetrabutylammonium hydroxide was found to be more effective in undoping to obtain more reproducible and reusable polymer resins. The undoped polymer resins were tried in the extraction of rare earth metal ions from the aqueous medium. Among them,

only PIII resin removes La(III), Eu(III) and Yb(III) and can be employed for the preconcentration of these metal ions. For batch extraction of La(III), Eu(III) and Yb(III) at neutral pH values, percent recoveries of 98.0 ± 1.0 , 90.7 ± 1.4 , 87.3 ± 4.0 , respectively, has been obtained. The sorption capacity is found as 1.3 mg of La(III) per gram of PIII resin. The PIII resin could be reused at least five times without significant change in its sorption capacity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2707–2711, 2008

Key words: chemical polymerization; preconcentration; rare earth elements; polypyrrole; crown ether

INTRODUCTION

Monocyclic polyethers called crown ethers are well known molecular hosts, able to complex alkali and alkaline earth cations, transition metal cations, and ammonium cations.^{1,2} The selective binding of guest molecules to conducting polymers can be a suitable approach for the extraction of cations. Therefore, considerable research has been devoted to polythiophenes substituted with crown ethers and/or polyether chains in the design of modified electrodes.^{3–8} In comparison to polythiophenes, the functionalization of polypyrroles with crown ethers for molecular recognition has been much less exploited due to the difficulties in their syntheses. Only few studies are reported. For example, benzocrown ether and azocrown ether substituted polymers **1**⁹ and **2**¹⁰ were synthesized, respectively but none of them showed any recognition toward alkali metal cations (see Scheme 1). On the other hand, azocrown ether substituted polymer **3**¹⁰ had minor voltammetric response toward Na⁺ and K⁺ in organic medium; unfortunately, the replacement of Li⁺ by those ions was found to be irreversible. Furthermore, most of

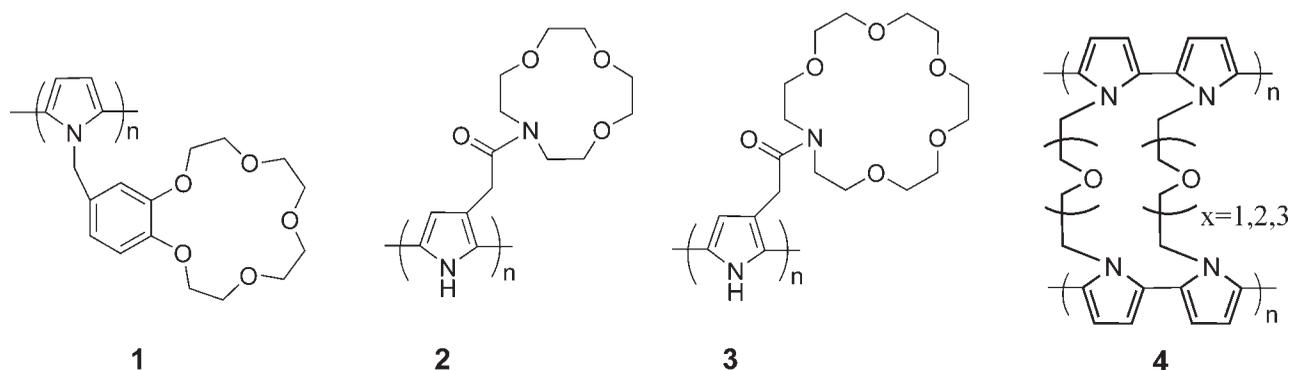
the polymers with crown ether appendages have solubility problems and water incompatibility.

Simonet et al. have recently synthesized monomers containing two pyrrolyl units linked by different length of polyether chains (see Scheme 1).¹¹ Macrocyclic cavities could be achieved via anodic polymerization, however, for the large scale synthesis of the polymer **4** an industrial type cell was needed. The complexing properties of such polymers have been investigated and a strong affinity toward Co²⁺, Cs⁺, K⁺, and Ag⁺ cations was reported. Recently, Cihaner synthesized *N*-polyetheral polypyrroles via anodic oxidation of corresponding monomer and its copolymer with pyrrole.^{12,13}

With the rapid growth of high technology sectors, the use of rare earth elements (REE) in various industrial activities and applications such as superconductors, lasercrystals, advanced ceramic materials, supermagnets, and nuclear technology has increased substantially. They are also employed in the manufacture of corrosion resistance materials, in the design of heat storage and dispersal systems, some polymerization processes and in agriculture. The precise determination of these elements is therefore very important. Whenever the concentration of the element to be determined is below the detection limit of the measurement technique, a preconcentration step is required. The enrichment techniques generally employed for the rare earth elements are liquid–liquid extraction,¹⁴ ion exchange,^{15,16} coprecipitation,^{17–20} and solid phase extraction.²¹

Correspondence to: A. M. Önal (aonal@metu.edu.tr)

Contract grant sponsor: TÜBİTAK; contract grant number: 104T423.



Scheme 1

The aim of this study is to obtain *N*-polyethereal polypyrroles in large scale via chemical polymerization and to investigate their performance for the pre-concentration of La(III), Eu(III), and Yb(III) from aqueous medium.

EXPERIMENTAL

Materials and methods

For spectroscopic determination of the REEs, an ICP-OES setup was used (Direct Reading Echelle, Leeman Labs). The instrument was operated applying an incident plasma power of 1.2 kW, with the plasma gas (Ar) coolant flow rate at 18 L min⁻¹, the auxiliary Ar flow at 0.5 L min⁻¹, and the nebulizer Ar flow set at 50 psi. The sample was transported to the nebulizer using a peristaltic pump with the pump flow rate set to 1.2 mL min⁻¹. Quantitative evaluations were based on peak height measurements. FTIR spectra of monomers and their polymers were taken with a Bruker Vertex 70 Spectrophotometer using KBr pellets.

La(III), Yb(III), Eu(III), Li(I), and Na(I) concentrations were determined at the following emission wavelengths: 333, 749 nm for La, 328, 937 nm for Yb, 381, 967 nm for Eu, 588, 995 nm for Na, 670, 784 nm for Li. For the batch sorption studies Nüve SL 350 model shaker was used to provide efficient mixing. Resin was filtered out on a vacuum filter Advantec MFS. For filtration Whatman No. 41 filter paper was used.

All reagents were of analytical grade. DI water was obtained from a Millipore water purification system. Glacial Acetic Acid (100%) used for buffer solution preparation was acquired from Merck KGaA Darmstadt, Germany. Other buffer solutions of pH 4 (citrate), pH 5 (phosphate), pH 8 (phosphate), and pH 10 (borate) were obtained from Fisher Scientific, Leicestershire, UK. Stock solutions (1000 mg L⁻¹) of La(III), Yb(III), Eu(III), Li(I), and Na(I) were obtained from Ultra Scientific, RI. Tetrabutylammonium hydroxide

(TBAOH; 0.1M) solution in diluted methanol and propanol were supplied from Merck KGaA Darmstadt, Germany. *N*-polyethereal pyrroles were synthesized according to a general procedure already described.¹¹ FeCl₃, chloroform, methanol, and ether were purchased from Aldrich.

Chemical polymerization of *N*-polyethereal polypyrrole resins

The polymers were synthesized according to a general procedure.²² The related monomer was dissolved in dry CHCl₃ (dried over MgSO₄) and a suspension of anhydrous FeCl₃ in CHCl₃ was added to the monomer solution for 1 h at 0°C. The reaction was performed under Ar atmosphere to remove the generated HCl as well as to keep the iron catalyst in its active Fe³⁺ oxidation state. The final concentration for the monomer and FeCl₃ was 0.05M and 0.4M, respectively. When the addition was complete, the mixture was stirred for 24 h at room temperature and the reaction mixture was poured into methanol, and polymer was precipitated. The precipitate was filtered and washed with methanol and ether, respectively, using Soxhlet apparatus. The black solid product was then dried under vacuum at 50°C.

Uptake measurements and recovery characteristics

Because as obtained polymer resins did not exhibit any affinity toward REE ions, they are reduced (undoped), prior to uptake studies, using 0.1M TBAOH solution. To assess the time required for the complete reduction of resin, six different batches were prepared. For each batch, 100 mg resin was suspended in 10.0 mL of 0.1M TBAOH solution and equilibrated at various (1, 2, 3, 4, 6, and 10 days) times. Then, they were washed with methanol and ether, respectively. Finally, the brown powders obtained were dried under Ar atmosphere and used for the uptake and recovery measurements.

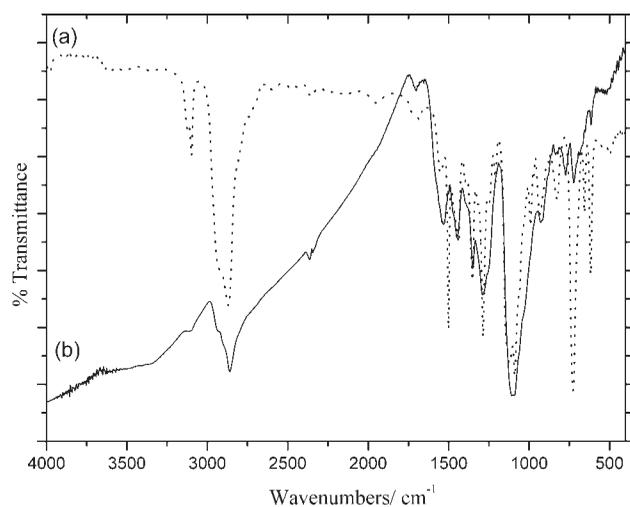


Figure 1 FT-IR spectra of (a) monomer MIII and (b) its polymer PIII.

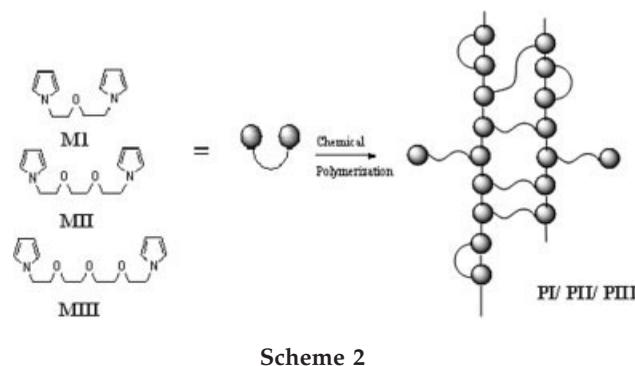
To measure the time required for the system to reach equilibrium, batch equilibration of 3 and 0.4 mg L⁻¹ solutions of La(III), Yb (III), and Eu(III) with 0.05 g resin were carried out up to 6 h for uptake studies. The pH dependence of the metal uptake was examined by batch equilibration of the resin with buffer solutions at pH values of 2, 4, 5, 8, and 10. For this purpose, 0.05 g resin was suspended in 10 mL buffer solutions containing 2 mg L⁻¹ La(III) and was equilibrated by gentle agitation. The resin was filtered out and the supernatant solution was analyzed for the metals using ICP-OES technique.

The metal binding parameters for the resin were appraised using standard aqueous solutions. The batch procedure was accomplished by equilibrating 0.05 g of the PIII resin with two different concentrations (3.0, 0.4 mg L⁻¹) of the metal (La (III), Yb (III), Eu(III)) solutions. The pHs of the solutions were monitored and found to remain within pH 5–10. The equilibration time was set as 3 and 6 h for 3.0 and 0.4 mg L⁻¹ concentrations of metal solutions, respectively. Afterward, the supernatant was separated from the resin and monitored for the metal concentrations by ICP for uptake studies. The adsorbed metals were recovered from the resin with 2M HNO₃ and determined by ICP-OES for the recovery studies. For investigation of sorbent capacity, 10 mL of 10 mg L⁻¹ La (III) solution was equilibrated with 0.05 g PIII resin for 2 h. The adsorbed La (III) ions were stripped from the resin with 2M HNO₃ and determined by ICP-OES.

RESULTS AND DISCUSSION

Characterization of polymer

The FTIR spectrum of the PIII polymer (Fig. 1) is consistent with the expected structure. The peaks at



2864 and 1096 cm⁻¹ are assigned to the methylene and etheric groups, respectively and they remain unchanged upon polymerization, which indicates that the polyetheric bridges between the pyrrole rings are not broken (see Scheme 2). The disappearance of the band at 726 cm⁻¹ and 3101 cm⁻¹ also confirms that the polymerization is carried out mainly via 2,5-coupling (α,α' -coupling). PI and PII have also similar FTIR spectra.

Optimization of extraction conditions

Because as obtained polymers did not give any response toward any cations, they were reduced (undoped) using chemical reducing agents. For this purpose, a reducing agent containing a cation, such as tetraalkylammonium, which can be replaced by other cations was preferred. As shown previously,¹¹ tetrabutylammonium cation in the resin has a rather fast exchange capability of cations between the solid and the liquid phases. Polymers were used as cation exchanger resins after achieving undoping process using TBAOH. To find the optimum time for the

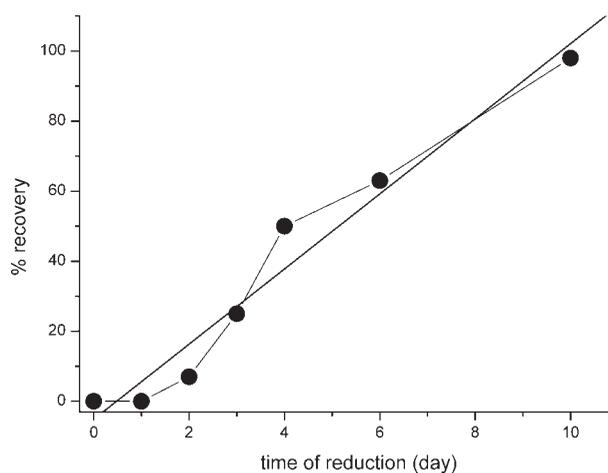


Figure 2 Change in the percent recovery for the extraction of 0.4 mg L⁻¹ La(III) solution by PIII resin depending on the span of undoping (reduction) process of conducting polymer PIII with 0.1M TBAOH.

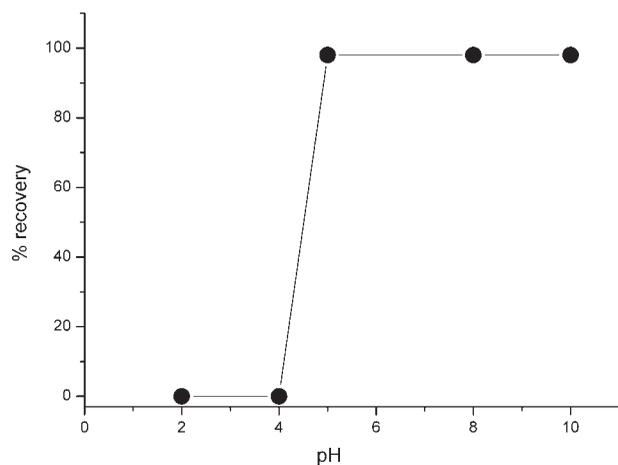


Figure 3 Batch equilibration of 2 mg L^{-1} La(III) with 0.05 g PIII resin as a function of pH. Equilibration time was 2 h.

reduction, conducting polymer PIII was undoped (reduced) at various times (1, 2, 3, 4, 6, and 10 days) using TBAOH. The capabilities of these PIII resins for the extraction of La(III) from aqueous solutions were then examined (see Fig. 2).

As can be seen from Figure 2, the 100% recovery of La(III) was achieved with the resin reduced in 10 days with 0.1 M TBAOH. Therefore, in the chemical preparation of resins for metal cation extraction studies, duration of reduction (undoping) was chosen as 10 days.

To optimize batch equilibration time 3.0 and 0.4 mg L^{-1} solutions of La(III), Yb (III), and Eu(III) with 0.05 g resin were carried out up to 6 h for uptake studies. The rate of the equilibration of PIII resin with REE ions was found to be rather slow. 4 h of shaking was needed for batch type extraction of 3.0 mg L^{-1} metal ion concentration. The uptake rate becomes even slower (6 h) at a concentration of 0.4 mg L^{-1} . However, aqueous solutions of these ions are stable and they do not undergo any observable change during lengthy periods of shaking. The long span of equilibration does not affect percent recoveries.

Batch equilibration studies of the partition of La (III) between PIII resin and solutions having various acidities showed that this metal was taken up almost 100% by the PIII resin over a pH range of 5–10 (Fig. 3). As expected, the percent recovery values changes in a way similar to the extraction of Yb(III) and Eu(III) with PIII resin, depending on the pH.

Potentially suitable eluting acids like HCl and HNO_3 were tried to recover the adsorbed REE ions. Because the yields using 2 M HNO_3 were higher than 95%, this acid was selected as the eluent for further work.

In the present study, the extraction efficiencies of PIII resin for La(III), Yb (III), and Eu(III) have been examined for a concentration range of 3.0 – 0.4 mg L^{-1} . The results are shown in Table I. High recoveries obtained for investigated concentrations indicate that, successful preconcentration of REE from aqueous solutions was possible with PIII resin. For La(III) ions, even lower concentrations were investigated. Recovery values of 98% and 75.5% were obtained for 0.1 and 0.04 mg L^{-1} concentrations of La(III) ions, respectively. Thus, the investigated resin might have significant analytical potential in the fields of trace determination of REE from natural waters.

Because the capacity of the sorbent is also an important factor that determines how much sorbent is required for quantitative removal of a specific amount of metal ion from the solution, the sorption capacity of the PIII resin is also measured. The sorption capacity of the PIII resin under optimum conditions is found as 1.3 mg of lanthanum per gram of PIII resin.

Regeneration of PIII resin

To assess the extent to which the performance of the PIII resin deteriorates following elution with 2 M HNO_3 , the same resin was employed for five consecutive loading/elution cycles for La(III). Of course, after each use the resin was reduced with TBAOH to regenerate its sorption capacity.

TABLE I
La(III), Yb(III), and Eu(III) Recoveries Obtained by Using PIII Resin

Cations	Spiked concentration (mg L^{-1})	Initial volume (mL)	Final volume (mL)	Enrichment factor	% Recovery	% Uptake
La	3	10	10	1	91.4 ± 4.8	99.1 ± 0.75
	0.4	40	8	5	98 ± 1	100
	0.1	40	8	5	98 ± 3	100
	0.04	100	5	50	75.5 ± 2	<DL
Eu	3	10	10	1	90.7 ± 1.4	99.9 ± 0.22
	0.4	40	8	5	90.5 ± 1.2	100
Yb	3	10	10	1	90.7 ± 3.1	99.9 ± 0.05
	0.4	40	8	5	87.3 ± 4.0	100

Recovery and up-take results are the average of three individual measurements.

TABLE II
La(III) Recoveries Obtained During the Successive Usage of PIII Resin

Number of loading/elution cycle	% Recovery	% Uptake
1st	96.0	100
2nd	96.0	100
3rd	97.3	100
4th	91.4	98.5
5th	90.0	100

As can be seen from Table II, excluding fourth loading/elution cycle result, the uptake values are all 100%. Although the percent recovery values show slight decrease at fourth and fifth loading/elution cycles of the PIII resin, they are still at acceptable levels for a preconcentration work ($\geq 90\%$).

Comparison of N-polyetheral polypyrrole (PI, PII, PIII) resins for the preconcentration studies

The undoped polymer resins PI and PII were also tried in the extraction of REE ions from aqueous medium and the results are tabulated in Table III. As seen from Table III, the percentage recovery values for PI and PII are almost eight times lower than that of PIII. This might indicate the presence of cavities with different sizes on the polymer backbone (see Scheme 2) which is contradictory to the polymer structure with uniform cavity size (polymer 4) suggested by Simonet et al.¹¹ To further investigate the significance of cavity size, the binding ability of PIII resin for Li(I) and Na(I) were studied. The results are depicted in Table IV.

As seen from Table IV, cavity size seems to be an important factor in determining the selectivity of the resin. While Li (I) was poorly adsorbed (recovery is 6%), Na(I) having larger ion size was taken up (recovery is 95%) by resin PIII effectively.

CONCLUSIONS

Chemical oxidation of the monomers (MI), (MII), and (MIII) containing polyetheral linkages has been successfully achieved yielding polymers PI, PII, and

TABLE III
La(III) Recoveries Obtained by Using N-Polyetheral Polypyrrole Resins (PI, PII, and PIII)

Type of resin	Initial volume (mL)	Final volume (ml)	Enrichment factor	% Recovery
PI	40	8	5	14
PII	40	8	5	12
PIII	40	8	5	98

TABLE IV
Li(I) and Na(I) Recoveries Obtained by Using PIII Resin

Spiked concentration	Initial volume (mL)	Final volume (mL)	Enrichment factor	% Recovery
0.4 mg L ⁻¹ Li(I)	40	8	5	6
0.4 mg L ⁻¹ Na(I)	40	8	5	95

PIII with pseudocages. FTIR spectra of the polymers indicate that polyether groups remain unchanged as in the case of their synthesis via electrochemical initiation.¹² The presence of these cages makes the newly synthesized N-polyetheral polypyrrole resins an effective solid phase complexing agent for trace quantities of lanthanum, europium and ytterbium ions. High recovery values obtained at low concentrations of these ions have shown that this novel resin represents a promising material for the preconcentration of REE ions from aqueous medium over a wide pH range.

References

- Pedersen, C. J. *J Am Chem Soc* 1967, 89, 7017.
- Pedersen, C. J. *Angew Chem Int Ed Engl* 1988, 27, 1021.
- Fabre, B.; Simonet, J. *Coord Chem Rev* 1998, 178–180, 1211.
- Roncali, J. *Chem Rev* 1992, 92, 711.
- Higgins, S. J. *Chem Soc Rev* 1997, 26, 247.
- Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J Mater Chem* 1999, 9, 1957.
- Tyler, D.; Pullen, A. E.; Swager, T. M. *Chem Rev* 2000, 100, 2537.
- Si, P.; Chi, Q.; Li, Z.; Ulstrup, J.; Møller, P. J.; Mortensen, J. *J Am Chem Soc* 2007, 129, 3888.
- Bartlett, P. N.; Benniston, A. C.; Chung, L.-Y.; Dawson, D. H.; Moore, P. *Electrochim Acta* 1991, 36, 1377.
- Yousoufi, H. K.; Hmyene, M.; Garnier, F.; Delabouglise, D. *J Chem Soc Chem Commun* 1993, 1550.
- Simonet, J.; Gache, Y.; Simonet-Gueguen, N.; Leclerc, O. *Denki Kagaku* 1994, 62, 1211.
- Cihaner, A. *J Macromol Sci Pure Appl Chem* 2006, 43, 1379.
- Cihaner, A. *J Electroanal Chem* 2007, 605, 8.
- Xu, Z.; Liu, C.; Zhang, H.; Ma, Y.; Lin, S. *Anal Sci* 2003, 19, 1625.
- Zhu, W.; de Leer, E. W. B.; Kennedy, M.; Alaerts, G. J. F. R.; Fresenius, J. *Anal Chem* 1998, 360, 74.
- Rimskaya-Korsakova, M. N.; Dubinin, A. V.; Ivanov, V. M. *J Anal Chem* 2003, 58, 870.
- Yokoyama, T.; Makishima, A.; Nakamura, E. *Chem Geol* 1999, 157, 175.
- Lakshatanov, L. Z.; Stipp, S. L. S. *Geochim Cosmochim Acta* 2004, 68, 819.
- Taicheng, D.; Hangting, C.; Xianjin, Z. *J Anal At Spectrom* 2002, 17, 410.
- Liu, X.; Byrne, R. H.; Schijf, J. *J Solution Chem* 1997, 26, 1187.
- Wang, Z.; Yan, X.; Wang, Z.; Zhang, Z.; Liu, L. *J Am Soc Mass Spectrom* 2006, 17, 1258.
- Anderson, M. R.; Selse, D.; Berggren, M.; Jarvinen, H.; Hjertberg, T.; Inganas, O.; Wennerstrom, O.; Österholm, J.-E. *Macromolecules* 1994, 24, 6503.