

# Aqueous Solution and Solid State Interactions of Lanthanide Ions with a Methacrylic Ester Polymer Bearing Pendant 15-Crown-5 Moieties

F. RUBIO,<sup>1</sup> F. GARCÍA,<sup>1</sup> H. D. BURROWS,<sup>2</sup> A. A. C. C. PAIS,<sup>2</sup> A. J. M. VALENTE,<sup>2</sup> M. J. TAPIA,<sup>1</sup> J. M. GARCÍA<sup>1</sup>

<sup>1</sup>Departamento de Química, Universidad de Burgos, Plaza Misael Bañuelos s/n, Burgos 09001, Spain

<sup>2</sup>Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Received 18 July 2006; accepted 11 December 2006

DOI: 10.1002/pola.21946

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

**ABSTRACT:** The interaction between trivalent lanthanide ions and poly(1,4,7,10,13-pentaoxacyclopentadecan-2-yl-methyl methacrylate), PCR5, in aqueous solution and in the solid state have been studied. In aqueous solution, evidence of a weak interaction between the lanthanides and PCR5 comes from the small red shift of the Ce(III) emission spectra and the slight broadening of the Gd(III) EPR spectra. From the Tb(III) lifetimes in the presence of H<sub>2</sub>O and D<sub>2</sub>O the loss of one or two water coordinated molecules is confirmed when Tb(III) is bound to PCR5. An association constant of the order of 200 M<sup>-1</sup> was obtained for a 1:1 (lanthanide:15-crown-5) complex from the shift of the polymer NMR signals induced by Tb(III). A similar association constant is obtained from the differences of the molar conductivity of Ce(III) solution at various concentrations in presence and absence of PCR5. When Tb(III) is adsorbed on PCR5 membranes, lifetime experiments in H<sub>2</sub>O and D<sub>2</sub>O confirm the loss of 5 or 6 water coordinated molecules indicating that in solid state the lanthanide(III)-PCR5 interaction is stronger than in solution. The adsorption of Ce(III) in PCR5 membranes shows a Langmuir type isotherm, from which an equilibrium constant of 39 M<sup>-1</sup> has been calculated. SEM shows that the membrane morphology is not much affected by lanthanide adsorption. Support for lanthanide ion–crown interactions comes from *ab initio* calculations on 15-crown-5/La(III) complex. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 1788–1799, 2007

**Keywords:** host-guest systems; lanthanide–crown ether interactions; macrocycles; metal-polymer complexes

## INTRODUCTION

At a molecular level, weak intermolecular forces govern many life processes. Thus, such noncovalent interactions, as electrostatic binding, H-bonding or hydrophobic interactions are the basis of the DNA double helix, the secondary, tertiary, and quaternary structure of proteins, part of the substrate recognition characteristics of

enzymes, the Na(I), K(I), and Ca(II) transport mechanisms in cell membranes, and so forth.

Considering the effectiveness of the naturally occurring chemical and biological processes involving such interactions, it is natural that people have tried to mimic nature at this level for commercial or scientific applications. One of the breakthroughs in this respect was the discovery in 1967 of the interaction of metal cation ions with cyclic oxyethylene sequences, which can be considered to be the birth of host–guest chemistry, one of the cornerstones of Supramolecular Science.<sup>1,2</sup> The term *crown ether* or *coro-*

Correspondence to: Prof. J. M. García (E-mail: jmiguel@ubu.es)

*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 45, 1788–1799 (2007)  
© 2007 Wiley Periodicals, Inc.

*nand* was coined to account for the ability of the host molecule to “crown” cation guest molecules through interaction of the lone pairs of the ether groups with electron deficient atoms or chemical groups, leading to an overall stabilization. The interaction of the ether groups with cations through ion–dipole interaction is particularly favored in crown ethers because the ether groups occupy conformationally favorable positions in an aliphatic cycle structure.

The ability of crown compounds to selectively interact with cations opens a wide variety of present and future technological application, including the fields of sensing in the manufacture of ion selective electrodes, the development of liquid membranes or supported liquid membranes employing the selective transport capabilities of these molecules, the production of selective extraction systems for purification, recovery or decontamination purposes, and the production of catalysts for organic and inorganic reactions.

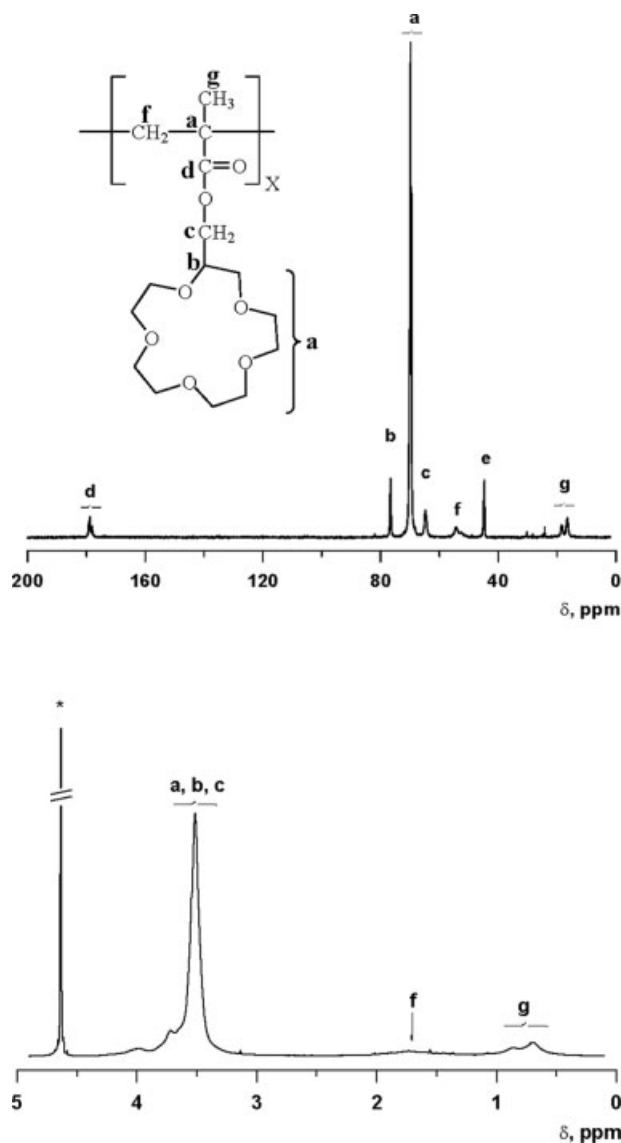
However, the discrete *coronands* are low molecular weight compounds, which limits their technological use because they are soluble in most solvents, and thus their separation and recovery is difficult. In addition, they have low thermal and chemical stability and need a physical support for most of their applications, with immobilization in such systems reducing their tendency to migrate. The preparation of polymers with crown or podand moieties chemically anchored to the backbone provides an excellent means of immobilization, and the inclusion of these supramolecules in a polymer structure opens the technological applications of these materials to areas, such as sensors,<sup>3</sup> actuators,<sup>4</sup> permselective membranes,<sup>5</sup> catalysts,<sup>6</sup> and so forth, all of which depend on the cation recognition capabilities of the crown compounds<sup>7,8</sup> described earlier. Thus, it is of great interest to study the interaction between cations and crown ethers bound to polymers. However, such studies are not easy, as we are frequently dealing with weak interactions in solution, as has previously been shown with the low association constants observed for the interaction between lanthanide ions and the crown ether polymer: poly(1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate), PCR4.<sup>9</sup> Although of great biological importance, metals such as alkali and alkaline earth ions are not good spectroscopic probes to study their interaction with polymers. These difficulties can partially be solved by using trivalent lanthanide ions as probes, as they can be detected with a

wide range of spectroscopic techniques, such as: fluorescence [Ce(III), Eu(III), Tb(III)], nuclear magnetic resonance (lanthanides are used as shift reagents), and electronic paramagnetic resonance at room temperature [Gd(III)]. In addition, there are few differences in behavior between the various lanthanide ions, which also have similar ionic radii and complexation characteristics to various biologically important alkaline earth and transition metal ions [Ca(II), Zn(II), Mg(II), Mn(II), Fe(II), and Fe(III)] and can replace them in many systems.<sup>10,11</sup> In the last few years we have studied the interaction of lanthanides with surfactants<sup>12,13</sup> polyelectrolytes<sup>14</sup> and uncharged polymethacrylate containing a pendant 12-crown-4 ether, PCR4,<sup>9</sup> in aqueous solution, mainly using spectroscopic techniques. It was suggested that the weak interaction observed between lanthanides and PCR4 in aqueous solution was partially due to the fact that the crown-4 cavity radius, 60–75 pm,<sup>15</sup> does not have the optimum size to incorporate trivalent lanthanide ions (ionic radii, around 100 pm).<sup>10</sup> We, therefore, report an extension of this work on the interaction of lanthanides with PCR4 to the interaction of lanthanides with the polymer poly(1,4,7,10,13-pentaoxacyclopentadecan-2-ylmethyl methacrylate), PCR5 (Fig. 1), which has the 15-crown-5 moiety with a cavity size radii between 85 and 110 pm,<sup>15</sup> similar to lanthanide ion radii. This is expected to make this polymer–crown system more favorable for interaction with this kind of cation. In addition, we extend the study in relation to with our previous work on PCR4,<sup>9</sup> by using ionic conductivity measurements to calculate the association constant between PCR5 and a model lanthanide cation, Ce(III) and, to study the interaction in both aqueous solution and in the solid state. We have determined the adsorption isotherms of trivalent lanthanide ions [using Ce(III)] with PCR5 membranes, and by using the luminescence characteristics of Tb(III) ions confirm that the interaction in the solid state is stronger than in aqueous solution as shown by the loss of a more coordinated water molecules when they interact with PCR5 membranes compared binding by crown ethers in aqueous solution.

## EXPERIMENTAL

### Reagents

Cerium(III), terbium(III), europium(III), lanthanum(III), and gadolinium(III) perchlorates (40%



**Figure 1.** Structure of PCR5, together with the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra (upper and lower spectra, respectively) along with signal assignments.

water solution), Ce(III) chloride and deuterium oxide (99.9%) were purchased from Aldrich and used without further treatment. 2,2'-Azobisisobutyronitrile (AIBN) (Fluka, 98%) was recrystallized twice from methanol, and dried under high vacuum at room temperature. Millipore-Q water was used to prepare all solutions.

### Apparatus and Methods

For steady-state luminescence spectral measurements, a Shimadzu RF-5301 PC instrument was used in right-angle configuration. Tb(III) luminescence lifetimes were measured, using the

Spex 1934D phosphorimeter accessory with a Jobin-Yvon-Spex Fluorolog 3-22 instrument. An integrating sphere was used when the interaction of Tb(III) and Ce(III) with PCR5 membranes was studied. Decays were analyzed using Origin 5.0 software. Electron paramagnetic resonance measurements were carried out in aqueous solutions with samples in the sealed capillary part of Pasteur pipettes; all spectra have been corrected for the background signal of the glass. Spectra were recorded on a Bruker EMX10/12 spectrometer, equipped with Bruker  $\text{N}_2$  temperature controller device BVT3000, operating at X band and calibrated with DPPH (2,2'-diphenyl-1-picrylhydrazyl). The NMR spectra of polymer were recorded on a Varian INOVA 400 spectrometer operating at 399.92 MHz ( $^1\text{H}$ ) and 100.57 MHz ( $^{13}\text{C}$ ), using  $\text{D}_2\text{O}$  or  $\text{DCCl}_3$  as solvent.

### $^1\text{H}$ and $^{13}\text{C}$ NMR Results

For Tb(III), the association constants between lanthanide and PCR5 in solution have been obtained from the shift of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PCR5 (8 wt %, corresponding to 0.25 M in terms of monomer units) solutions in  $\text{D}_2\text{O}$  with addition of various concentrations of the cation ( $2 \times 10^{-4}$ –0.2 M). The strong paramagnetism of Tb(III) limits the maximum cation concentration to 0.2 M for such studies. Unsuccessful attempts were made using the same method to obtain association constants for lanthanum(III) and europium (III). Although small shifts were seen with Eu(III), quantification of the complexation behavior failed because of the small lanthanide induced chemical shifts compared with the experimental errors.

All luminescence, NMR and EPR spectra have been registered at 20 °C. Solution electrical resistances were measured with a Wayne-Kerr model 4265 Automatic LCR meter at 1 kHz. A dip-type conductance cell with a cell constant of  $0.0334 \text{ cm}^{-1}$ , uncertainty of 0.02%, was used. The cell constant was determined to  $\pm 0.02\%$  from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data from Barthel et al.<sup>16</sup> Measurements were made at  $(25.00 \pm 0.01) \text{ }^\circ\text{C}$  in a Grant thermostat bath. In a typical experiment a PCR5 solution (of concentration 4.9 mM) was placed in the conductivity vessel; then, aliquots of the Ce(III) solution were added in a stepwise manner using micro-pipettes. The conductance of the solution was

measured after each addition. All solutions were freshly prepared just before each experiment.

The morphologies of the polymer films, previously coated with a gold film, were analyzed by scanning electron microscopy (SEM), using a Jeol/Scanning Microscope, model 5310 operating under low vacuum at 20 kV.

### Synthesis of Monomer and Polymers

1,4,7,10,13-pentaoxacyclopentadecan-2-ylmethanol and 1,4,7,10,13-pentaoxacyclopentadecan-2-ylmethyl methacrylate (CR5MA) were prepared according to the synthetic procedures described by Tiemblo et al.<sup>17</sup> and García et al.<sup>18</sup> The radical polymerization of CR5MA to give linear PCR5, and the subsequent purification were accomplished following the procedure described by García et al.<sup>19</sup>

### Membrane Preparation

The membranes were prepared by radical polymerization of pure CR5MA, using 1,2-ethanedioldimethacrylate as crosslinking agent and AIBN (0.2 wt %) as initiator. The nominal crosslinking ratio, that is, the ratio between the number of moles of monomer to the crosslinking agent, was  $\sim 100$ . The addition of a crosslinking agent is necessary to obtain membranes with adequate mechanical properties. The reaction was carried out as outlined in previous articles.<sup>20,21</sup>

### Polymer Characterization

The chemical structure of the linear PCR5 (Fig. 1) was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The tacticity of the polymer, determined by <sup>13</sup>C NMR spectroscopy, gave an average molar fraction of syndiotactic dyads of  $0.82 \pm 0.05$ . Comparison of this with the values of the triad and pentad units indicates Bernoullian stereochemical control.<sup>22</sup> The predominance of syndiotactic over isotactic sequences is similar to that found for other methacrylic polymers.<sup>23</sup>

## RESULTS AND DISCUSSION

The results of our study are organized in three different sections. In the first, the results of the interaction of PCR5 in solution with lanthanides are shown, in the second, we report the interaction of lanthanides with PCR5 membranes, while in the last section we present a theoretical simulation carried out in gas phase.

### Interaction in Solution

#### Magnetic Resonance Spectroscopic Results in D<sub>2</sub>O

<sup>1</sup>H and <sup>13</sup>C NMR Results. Upon addition of Tb(III) ( $2 \times 10^{-4}$ –0.2 M) to PCR5 (8 wt %, corresponding to 0.25 M in terms of monomer units) solutions in D<sub>2</sub>O, shifts in the proton and carbon resonances to higher magnetic fields and signal broadening are observed.

The chemical shifts of all hydrogen and carbon nuclei decrease linearly with Tb(III) molar concentrations. The slopes of the linear fitting are shown in Table 1. Although the differences are small, the changes in chemical shifts are slightly higher for carbon or hydrogen atoms of the crown ether pendant group (12-crown-5) or for the atoms close to them (atoms a or b and c, respectively, according to the nomenclature of Fig. 1) confirming that the lanthanide interacts with PCR5 mainly through the crown ether group, as previously observed for poly(1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate) PCR4.<sup>9</sup>

Comparing the linear fittings for similar atoms in the proton and carbon atom-chemical-shifts versus Tb(III) molar concentrations for PCR4 and PCR5, we observe that the slopes are lower in the case of PCR4 for the majority of the atoms, as shown in Table 1. This is clear evidence that the lanthanide–crown polymer interaction is stronger in the case of PCR5 than in the case of PCR4. The difference in the chemical shifts is mainly a consequence of differences in the proximity between lanthanide and the crown moiety due to steric factors.

**Table 1.** Slopes of the Linear Fittings of Proton and Carbon Atom-Chemical-Shifts versus Tb(III) Molar Concentrations Interacting with PCR4 and PCR5

	C (a)	C (b)	C (c)	C (d)	C (e)	C (f)	C (g)	H (a–c)	H (f)	H (g)
PCR4	–10.9	–9.8	–9.3	–7.7	–7.7	–8.8	–7.2	–10.6	–8.3	–8.7
PCR5	–10.5	–10.7	–10.9	–9.4	–9.8	–10.3	–9.4	–11.3	–9.9	–10.2

The chemical shift increments of the proton and/or carbon resonances obtained from the difference between the polymer–lanthanide chemical shifts and those of the polymer are used to calculate the stability constant for a 1:1 (lanthanide: 15-crown-5) stoichiometry obtaining a very good fitting. A 1:1 stoichiometry is generally proposed in studies of the interaction between lanthanides trivalent ions and ligands containing 12-crown-4, 15-crown-5, and 18-crown-6 moieties.<sup>7–9,24</sup> This stoichiometry is obtained from Job's plot in some cases.<sup>7</sup> Although, for smaller ions such as Li(I) interacting with 12-crown-4 system, both 1:1 and 1:2 (metal ligand) complexes seem to be important,<sup>25</sup> in our case, from the good fitting of both NMR and conductivity data (see below) with a model 1:1, the ion and cavity radii, and the maximum Ce(III) adsorbed per crown in the Ce(III) isotherm, we appear to have evidence that the 1:1 complex is the dominant species under our experimental conditions.

We will now address the use of the shift increments of proton and carbon resonances to calculate the stability constants.

*Determination of Stability Constants.* As discussed in the previous section, on the assumption that a 1:1 complex (C-L) is formed between the lanthanide ion (L) and crown (C)



the stability of the complex (C-L) can be described in terms of an association constant,  $K$ , defined by

$$K = \frac{[C-L]}{[C][L]} \quad (2)$$

where  $[C]$  and  $[L]$  represent the concentration of free (noncomplexed) species, crown, and lanthanide, respectively, and  $[C-L]$  is the concentration of the 1:1 complex.

From eq 2 and the mass balance equations

$$[C]_t = [C-L] + [C] \quad (3)$$

$$[L]_t = [C-L] + [L] \quad (4)$$

where  $[C]_t$  and  $[L]_t$  represent the total concentration of crown and lanthanide, respectively, the association constant can be rewritten as

$$K = \frac{f}{(1-f)([C]_t - f[L]_t)} \quad (5)$$

where  $f$  is the fraction of lanthanide ions complexed with the crown PCR5.

*NMR Data.* Assuming fast exchange conditions and a 1:1 complex, the observed chemical shift for a guest atom is expressed as

$$\delta_{\text{obs}} = (1-f)\delta_C + f\delta_{C-L} \quad (6)$$

where  $\delta_C$  and  $\delta_{C-L}$ , represent the chemical shift of a given nucleus when free and complexed, respectively.

The chemical shift displacement of a given nucleus of the crown, C, can be expressed as

$$\Delta\delta_{\text{obs}} = \frac{\Delta\delta_{C-L}}{[C]_t} [C-L] \quad (7)$$

which, after some algebraic manipulation and simplification results in,

$$\Delta\delta_{\text{obs}} = \frac{\Delta\delta_{C-L}}{2[C]_t} \left\{ [L]_t + [C]_t + \frac{1}{K} \right\} - \left( \left( [L]_t + [C]_t + \frac{1}{K} \right)^2 - 4[L]_t[C]_t \right)^{1/2} \quad (8)$$

See ref. 26 for the complete derivation of the earlier equation, and refs. 9 and 25 for recent discussion of problems associated with this method for the estimation of the association constant.

The use of eq 8 in a least-squares fit to our NMR data, has produced some more or less consistent values for the association constant. The 2:1 complex counterpart was, in contrast, incapable of fitting the data. The stability constants for complexes involving terbium are between 94 and 293 as extracted from proton chemical shifts, and from 70 to 275 using <sup>13</sup>C data.

The fact that NMR shifts depend on lanthanide concentration in aqueous solution implies that there is an equilibrium between complexed and uncomplexed pendent crown ether structure with metal ion in D<sub>2</sub>O, and that this equilibrium is too fast to be observed on the NMR timescale (fast exchange limit), such that only a single average signal is recorded for each nucleus.

### Conductivity

For practical reasons, electrical conductivity measurements were made, using Ce(III) instead of Tb(III). However, results for the two ions

should be comparable. Figure 2 shows the variation of the molar conductivity,  $\Delta\Lambda$ , of  $\text{CeCl}_3$  in the presence and absence of PCR5 ( $4.9 \times 10^{-3}$  M) for several  $\text{CeCl}_3$  concentrations,  $\Delta\Lambda = \Lambda_{\text{L+C}} - \Lambda_0$ . When the concentration ratio  $[\text{PCR5}]/[\text{CeCl}_3]$  increases, the difference of molar conductivities with and without PCR5,  $\Delta\Lambda$ , also increases, clearly suggesting that complexation between the salt or dissociated ions, and the polymer PCR5 is occurring.

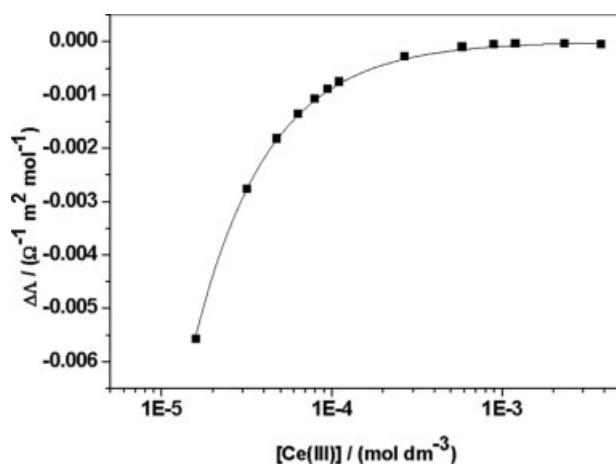
If we denote the specific conductance of lanthanide ion and complex as  $\kappa_{\text{L}}$  and  $\kappa_{\text{C-L}}$ , respectively, we may write<sup>27,28</sup>

$$\Delta\Lambda = \Lambda_{\text{L+C}} - \Lambda_0 = f(\kappa_{\text{L}} - \kappa_{\text{C-L}}) \quad (9)$$

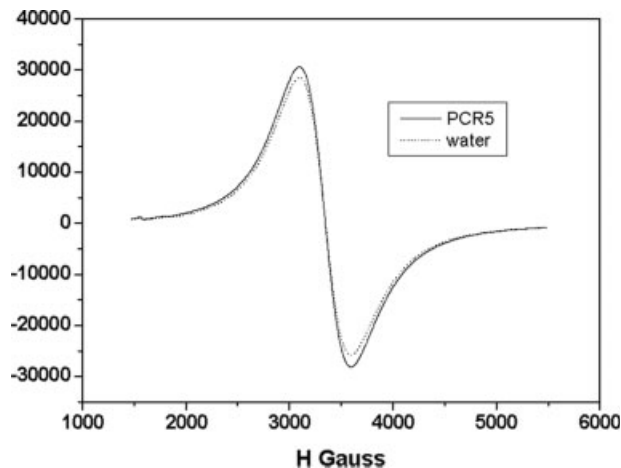
It follows from eqs 5 and 9 that:

$$\Delta\Lambda = \frac{\Delta\kappa}{2K[\text{L}]_{\text{t}}} [K([\text{L}]_{\text{t}} + [\text{C}]_{\text{t}}) + 1 - (K([\text{L}]_{\text{t}} + [\text{C}]_{\text{t}}) + 1)^2 - 4K^2[\text{L}]_{\text{t}}[\text{C}]_{\text{t}}]^{1/2} \quad (10)$$

where  $\Delta\kappa$  is the difference of ionic conductivity of the complexed and noncomplexed  $\text{Ce}^{3+}$  ions, and other symbols have the same meaning as described before. In fact, as should be expected, the earlier equation corresponds to eq 8 when NMR parameters are replaced by those extracted from conductivity measurements. A nonlinear least-squares fit of eq 10 to the experimental data (Fig. 2) is performed to determine



**Figure 2.** Effect of cation concentration on the difference between the molar conductivity of  $\text{CeCl}_3$  in the presence ( $\Lambda_{\text{L+C}}$ ) and absence ( $\Lambda_0$ ) of PCR5 (4.9 mM) at 298.15 K,  $\Delta\Lambda = \Lambda_{\text{L+C}} - \Lambda_0$ . Solid line represents the difference of the molar conductivities predicted by eq 10, assuming 1:1 (Ce(III):PCR5) association (see text for further details).



**Figure 3.** EPR spectra of Gd(III) ( $1 \times 10^{-1}$  M) in PCR5 (1% solution) and in aqueous solution.

the unknown values for the variables.<sup>29</sup> The best values of the two fitting parameters calculated using this procedure, and taking  $[\text{C}]_{\text{t}} = [\text{CeCl}_3] = 4.9$  mM, are:  $K = 113$  and  $\Delta\kappa = 2.0 \times 10^{-5} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$  (correlation coefficient = 0.99921 and reduced chi square =  $2.129 \times 10^{-9}$  (---) see solid line in the Fig. 2).

### EPR Results

Gd(III), due to its high electron relaxation times in comparison to the other paramagnetic lanthanides, is the only one that gives EPR spectra at room temperature.<sup>10</sup> The EPR spectra of Gd(III) at five Gd(III) concentrations ( $1 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $4 \times 10^{-2}$ , and  $1 \times 10^{-1}$  M) were measured in aqueous PCR5 solutions (1%) and in pure water at 20 °C. As can be seen in Figure 3, Gd(III) spectra are quite similar in the absence and presence of PCR5 and only a slight broadening of the signal is observed on addition of PCR5. This is similar to what was previously observed upon addition of other polyelectrolytes, such as poly(vinyl sulfonate).<sup>14</sup> Small changes in the coordination of lanthanide–water complexes or in viscosity could justify the small broadening of the signal. However, from the similarity of the spectra we can conclude that Gd(III) is only weakly bound to PCR5 in aqueous solution, as was previously reported for the case of PCR4.<sup>9</sup>

### Luminescence Results

A number of intrinsic luminescent probes have been used to study the interaction between lanthanides and PCR5 in aqueous solution. One of

**Table 2.** Lifetime of Tb(III) in PCR5 (1%) in H<sub>2</sub>O or D<sub>2</sub>O solutions

Tb Concentration (M)	$\tau_{D_2O}$ (ms)	$\tau_{H_2O}$ (ms)
$6.0 \times 10^{-5}$	1.48	0.42
$1 \times 10^{-4}$	1.42	0.39
$2 \times 10^{-4}$	1.35	0.41

the most important is Tb(III), whose lifetime measurements permit the determination of the number of coordinated Tb(III) water molecules lost upon interaction with the crown polymer. The basis of the method is the fact that the Tb(III) lifetime increases in D<sub>2</sub>O relative to H<sub>2</sub>O due to the reduced coupling of the lower energy O—D oscillator compared with O—H on the deactivation of the excited lanthanide ions. These changes depend directly on the number of coordinated water molecules and provide a quantitative method for determining this.<sup>30–32</sup> Tb(III) fluorescence decays were measured for three different metal ion concentrations ( $6.0 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and  $2 \times 10^{-4}$  M) in PCR5 solutions at 1% (weight/volume, w/v) aqueous (or D<sub>2</sub>O) solutions at 20 °C. All the decays were monoexponential, and from the fits, the lifetimes were determined (Table 2).

From these results, the average number of water molecules coordinated to Tb(III) when it is interacting with PCR5 in aqueous solution is 7.3, identical to what was previously determined for Tb(III)-PCR4 system.<sup>9</sup> However, in aqueous solution, Tb(III) coordinates between eight and nine water molecules,<sup>33</sup> indicating that, as a consequence of the interaction with both PCR4 and PCR5, a loss of between one and two water molecules occurs and at the level of the primary coordination sphere there are no significant differences in the interaction between these two polymers and Tb(III).

A second evidence for the weak interaction between Tb(III) and PCR5 comes from the Ce(III) luminescence. The spectroscopically allowed  $4f \rightarrow 5d$  Ce(III) emission<sup>34</sup> is red-shifted 1 nm with respect to the emission in aqueous solution, when Ce(III) ( $4 \times 10^{-4}$  M) interacts with PCR5, similar to what was previously observed in the case of PCR4.<sup>9</sup> This small red-shift can be attributed to the weak interaction of the lanthanide to the noncharged crown ether group.

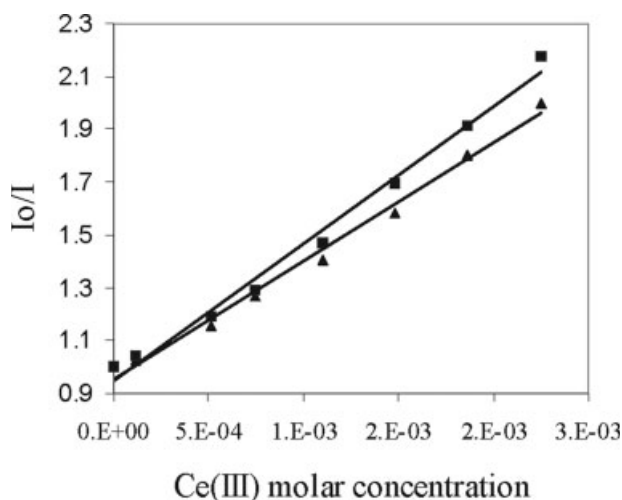
The third piece of luminescence experimental evidence for the interaction between lanthanides

and PCR4 and PCR5 comes from the quenching of Tb(III) ( $1.0 \times 10^{-2}$  M) emission by Ce(III) (from  $1.2 \times 10^{-4}$  to  $2.6 \times 10^{-3}$  M). Quenching follows good Stern–Volmer kinetic as seen in Figure 4 for both polymers and is probably due to energy transfer to a low-lying state of Ce(III), which is supported by the increase of the Ce(III) emission intensity.

From the experimental results, we observe that the quenching process is slightly more efficient with PCR5 than with PCR4 and is similar to the quenching process in aqueous solution as has previously been discussed.<sup>9</sup> These results, in agreement with the NMR results, show that, in spite of the similarities between PCR4 and PCR5, when interacting with lanthanides in solution, the interaction with PCR5 is slightly stronger favoring higher induced shifts of the NMR signals and a more efficient quenching of Tb(III) luminescence by Ce(III).

### Interaction in the Solid State

Luminescence is a very good technique to study the interaction between lanthanides and PCR5 membranes. The adsorption of lanthanides in PCR5 membranes has been probed by the loss of coordinated water molecules of Tb(III) upon interaction with PCR5 membranes and by the shift in Tb(III) emission spectra when the lanthanide is adsorbed in the membrane. The



**Figure 4.** Stern Volmer plot ( $I_0/I$ ) of Tb(III) ( $10^{-2}$ ) emission at 544 nm versus Ce(III) molar concentration with PCR4 (triangles) and with PCR5 (squares).  $I_0$  and  $I$  are the Tb(III) emission intensities without and with Ce(III), respectively.

**Table 3.** Lifetime of Tb(III) in PCR5 Membranes in H<sub>2</sub>O or D<sub>2</sub>O

Tb: 15-Crown-5 Mole Ratio	$\tau_{D_2O}$ (ms)	$\tau_{H_2O}$ (ms)
5:1	0.60	0.41
7.5:1	0.62	0.40
8.9:1	0.57	0.42

adsorption isotherm has been quantitatively study by the emission of nonadsorbed Ce(III).

### Tb(III) Experiments

Three previously weighed pieces of PCR5 membranes were put in contact with separate 1-mL samples of aqueous solutions of Tb(III) perchlorate at different concentrations for 36 h at room temperature, stirring from time to time. Swelling of the membranes was observed. The molar ratios of Tb(III) to crown 15-crown-5 moieties were: 5:1, 7.5:1, and 8.9:1 for the three samples. The lifetime of the adsorbed Tb(III) was measured at 544 nm by placing the membranes in an integrating sphere. Afterwards, these membranes were removed from the integrating sphere and placed in D<sub>2</sub>O for a half of hour to exchange water for D<sub>2</sub>O in the Tb(III) coordination sphere. Longer times of contact between membranes and D<sub>2</sub>O were not suitable as membranes become very fragile when soaking twice. However, water molecules bound to lanthanides are very labile, with residence times typically of the order of tens of ns,<sup>35</sup> such that substitution by D<sub>2</sub>O should be complete within this time. The lifetime of the adsorbed Tb(III) luminescence was measured again in the integrating sphere. Lifetimes are shown in Table 3.

The average number of water molecules coordinated to Tb(III) when it is interacting with PCR5 membranes is 3 while it is 7.3 when Tb(III) is interacting with PCR5 in aqueous solution. This suggests that the interaction between lanthanides and PCR5 in solid state is much stronger than in aqueous solution. It seems that, in solution, water molecules compete strongly with ether groups to coordinate lanthanides. As in aqueous solution Tb(III) coordinates between eight and nine water molecules,<sup>33</sup> indicates that a loss of between five and six water molecules is produced when Tb(III) is adsorbed in PCR5 membranes, around a water molecule per ether group indicating that a similar interaction between terbium atoms and all

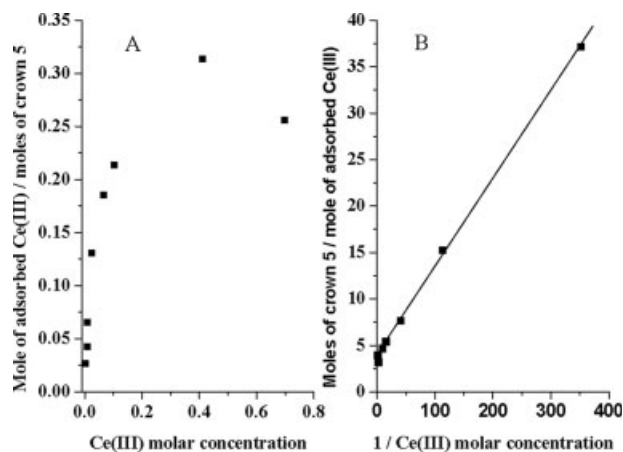
the oxygen atoms of 15-crown-5 moieties is produced.

Another piece of experimental evidence for the interaction between Tb(III) and PCR5 membranes comes from the 1-nm red shift of the Tb(III) emission spectra when Tb(III) is adsorbed on PCR5 membranes with respect to the emission of Tb(III) in aqueous solution. This cannot be due to scattering, which would induce a blue shift, and is similar to the shift observed in the Ce(III) emission spectra when it interacts with PCR5 in aqueous solution as shown in previous sections.

### Ce(III) Sorption Isotherm

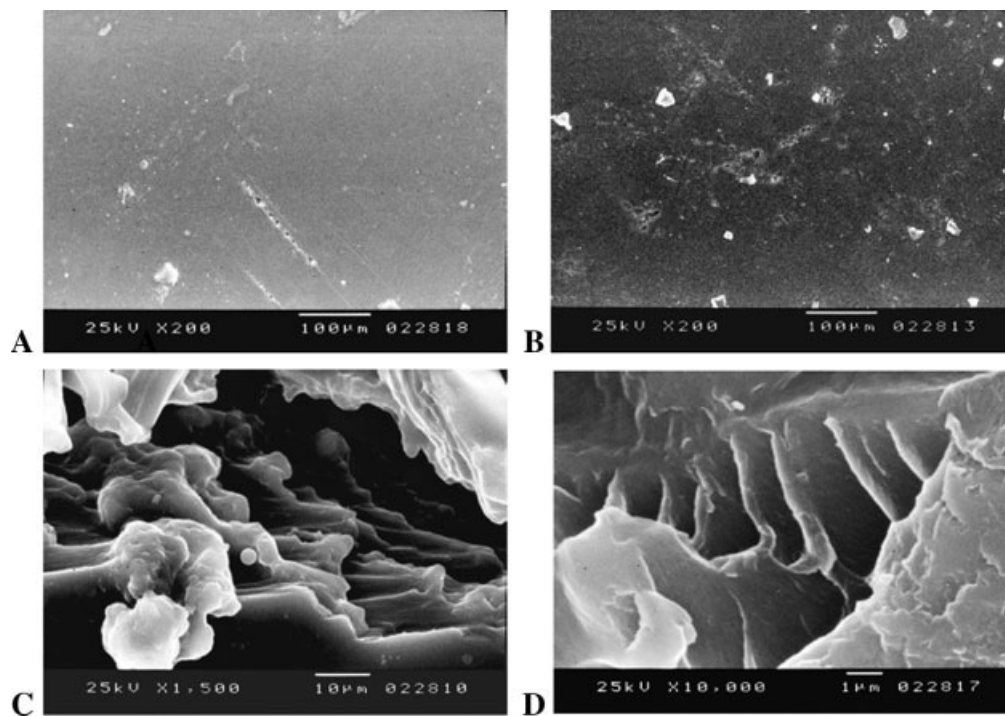
Ce(III) sorption isotherm has been obtained from the emission spectra of the nonadsorbed Ce(III) in the supernatant obtained after a week of being in contact eight pieces of PCR5 membranes of a weight between 0.02 and 0.03 g with 5 mL of Ce(III) perchlorate aqueous solutions with concentrations between  $2.84 \times 10^{-3}$  M and 0.70 M at 25 °C. The moles Ce(III) to moles of crowns ratios ranged from 0.20 to 42.42. And the free Ce(III) was estimated from a calibration curve in the concentration range between  $2.4 \times 10^{-3}$  and  $7.3 \times 10^{-3}$  M, in which the Ce(III) emission increases linearly with Ce(III) concentration. The samples were diluted to get Ce(III) concentrations in the range of the calibration curve.

The adsorption isotherm [Fig. 5(A)] suggests a strong sorption of Ce(III) by the 15-crown-15 followed by a plateau, which is reached for a concentration of Ce(III) of 0.27 [mol Ce(III)/mole of crown]. This approach can be mathematically



**Figure 5.** Adsorption isotherm (A), Langmuir isotherm linear fitting.





**Figure 6.** SEM pictures of PCR5 membrane surface before and upon Ce(III) adsorption (A and B, respectively) and of PCR5 membrane edges before and upon Ce(III) adsorption (C and D, respectively).

expressed, using a Langmuir-type isotherm, which in its linear form can be written as<sup>36</sup>

$$\frac{\text{moles of crown}}{\text{moles of adsorbed Ce(III)}} = \frac{1}{w_{\max}} + \frac{1}{K_e w_{\max} [\text{Ce}]} \quad (11)$$

where  $w_{\max}$  is the maximum ratio of Ce(III) adsorbed moles per mol of crown and  $K_e$  is the adsorption equilibrium constant, the ratio between the kinetic constant of the adsorption and desorption processes. A good linear fit is obtained, Figure 5(B).

The adsorption equilibrium constant obtained,  $39.1 \text{ M}^{-1}$ , is of a similar magnitude to the binding constants determined in solution by NMR and electrical conductivity. Although the heterogeneous sorption processes involved in the Langmuir isotherm involve both physical interaction of the lanthanide ion with the surface and binding by the crown, and care is needed in comparison with association in homogeneous solution, the agreement is encouraging and indicates that complexation by the crown must be one of the important factors in lanthanide binding to the membrane.

### Microscopy

A SEM study was made of PCR5 membranes used for obtaining the Ce(III) isotherm before [Fig. 6(A,C)] and after Ce(III) sorption [Fig. 6(B,D)]. Figure 6(A,B) shows that the surfaces of PCR5 membranes are compact and some phase separation is observed with the formation of some circular structures on the surfaces. These kind of structures are not much affected by Ce(III) adsorption and seem to be characteristic of polymers containing crown ethers as they have been also observed in polyamide polymers bearing benzo-18-crown-6 moieties.<sup>37</sup>

However, one marked feature involves the “lamellar structures” observed at the edge of PCR5 membranes, Figure 6(C,D). From the presence of a quaternary carbon atom in the polymer structure (Fig. 1), no kind of ordered polymer structure is anticipated, and it is impossible to say whether these are intrinsic lamellae within the membranes or are artifacts induced in preparation of samples for SEM measurements. Small Angle X-ray Scattering experiments are planned to check for the presence of regular structures in these membranes.

**Table 4.** Energies and Selected Geometry Parameters for (12-Crown-4)-La(III) Interaction

	Mean Distance Cation-O <sub>crown</sub> (Å)	<i>E</i> Total (au)	<i>E</i> <sub>bond</sub> Total (kJ mol <sup>-1</sup> )	<i>E</i> <sub>bond</sub> (kJ mol <sup>-1</sup> )
12-Crown-4	–	–615.267074 <sup>a</sup>	–	–
(12-Crown-4)-La(III)	2.422	–645.642188	–1,490	–373
15-Crown-5	–	–769.095780 <sup>a</sup>	–	–
(15-Crown-5)-La(III)	2.467	–799.567721	–1,744	–349

<sup>a</sup> Molecule in the complex geometry.

From these SEM results it can be concluded that only a slight change of the morphology of PCR5 polymer membranes is observed upon Ce(III) adsorption.

### Molecular Modeling: Methodology and Results

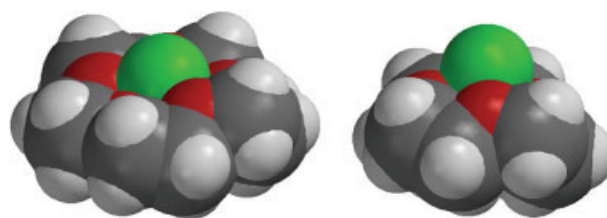
To get an insight into the crown–metal ion interactions, theoretical studies have been performed, using gas phase density functional theory (DFT) calculations.<sup>38</sup> The interaction of discrete 12-crown-4 or 15-crown-5 molecules with La(III) was studied, where La(III) is taken as a representative example of the different trivalent lanthanides.

The geometry optimizations and energy evaluations were performed with DFT methods employing pseudopotentials at the RB3LYP/LACVP\* level of theory for La(III) associated with the standard 6-31G\* basis set for lighter elements. The bonding energies are defined as  $E_{\text{bond}} = \{E(\text{cation–molecule complex}) - [E(\text{molecule in the complex geometry}) + E(\text{cation})]\}$  where the cation is La(III) and the molecule is 12-crown-4 or 15-crown-5.

Results of the bond energy ( $E_{\text{bond}}$ ) and the mean distance between cation and crown oxygen atoms of [crown-La(III)] complex in the gas phase are shown in Table 4. As expected, the bonding energy of the (15-crown-5)-La(III) is higher than the  $E_{\text{bond}}$  of (12-crown-4)-La(III) since the La(III) fits better in the crown cavity of 15-crown-5 than in that of 12-crown-4. However, it is noteworthy that the mean distance between the La(III) and the crown oxygens is shorter in the (12-crown-4)-La(III) complex, suggesting that the individual bond energy per oxygen is higher in the crown-4. This is reasonable because although the larger cavity of 15-crown-5 can better accommodate the metal ion, at the same time it implies greater distances between the oxygens and the cation (Fig. 7).

The  $E_{\text{bond}}$  and the mean distances between the cation-O<sub>crown</sub> can be compared with the theoretical results obtained in the interactions of polyglymes with different cations. Polyglymes

are open chain counterpart of the crown ether and usually exhibit less cation affinity than comparable crown compounds due to unfavorable enthalpic and entropic effects. However, their higher conformational flexibility allows them to engage in multiple bridging and helical binding modes that the crowns cannot adopt.<sup>39,40</sup> Johansson et al.<sup>41</sup> have studied the interaction of tetra, penta, and hexaglyme–Li(I) complex. Due to the previously noted higher ability of crown compounds to complex molecules compared with those with an open structure, the bond energy per oxygen atom found in 12-crown-4:metal or 12-crown-4:metal complex are higher than those obtained in the interaction between lithium ion and the open polyoxyethylene units, although contributions due to the differences in the metal ion charge and radii also have to be taken into account. The distances between the cation and the crown oxygens are higher for the crown–metal complex in our systems than those calculated by Johansson et al.<sup>41</sup> This is due to the larger ionic radii of La(III) compared with Li(I). If the radii of both metals were subtracted from the distance discussed earlier, this value would be approximately the same for both systems. Considering a closer guest–host complex, as in the solid state [Tb(OH<sub>2</sub>)<sub>5</sub>(12-crown-4)]Cl<sub>3</sub>·2H<sub>2</sub>O, the distances between La(III) and the crown oxygens are similar to that one theoretically determined in our systems.<sup>9</sup>



**Figure 7.** CPPK model of crown-La(III) complexes [left: (15-crown-5)-La(III); right: (12-crown-4)-La(III)]. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

## CONCLUSIONS

The interaction between trivalent lanthanides and PCR5 in aqueous solution and solid state has been confirmed by several spectroscopic techniques and by ionic conductivity. The interaction seems to be stronger in the solid state as is shown from the loss of five or six water coordinated molecules when Tb(III) is adsorbed in PCR5 membranes and between one and two when is interacting in aqueous solution. This indicates that, in aqueous solution, water, and ether groups compete to coordinate the lanthanides and the lanthanide-15-crown-5 interaction is stronger in absence of water. The small broadening of Gd(III) EPR signal is also a good indicative of the weak interaction in aqueous solution. A complex of an stoichiometry 1:1 (lanthanide:15-crown-5) is proposed and good fittings of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR polymer signal shifts induced by Tb(III) and Ce(III) ionic conductivity in the presence of PCR5 conductivity are obtained with this model. The association constants obtained with these two techniques are in reasonably good agreement. The adsorption of Ce(III) is followed by metal ion emission spectra and shows a Langmuir type isotherm with a maximum amount of Ce(III) adsorbed per mole of crown around 0.27, which practically rules out the possibility of a 1:2 model. From SEM studies, we conclude that no significant alteration of the morphology of PCR5 membranes is observed upon Ce(III) adsorption. The comparison between the bond energies in the 12-crown-4/La(III) and 15-crown-5 system and the Tb(III) emission quenching by Ce(III) let us conclude that the lanthanide interaction is stronger for PCR5 system than for PCR4 as was expected from the cavity radii of 15-crown-5 being closer to lanthanide radii than that of 12-crown-4.

Financial supports from Acci3n Integrada Hispano-Portuguesa (HP2003-0077, Acç3o E/405), Spanish Junta de Castilla y Le3n and European Union (F.S.E.) (Bu09/01 and BU003A05), and Ministerio de Ciencia y Tecnolog3a (FEDER-Plan Nacional de Investigaci3n Cient3fica, Desarrollo e Innovaci3n Tecnol3gica, MAT-2005-01355) are gratefully acknowledged. H.D. Burrows, A.A.C.C. Pais, and A.J.M. Valente also thank POCTI, FCT, and FEDER for financial support.

## REFERENCES AND NOTES

- Pedersen, C. J. *J Am Chem Soc* 1967, 89, 7017.
- Pedersen, C. J. *J Am Chem Soc* 1967, 89, 2495.
- Drake P. L.; Price, G. *J Polym Int* 2000, 49, 926.
- Shinkai, S.; Takeuchi, M.; Ikeda, A. In *Polymer Sensors and Actuators*; Osada, Y.; De Rossi, D. E., Eds.; Springer: Berlin, 2000; Chapter 6.
- Sata, T.; Sata, T.; Yang, W. *J Membr Sci* 2002, 206, 31.
- Watanabe, H.; Iijima, Y.; Fukuda, W.; Tomoi, M. *React Funct Polym* 1998, 37, 101.
- Bekiari, V.; Judeinstein, P.; Lianos, P. *J Lumin* 2003, 104, 13.
- Sousa, C.; Gameiro, P.; Freire, C.; Castro, B. *Polyhedron* 2004, 23, 1401.
- Tapia, M. J.; Burrows, H. D.; Garc3a, J. M.; Garc3a, F.; Pais, A. A. C. C. *Macromolecules* 2004, 37, 856.
- B3nzli, J. C. G.; Choppin, G. R. *Lanthanides Probes in Life, Chemical and Earth Sciences*; Elsevier: Amsterdam, 1989; Chapters 4, 6 and 7.
- Elbanowski, M.; Makowska, B. *J Photochem Photobiol A* 1996, 99, 85.
- Tapia, M. J.; Burrows, H. D.; Azenha, M. E. D. G.; Miguel, M.; da, G.; Pais, A. A. C. C.; Sarraguça, J. M. G. *J Phys Chem B* 2002, 106, 6966.
- Burrows, H. D.; Tapia, M. J. *Langmuir* 2002, 18, 6706.
- Tapia, M. J.; Burrows, H. D. *Langmuir* 2002, 18, 1872.
- Khopkar, S. M. *Analytical Chemistry of Macrocyclic and Supramolecular Compounds*; Springer-Verlag: Berlin, 2002; Chapter 5.
- Barthel, J.; Feuerlein, F.; Neuder, R.; Wachter, R. *J Sol Chem* 1980, 9, 209.
- Tiemblo, P.; Guzm3n, J.; Riande, E.; Garc3a, F.; Garc3a, J. M. *Polymer* 2003, 44, 6773.
- Garc3a, F.; Garc3a, J. M.; Rubio, F.; Tiemblo, P.; Guzm3n, J.; Riande, E. *Polymer* 2004, 45, 1467.
- Garc3a, F.; De la Peña, J. L.; Delgado, J. J.; Garc3a, N.; Guzm3n, J.; Riande, E.; Calle, P. *J Polym Sci Part A: Polym Chem* 2001, 39, 1843.
- Tiemblo, P.; Laguna, M. F.; Garc3a, F.; Garc3a, J. M.; Riande, E.; Guzm3n, J. *Macromolecules* 2004, 37, 4156.
- Compañ, V.; Tiemblo, P.; Garc3a, F.; Garc3a, J. M.; Guzm3n, J. Riande, E. *Biomaterials* 2005, 26, 3783.
- Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley: New York, 1980; p 328.
- Matsumoto, A.; Mizuta, K.; Otsu, T. *Macromolecules* 1993, 26, 1659.
- Peluffo, F.; Torres, J.; Kremer, C.; Dom3nguez, S.; Mederos, A.; Kremer, E. *Inorg Chim Acta* 2006, 359, 2107.
- Masiker, M. C.; Mayne, C. L.; Eyring, E. M. *Magn Reson Chem* 2006, 44, 220.
- Cabrer, P. R.; Alvarez-Parrilla, E.; Mejjide, F.; Seijas, J. A.; N3ñez, E. R.; Tato, J. V. *Langmuir* 1999, 15, 5489.
- Satake, I.; Yoshida, S.; Hayakawa, K.; Maeda, T.; Kusumoto, Y. *Bull Chem Soc Jpn* 1986, 59, 3991.

28. Palepu, R.; Reinsborough, V. C. *Can J Chem* 1988, 66, 325.
29. Cabaleiro-Lago, C.; Nilsson, M.; Valente, A. J. M.; Bonini, M.; Söderman, O. *J Colloid Interface Sci*, in press.
30. De Horrocks, W., Jr.; Sudnick, D. R. *Acc Chem Res* 1981, 14, 384.
31. Beeby, A.; Clarkson, I. M.; Eastoe, J.; Faulkner, S.; Warne, B. *Langmuir* 1997, 13, 5816.
32. Frey, S. T.; De Horrocks, W., Jr. *Inorg Chim Acta* 1995, 229, 383.
33. De Horrocks, W., Jr.; Sudnick, D. R. *J Am Chem Soc* 1979, 101, 334.
34. Kaizu, Y.; Miyakawa, K.; Okada, K.; Kobayashi, H.; Sumitani, M.; Yoshihara, K. *J Am Chem Soc* 1985, 107, 2622.
35. Bünzli, J.-C. G. *Acc Chem Res* 2006, 39, 53.
36. Atkins, P.; Paula, J. *Physical Chemistry*, 7th ed.; Oxford University Press: Oxford, 2002; Chapter 28.
37. Calderón, V.; Schwarz, G.; García, F.; Tapia, M. J.; Valente, A. J. M.; Burrows, H. D.; García J. M. *J Polym Sci Part A: Polym Chem* 2006, 44, 6252.
38. Spartan'04, Wavefunction, Inc., Irvine, CA.
39. Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, 2000; Chapter 3, pp 92–94.
40. Calderón, V.; García, F. C.; de la Peña, J. L.; Maya, E. M.; García, J. M. *J Polym Sci Part A: Polym Chem* 2006, 44, 2270.
41. Johansson, P.; Tegenfeldt, J.; Lindgren, J. *Polymer* 1999, 40, 4399.