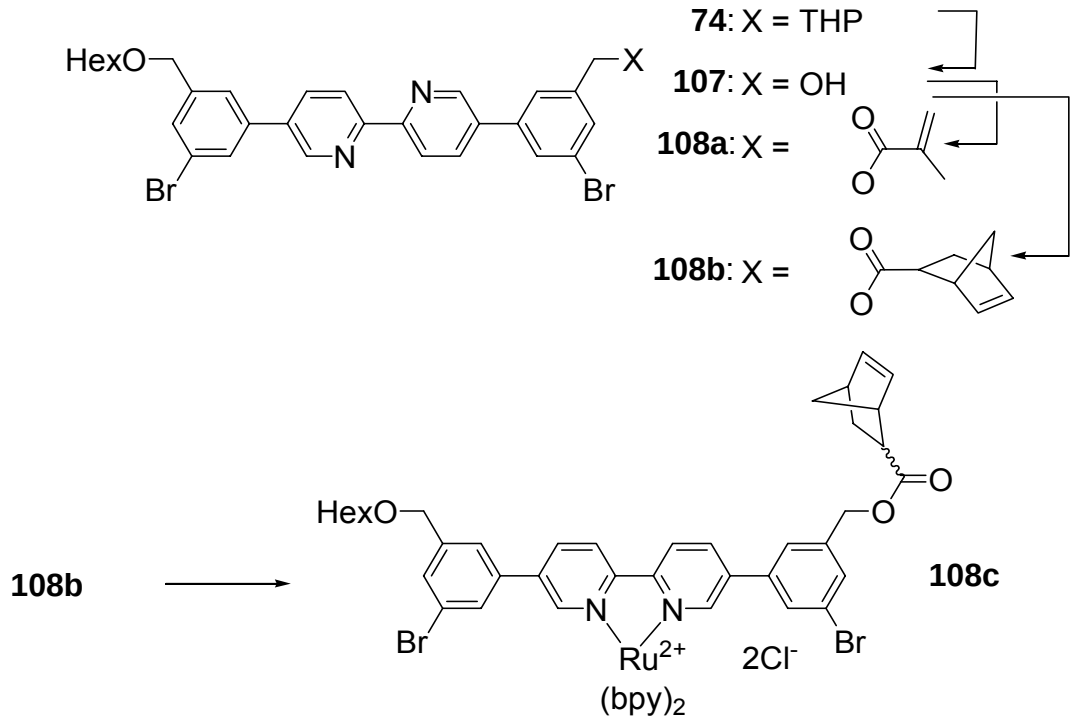
4.4. Polymerization of macrocycles with pendant polymerizable unit

In modern scientific polymer chemistry there has been a clear trend away from conventional polymers like polystyrene and polyacrylate. Several groups worldwide showed that rather complex monomers can be successfully subjected to polymerization and a whole variety of unprecedented polymers have been realized.[72] Inspired by this it was an obvious question whether macrocycles can also be equipped with polymerizable units and converted into polymers. Additionally, in such polymers the macrocycles may organize into supramolecular structures with channels in which the cycles lay directly on top of each other (cylindrical stacks). Such polymers could show properties ranging from liquid crystalline behavior to one-dimensional charge flow and alike. Another promising approach into cylindrical stacks was reported by Höger. He attached flexible oligomeric chains to several corners of hexagonal cycles. Dynamic light-scattering experiments showed that these cycles aggregate and actually form hollow cylinders.[73]

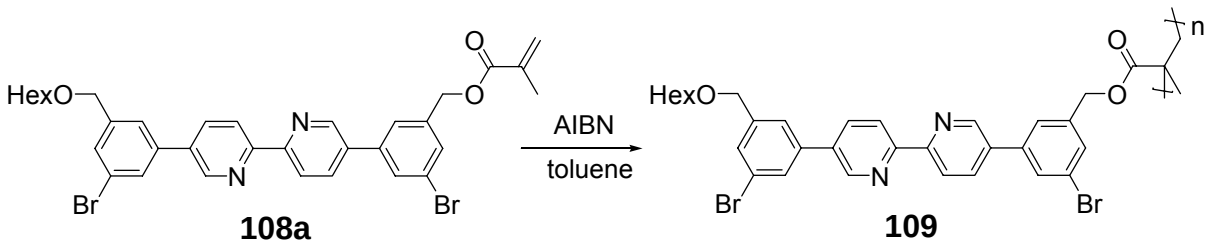
This chapter describes the synthesis of two new cycles which have either one methacrylic ester group for free radical polymerization or one norbornenic ester for ROMP polymerization, respectively. The first successful oligomerizations of such monomers which, because of their respectable molar mass, can also be considered macromonomers are also described.

4.4.1. Model compounds and reactions

In order to find optimum conditions for both the attachment of the polymerizable units and the polymerizations themselves, model reactions were done. The non-cyclic compound **74c** was chosen as starting material. For its synthesis see chapter 4.2., p. 48. The deprotection of compound's **74c** THP group went best with hydrochloric acid and proceeded virtually quantitatively to give **107** (Scheme 52). Model monomers **108a** and **108b** were obtained by treating the alcohole **107** with freshly distilled methacrylic acid chloride and 5-norbornene-2-carboxylic acid, respectively, in yields of 98% and 85%. The norbornenic unit was introduced by active ester chemistry using the commercially available *exo/endo* (2:8) mixture of norbornenic acid. For this test purpose the use of an *exo/endo* mixture was considered acceptable.



Scheme 52. Synthesis of monomers **108a** and **108c** for FRP and ROMP, respectively.



Scheme 53. FRP of monomer **108a** to oligomer **109** using AIBN as initiator and toluene as solvent.

The free radical polymerization of **108a** (Scheme 53) was done in toluene at 60°C using AIBN as initiator and gave an oligomeric material which was separated from the unreacted monomer by preparative GPC. Figure 59 shows the ^{1}H NMR spectra of **108a** and the corresponding polymerization product. It contains characteristic signals of the monomer and a set of broad signals which were assigned to polymer **109**. The molar mass and its distribution was analyzed by GPC versus polystyrene standard. The elution curve showed M_p = 20,300 g/mol and M_w = 27,600 with a polydispersity index PDI = 1.56 (Figure 60). This mass values correspond to degrees

of polymerization P_p = 30 and P_w = 40. Since GPC is a relative method these values have to be treated with care. They can easily differ from the actual ones by a factor of 2 or 3 in both directions. Nevertheless it can be concluded with certainty that the polymer formed is still in the higher oligomeric regime.

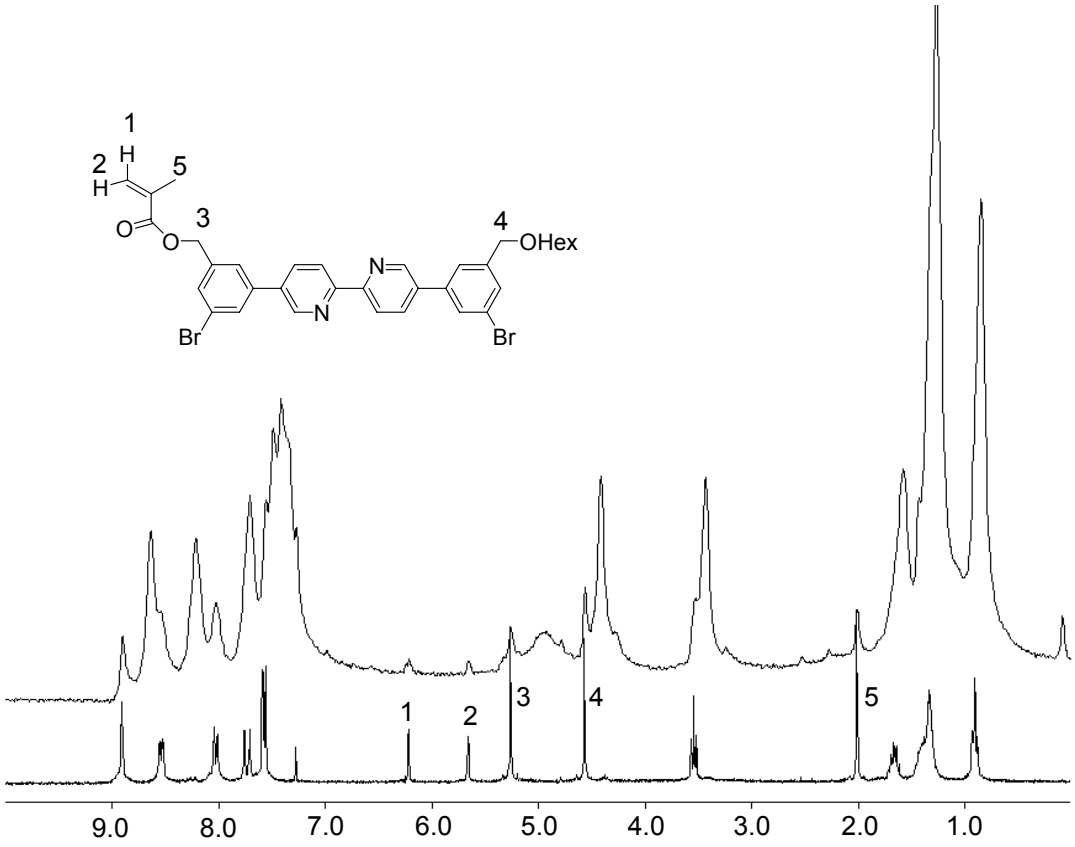


Figure 59. Comparison of the ^{1}H NMR spectra ($CDCl_3$, 270 MHz, 20 °C) of monomer **108a** (bottom) and the raw polymerization product (top).

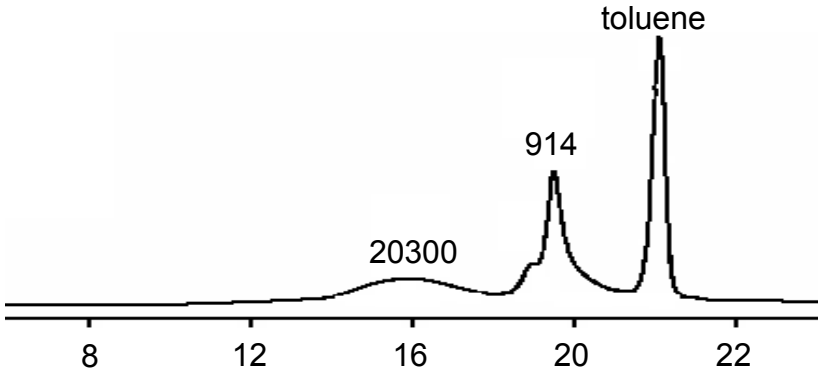
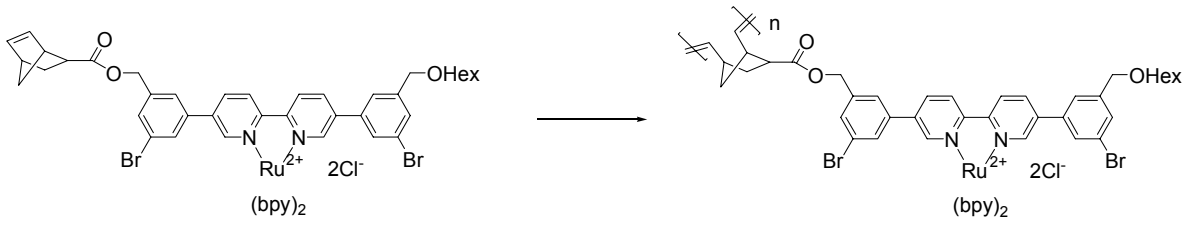


Figure 60. GPC elution curve of the raw product of the polymerization of monomer **108a** using THF as solvent and polystyrene as standard. The peak numbered with 914 is due to unreacted monomer and the broad signal represents polymer **109**.

Whereas the radical polymerization went smoothly from the beginning, the alternative approach by ROMP initially faced problems. Thus, exposure of monomer **108b** to the commonly used ROMP catalyst, the so-called Grubbs generation I Ru-catalyst, led to unreacted material.[74] It was concluded that there may have been a detrimental complexation of the catalyst to the monomer's bipyridine unit. It was therefore decided to protect the bipyridine unit prior to polymerization. This was achieved by complexing **108b** with $Ru(bpy)_2Cl_2$ to give **108c** (Scheme 52). After isolation as mixture of diastereoisomers, the Ru-complex **108c** was subjected to the same polymerization conditions with Grubbs catalyst which had failed in the above experiment. Fortunately, this time polymerization took place and polymer **110** was isolated (Scheme 54).



108c **110**

Scheme 54. ROMP polymerization of **108c** to **110** in DCM using Grubbs generation I catalyst.

Polymer **110** carries two positive charges per repeat unit and is thus a polyelectrolyte. An accurate molar mass determination of polyelectrolytes is a rather complex matter and was therefore not even tried in this (model) case. It was just confirmed by ^{1}H NMR spectroscopy that the polymerization had actually taken place. The indicator was the complete disappearence of **108c**'s olefinic signals (Figure 61). The oligomeric/polymeric product was soluble in chloroform, DMF, and NMP, but not in THF.

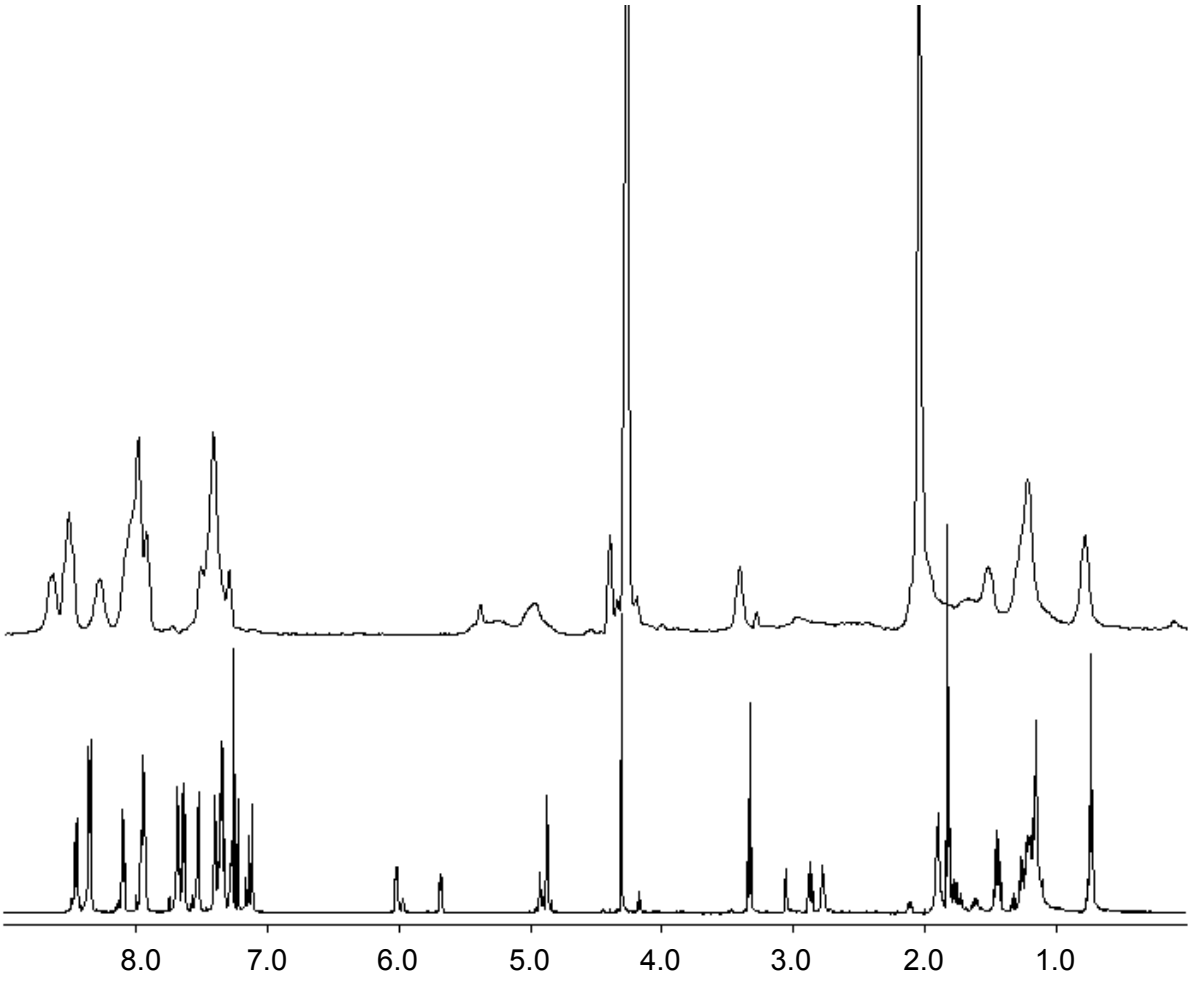
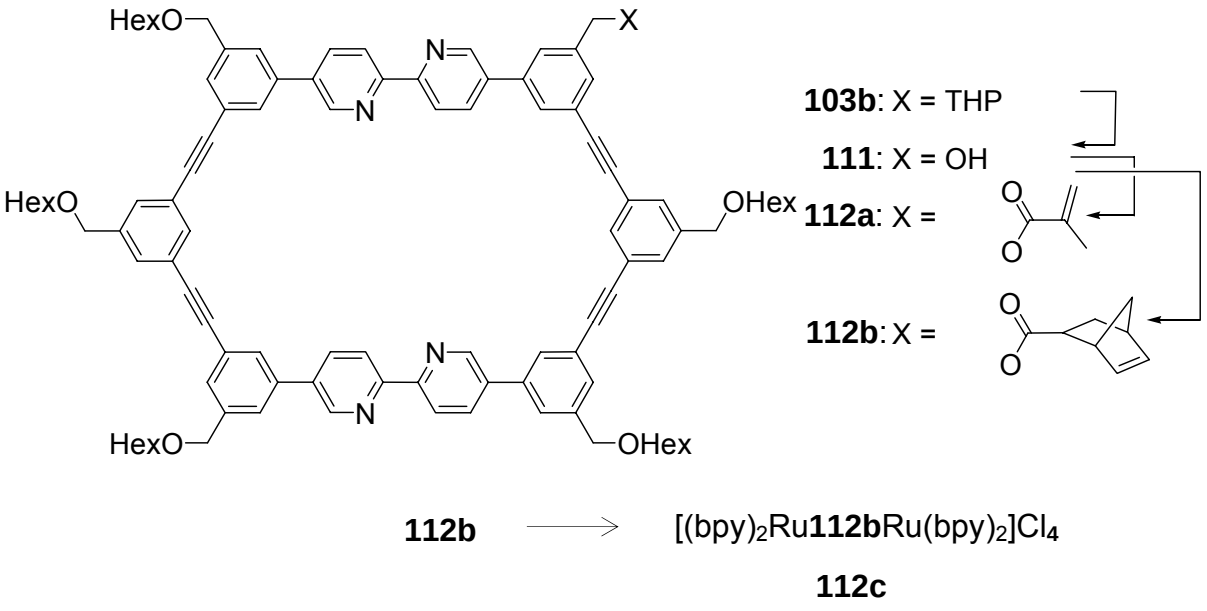


Figure 61. Comparison of the ^{1}H NMR spectra of monomer **108c** (bottom) and of its polymerization product **110** (top), (CD_3NO_2, 270 MHz, 20 °C).

4.4.2. Syntheses of macrocyclic macromonomers and their polymerization

The macrocycle **103b** has two bipyridine units in its structure, five hexyl groups to keep it tractable, and a THP protected alcohol for further functionalization. The synthesis of **103b** used the symmetrical and non-symmetrical building blocks **74b** and **102b**, and was already described before (Chapter 4.2). The deprotection of **103b** at its THP group was done in hydrochloric acid (Scheme 55). The reaction went cleanly as was supported by the ^{1}H NMR spectrum of the raw alcohol **111** which did not show any signal corresponding to THP. Also in the FAB(+) mass spectrum of **111** no signal of protected macrocycle **103b** was observed. Concentration dependent NMR measurements of pure alcohol **111** showed the cycles tendency to self-associate. All aromatic signals were increasingly up-field shifted with increasing

concentration. This effect was not quantified, an association constant not determined. It is reasonable to assume that the association is due to π–π– as well as hydrogen bonding interactions.

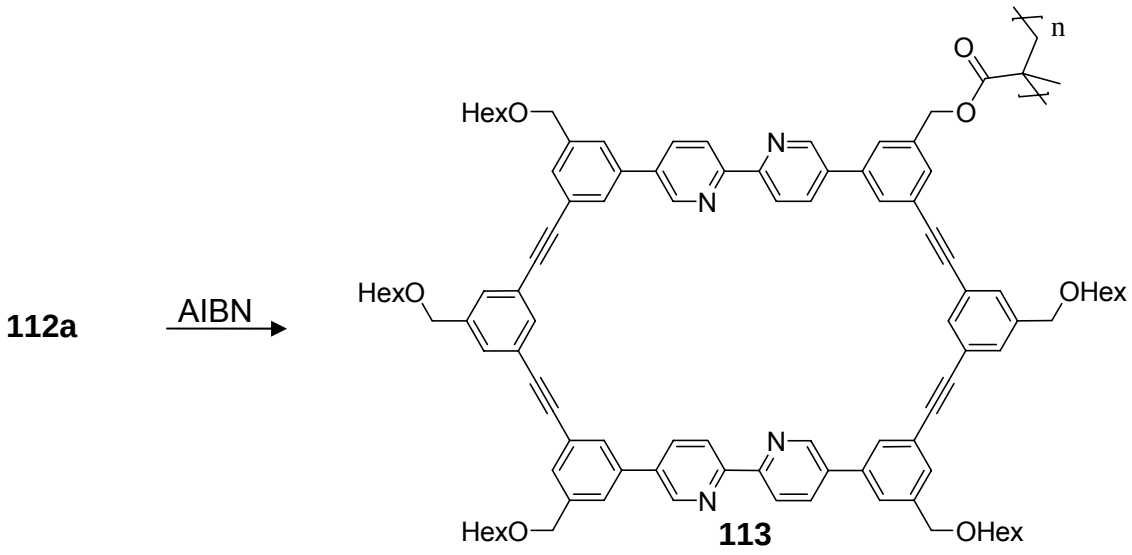


Scheme 55. Synthesis of the macromonomers **112a** and **112c**.

For the synthesis of the macrocyclic macromonomer **112a** for FRP alcohol **111** was reacted in a standard procedure with freshly distilled methacrylic acid chloride (Scheme 55). This gave the product on the 200 mg scale. The characterization of **112a** rests upon the ^{1}H and ^{13}C NMR spectra including full signal assignment, its mass spectrum, and correct data from combustion analysis (Figure 62).

In macromonomer polymerization the application of an as high as possible concentration is essential. Otherwise the concentration of the polymerizable units is so low that the polymerization is slowed to the extent that side reactions can take over.[75] This is why the polymerization of **112a** was performed in highly concentrated solutions (for macrocycles) with molarities of up 0.11 M. Few solvents and initiators were tried for the polymerization. The first successful polymerization of **112a** was achieved in benzene with AIBN as initiator precursor (Scheme 56). The product (**113**) was isolated by preparative GPC and structurally analyzed by ^{1}H and ^{13}C NMR spectroscopy. Figure 62 compares the ^{1}H NMR spectra of monomer **112a** and polymer **113**. As expected the olefinic signals of **112a** are absent in the spectrum of the polymer and all signals are broadened. It is noteworthy that the signals associated with the cyclic substituent on **113**'s backbone suffer a considerable

highfield shift of approximately 0.5 ppm. This reflects the cycles' close proximity and thus their mutual influence.[1c,d]



Scheme 56. FRP of macrocycle **112a** in benzene and AIBN as initiator.

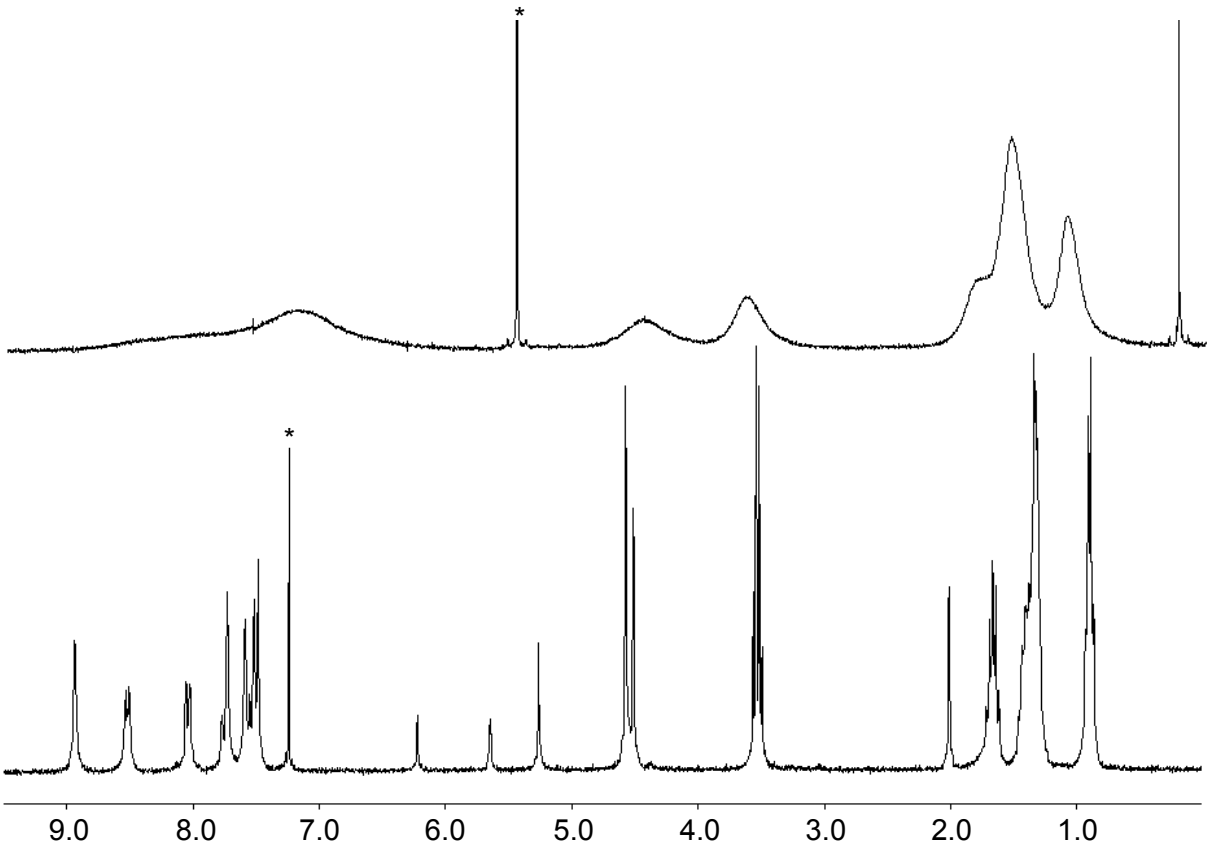


Figure 62. ^{1}H NMR spectra of **112a** (bottom) (*: $CDCl_3$, 270 MHz, 20 °C) and of corresponding polymer **113** (top) (*: CD_2Cl_2, 270 MHz, 20 °C).

The molecular weight of the product was determined by GPC referenced to PS (polystyrene). The elution curve revealed a monomodal distribution with the results: M_n = 10,500, M_p = 13,800, M_w = 14,000, PDI = 1.35 (Figure 63). This M_n value corresponds to a degree of polymerization P_n = 7. As already mentioned above these values can just be considered rough estimations. The ^{1}H NMR spectrum of **113** (Figure 62) has very broad signals which makes it likely that the actual molar masses are higher. Unfortunately also a MALDI-TOF mass spectrometric analysis of the product did not shed more light onto this important point. Recorded in dithranol as matrix it showed only oligomers up to the sixteenmer with the tetramer being the strongest signal which obviously cannot be the case (Figure 64). Unfortunately it could not be clarified whether there are, in fact, no higher molar mass components or whether they have been decomposed by the laser beam in the attempt to get them into gas phase.

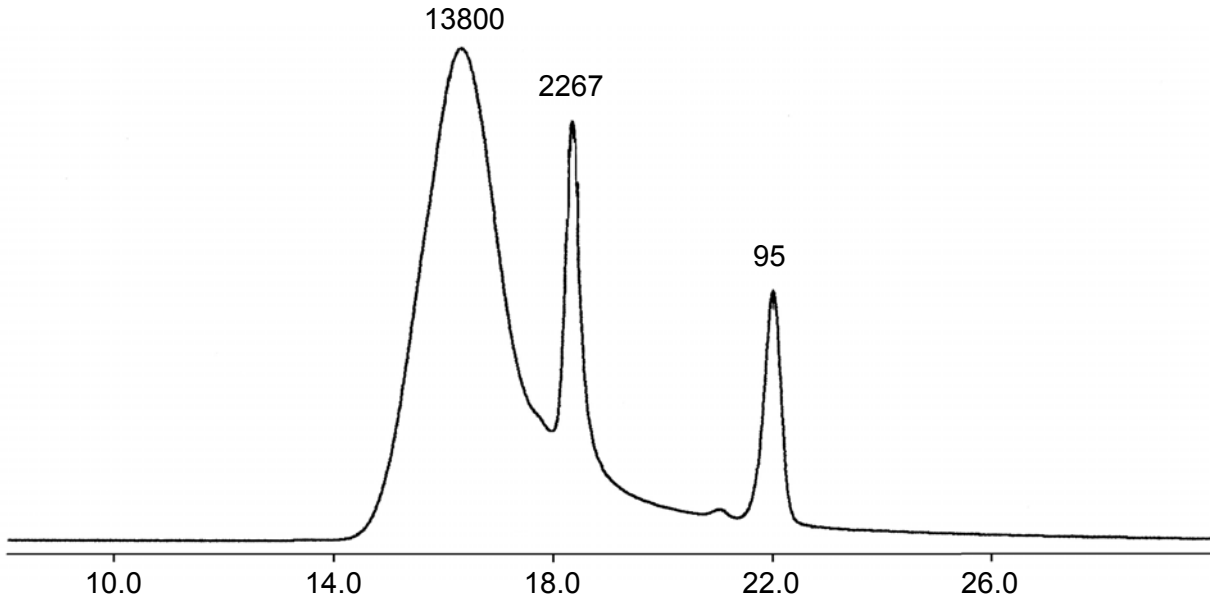


Figure 63. GPC elution curve of the raw product obtained from FRP of monomer **112a**. The curve shows a monomodal distribution with the results: M_n = 10,500, M_p = 13,800, M_w = 14,000, PDI = 1.35. The M_n value corresponds to a degree of polymerization P_n = 7

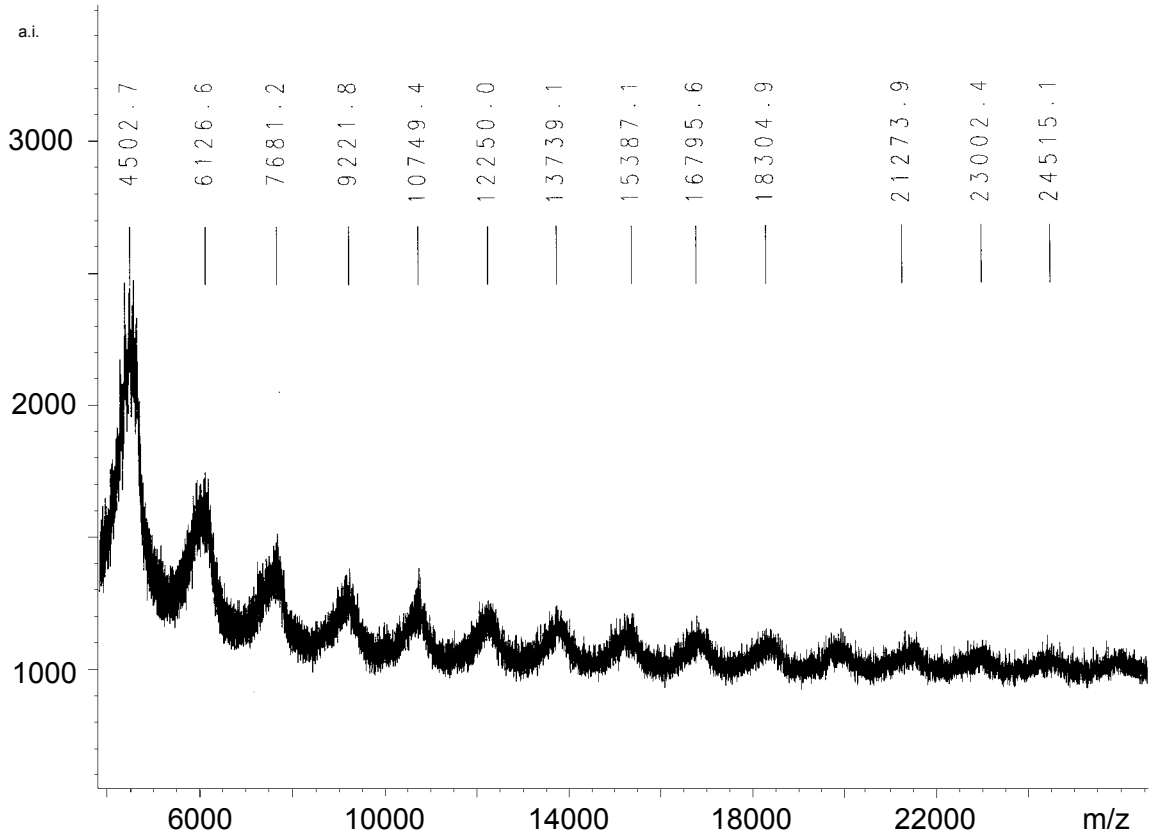


Figure 64. MALDI-TOF spectrum of oligomer **113** in dithranol matrix (reflector mode).

It is well-known for the ROMP of *endo*/*exo*-norbornene esters that the *exo* isomer reacts significantly faster than the *endo* isomer.[76] Recently, a detailed mechanistic investigation for the ROMP of *endo*- and *exo*-dicyclopentadiene has shown that the rate difference between the two isomers is primarily due to steric interactions between the growing polymer chains and the incoming monomer.[77] Therefore, the utilization of isomerically pure *exo* monomers could lead to better polymerizations. Isomerically pure *exo*-norbornene acid was synthesized via isomerization of the corresponding norbornene methyl ester from an 80:20 to a 45:55 *endo*/*exo* mixture followed by hydrolysis to the norbornene acid and removal of excess *endo* isomer by selective iodolactonization.[78] The functionalization of *exo*-norbornene acid was carried out via DCC/DMAP-assisted esterfication with alcohol **111** to give the corresponding *exo*-**112b** in 96% yield (Scheme 55). The raw product was dissolved in a small amount of THF and the macrocycle was precipitated by addition of methanol to this solution. The macrocycle was used without additional purifications, its high purity is reflected by the ^{1}H NMR spectrum (Figure 65). **112b**

showed concentration dependent ^{1}H NMR chemical shifts in $CDCl_3$, indicating an aggregation tendency.

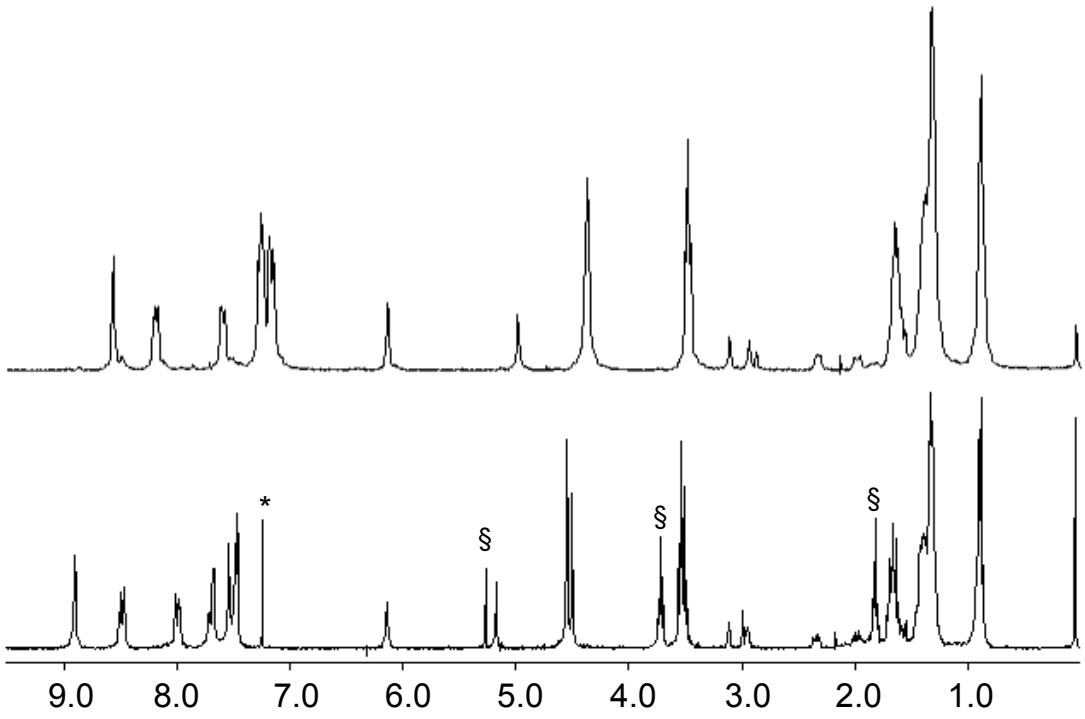


Figure 65. ^{1}H NMR spectra of monomer **112b** at a) higher and b) lower concentrations (*: $CDCl_3$, 270 MHz, 20 °C, §: traces of solvents).

The macromonomer **112a** was converted into its Ru complex **112c** by refluxing it with excess of $[Ru(bpy)_2Cl_2]$ in a mixture of ethylene glycol and dioxane (Scheme 55). After removal of solvent, the remaining brownish solid was purified by column chromatography through silica gel. For a better characterization of **112c**, a small part of the complex was precipitated as hexafluorophosphate. The resulting precipitate was fully characterized and gave correct elemental analysis. Figures 66 and 67 show the ^{1}H NMR spectrum and MALDI-TOF mass spectrum of **112c**.

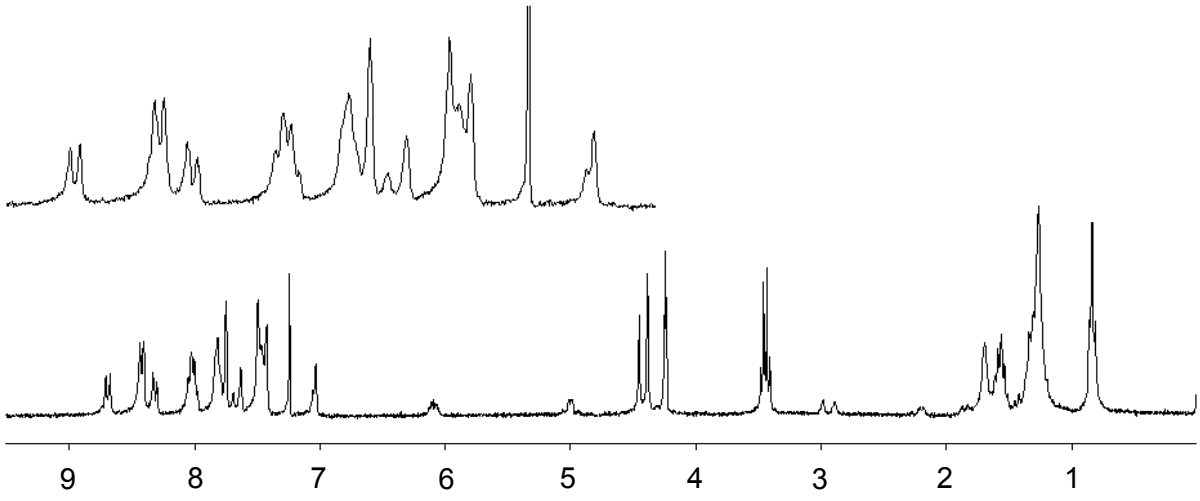


Figure 66. ^{1}H NMR spectrum of macromonomer **112c** (as PF_6 salt) ($CDCl_3$, 270 MHz, 20 °C).

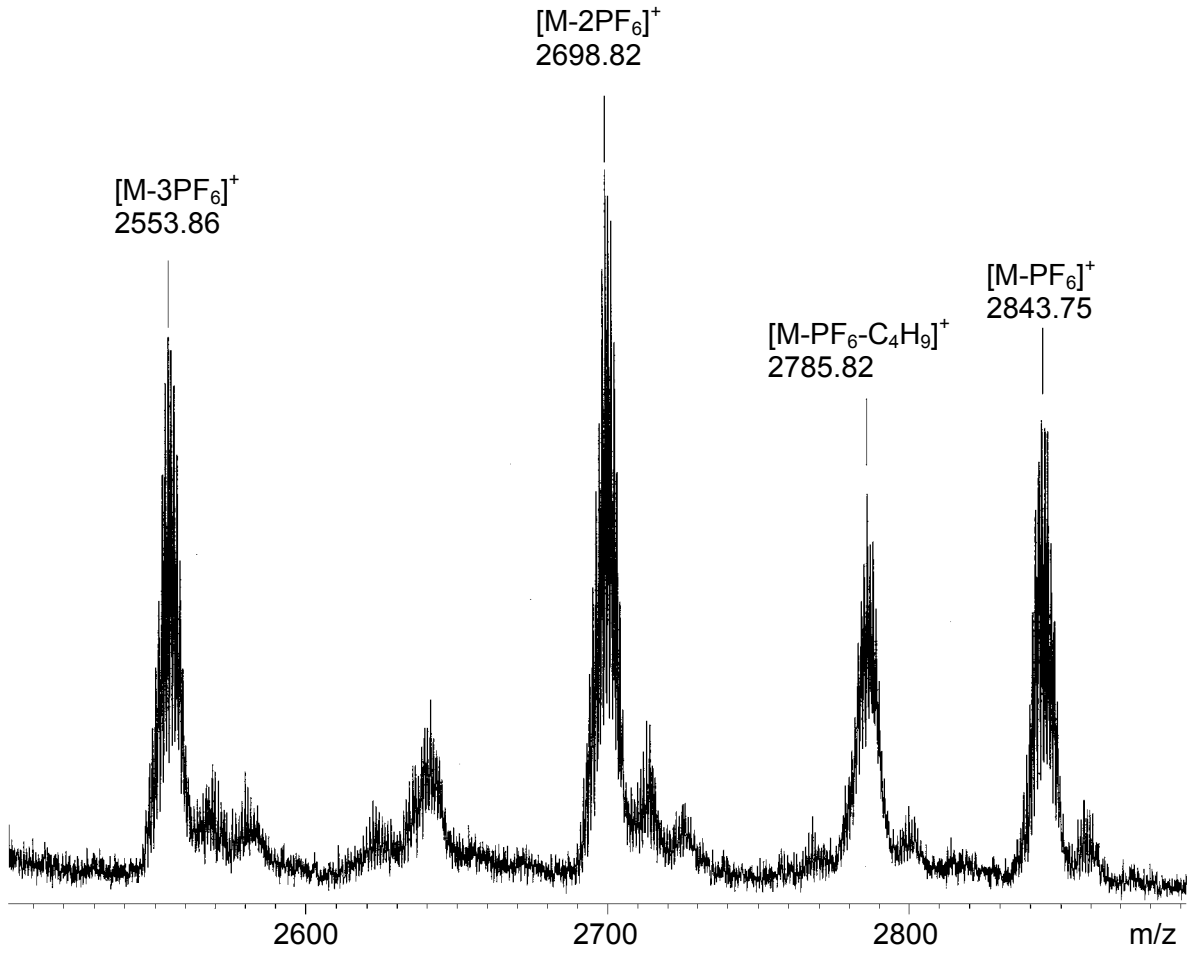
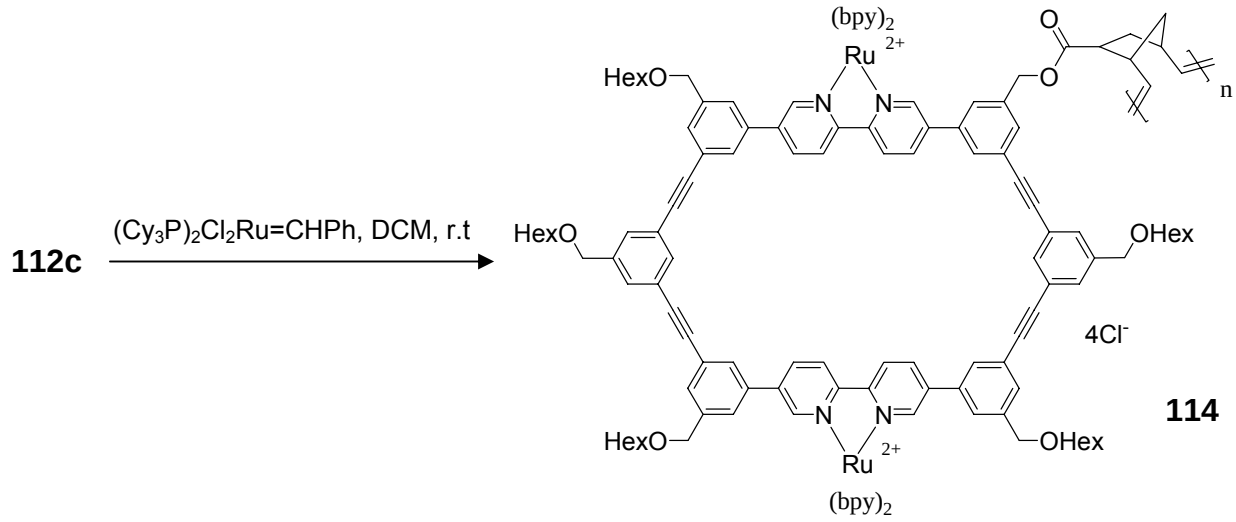


Figure 67. MALDI-TOF mass spectrum (dithranol matrix) of macromonomer **112c** (as PF_6 salt).

For the polymerization **112c** was used as the chloride salt because of its better solubility compared with the corresponding PF_6 salt. Using the same reaction conditions as described for the model compound **110** polymer **114** was obtained (Scheme 57). The ^1H NMR spectrum of **114** shows the ring-opened norbornene and gives no evidence for end groups. Especially characteristic is the disappearance of the norbornenic olefin signals of monomer **112c** at δ = 6.1 ppm with concommitant appearance the olefinic signals of **114** which absorb at δ = 4.9 and 5.3 ppm as is typical for norbornene ROMP polymers (Figure 68).[79] The polymerization was carried out in dichloromethane solution from which the polymer precipitated. GPC measurements could not yet be performed because of **114**'s polyelectrolyte character.



Scheme 57. ROMP of macrocycle **112c** using $(Cy_3P)_2Cl_2Ru=CHPh$ as initiator in DCM.

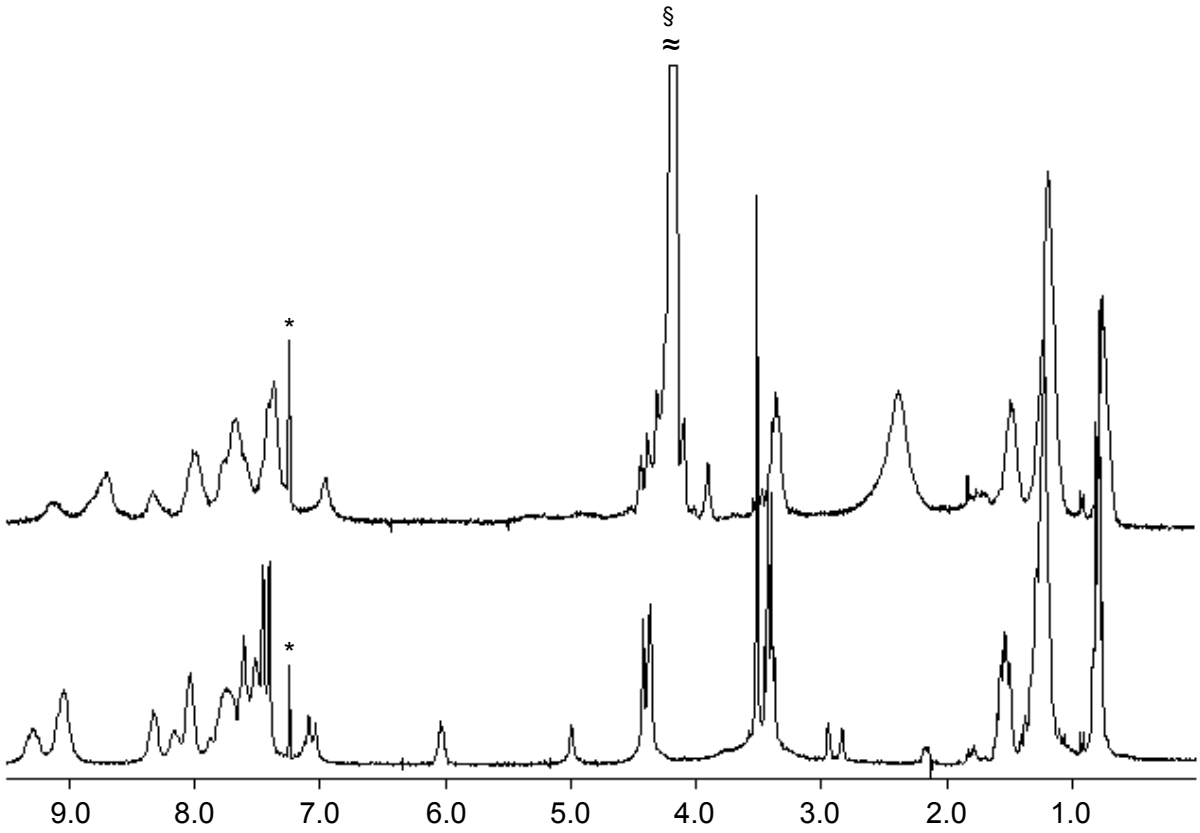


Figure 68. ^{1}H NMR spectra of macromonomer **112b** as Cl salt (*: $CDCl_3$, 270 MHz, 20 °C) and corresponding polymer as Cl salt (*: $CDCl_3$, §: CD_3NO_2, 270 MHz, 20 °C).

This exploratory work has shown that FRP and ROMP can be used in the polymerization of bipyridine macrocycles **112a** and **112c**. Further work will be required specifically in regard to the molecular weight determination. Such polymers represent a new class of polymeric materials which may lead to interesting properties.