Coordination polymers from kinetically labile copper(I) and silver(I) complexes: True macromolecules or solution aggregates?

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SUMMARY: Copper(I) and silver(I) coordination polymers have been prepared via conversion of equimolar amounts of *o*-phenanthroline-based *bis*-bidentate ligand monomers, and $[Cu(CH_3CN)_4]PF_6$ or $AgBF_4$ as the respective metal comonomers. Using NMR spectroscopy, the homogeneous constitution of the diamagnetic products has been proved, and their average chain length has been estimated to be $P_n \geq 20$. Moreover, NMR studies showed the multinuclear complexes to be open (dynamic) solution aggregates when dissolved in solvents that contain coordinating species like acetonitrile or pyridine. When strictly non-coordinating solvents are used, on the other hand, the multinuclear complexes were found to be "true" polymers, *i.e.* macromolecules with a constant number of repeating units per individual chain in time. At very high dilution, finally, transformation of the originally formed chain molecules into cyclic oligomers was observed when coordinating solvents are used, but not in the case of non-coordinating solvents.

Introduction

High-molecular-weight chain molecules **A** held together by transition-metal complexes, *i.e.* transition-metal coordination polymers, are of considerable interest in macromolecular and supramolecular science because of their electronic, magnetic, optic, catalytic, and solution properties[1,2]. Much effort has been spent, therefore, during recent years to make available a broader variety of such species. Most of the thus developed well-defined polymers are based on thermodynamically stable and *kinetically inert* transition-metal complexes. This selection is reliable because the characterization of the resulting polymers is possible in solution, using essentially the same techniques as are applied for conventional macromolecules. In contrast to this, well-defined coordination polymers from *kinetically labile* transition-metal complexes are still nearly unknown. This is mainly due to the fact that such species decompose simultaneously with their dissolution. Consequently, characterization is possible only in the solid state, and determination of the solution properties is precluded.

Recently, we lined out a number of requirements that we assumed to be essential for obtaining

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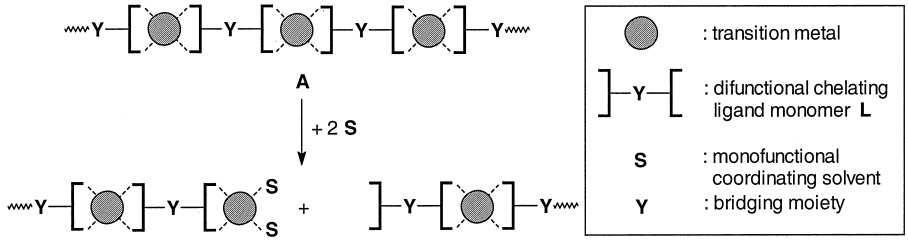
readily soluble and thus fully characterizable coordination polymers even from kinetically labile transition-metal complexes[3,4]. The key aspect of our concept was the assumption that coordination polymers decompose exclusively via displacement of the original ligand monomers **L** by coordinating solvent molecules **S** (Scheme 1): even if **S** is not a chelating ligand, it nevertheless can compete successfully for the metal ions because it is present in large number.

Scheme 1



To avoid decomposition according to Scheme 1, coordination polymers **A** from kinetically labile metal complexes must be designed in a way that they are also soluble in strictly non-coordinating solvents. In these media, ligand-exchange should be excluded and hence, the dissolved multinuclear complexes should behave like "true" polymers. In order to probe this concept, we had to take measures to make soluble the coordination polymers — which are polyelectrolytes in general and thus prefer highly polar solvents — also in less polar, non-coordinating media. Attachment of flexible *n*-hexyl side chains was assumed to be one possible method to achieve this goal. Indeed, we were able to verify our hypothesis by means of coordination polymers **1a** and **1b** (Figure 1)[3,4]. Careful analysis of these multinuclear complexes showed them to be well-defined macromolecules in non-coordinating solvents like 1,1,2,2-tetrachloroethane (TCE), but open solution aggregates in the presence of coordinating solvents like acetonitrile or pyridine.

In continuation of this basic work it was of interest to find out to what extent the above strategy can be generalized. One aspect in this regard was the question concerning benefit of the *n*-hexyl side chains of **1**: in addition to their solubilizing effect, they might additionally protect the metal complexes against the attack of coordinating solvent molecules because of their steric demand. A second aim was to find out whether or not entropy forces the kinetically labile multinuclear complexes to decompose in highly diluted solution: cyclooligomerization and/or formation of oligomeric helicates may cause chain degradation and hence prevent full determination of the

properties of the polymeric chains in solution. To consider the above aspects, we have prepared the novel copper(I) and silver (I) coordination polymers **2a,b** and **3a,b** (Figure 1).

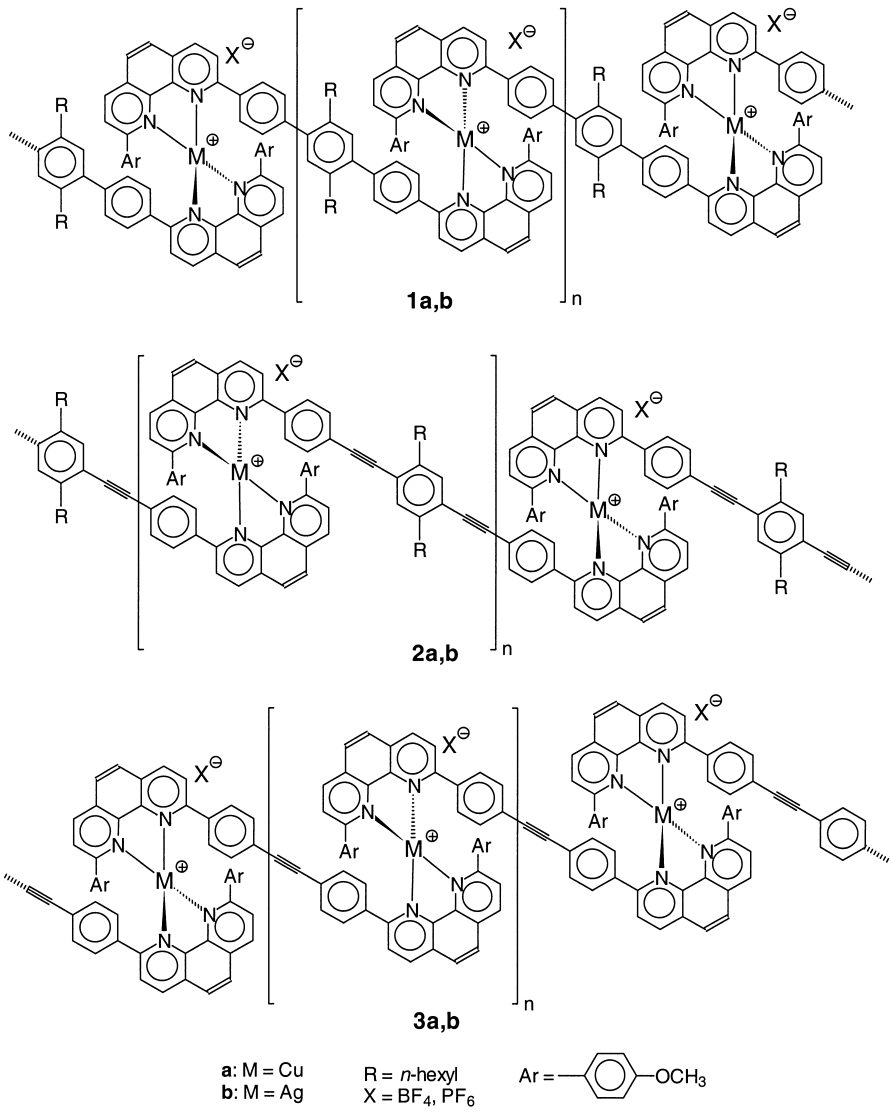
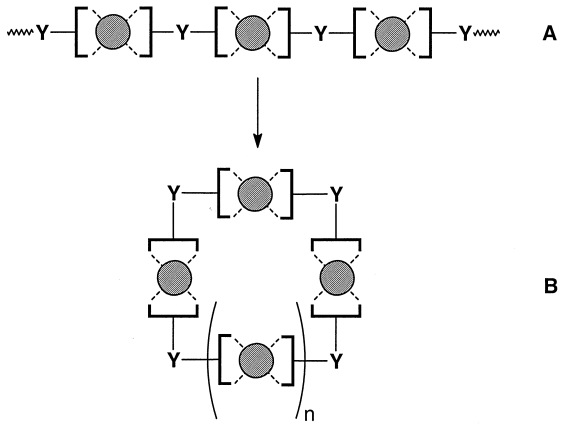


Fig. 1: Coordination polymers **1a,b** - **3a,b**.

In polymers **2**, the *n*-hexyl side chains have a larger distance from the neighboring metal complexes than in polymers **1**, and in polymers **3**, side chains are completely absent. Moreover, because the bridging units **Y** are conformationally rigid in all cases, formation of low-molecular-weight helicates should be rather unlikely. Cyclooligomerization according to Scheme 2, therefore, should be the only way of chain degradation at high dilution except for the destruction of the metal complexes as a whole. Finally, because all other features are quite similar in the three target systems shown in Figure 1, the detailed comparison of the coordination compounds **1** - **3** should provide a deeper insight into the general validity of our concept.

Scheme 2



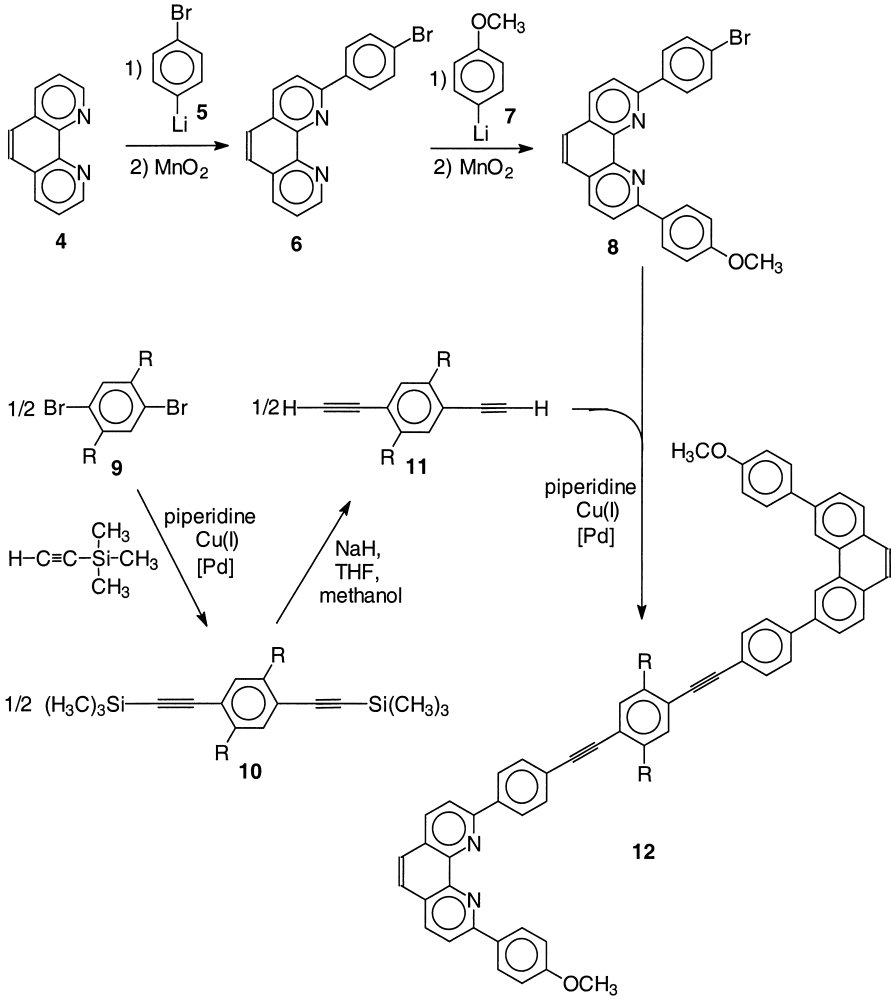
Monomer synthesis

2(*p*-Bromophenyl)-9(*p*-methoxyphenyl)-*o*-phenanthroline **8** was the central intermediate required for the synthesis of compounds **12** and **15**, the ligand monomers of polymers **2a,b** and **3a,b**. For its synthesis, *o*-phenanthroline **4** was treated with a slight excess of *p*-bromophenyllithium **5** in diethyl ether at - 10 °C. The formed intermediate was dehydrogenated using MnO_2, leading to 2-(*p*-bromophenyl)-*o*-phenanthroline **6**[4]. Then, the arylation-rearomatization sequence was repeated with compound **6**, however, using *p*-methoxyphenyl lithium **7** as the arylating agent. From this process, the desired key compound **8** was obtained in approx. 80 % yield.

2,5-Dihexyl-1,4-diethinylbenzene **11** was another starting material required for the synthesis of **12**. It was prepared via Pd-catalyzed condensation of 1,4-dibromo-2,5-dihexylbenzene **9**[5] and

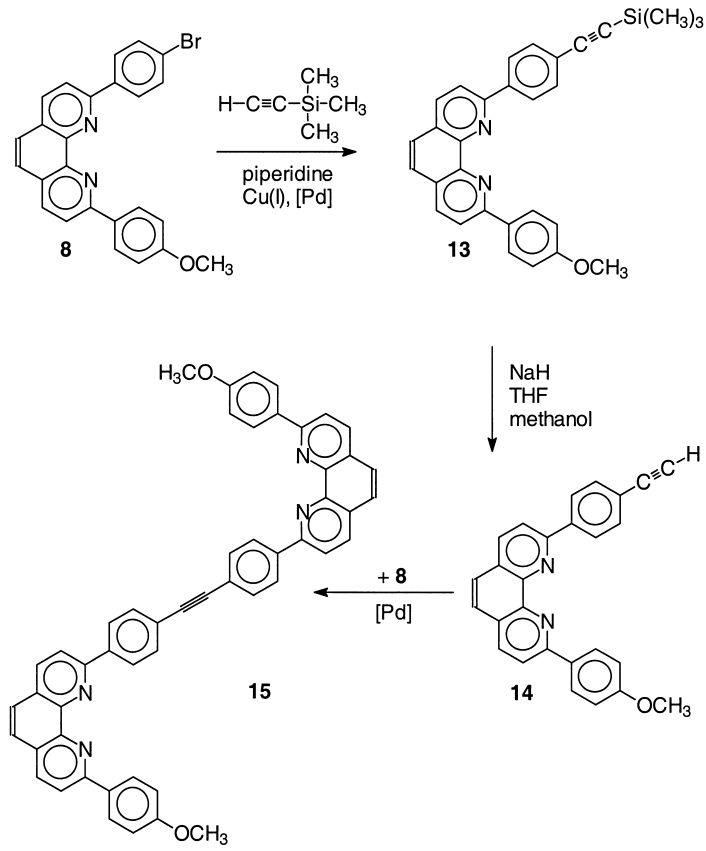
trimethylsilylacetylene in the presence of catalytic amounts of [$Pd(PPh_3)_4$] and CuI, using piperidine as both, solvent and base. The cleavage of the trimethylsilyl protecting groups of **10** was achieved in a mixture of THF, methanol, and sodium hydride. Pure **11** was isolated as a yellow oil (30% yield) which was subsequently treated with a twofold molar excess of **8** under Pd-catalysis. The desired *n*-hexyl substituted ligand monomer **12** was obtained in 60-70% yield.

Scheme 3



9-(*p*-Methoxyphenyl)-2(*p*-ethinylphenyl)-*o*-phenanthroline **14** was required for the synthesis of ligand monomer **15**. It was prepared in an overall yield of 80% via Pd-catalyzed condensation of equimolar amounts of **8** and trimethylsilylacetylene, followed by cleavage of the trimethylsilyl protecting groups of intermediate **13**. Heating equimolar amounts of **8** and **14** in the presence of $[Pd(PPh_3)_4]$, CuI and piperidine resulted in the pure yellow solid **15** (40% yield).

Scheme 4

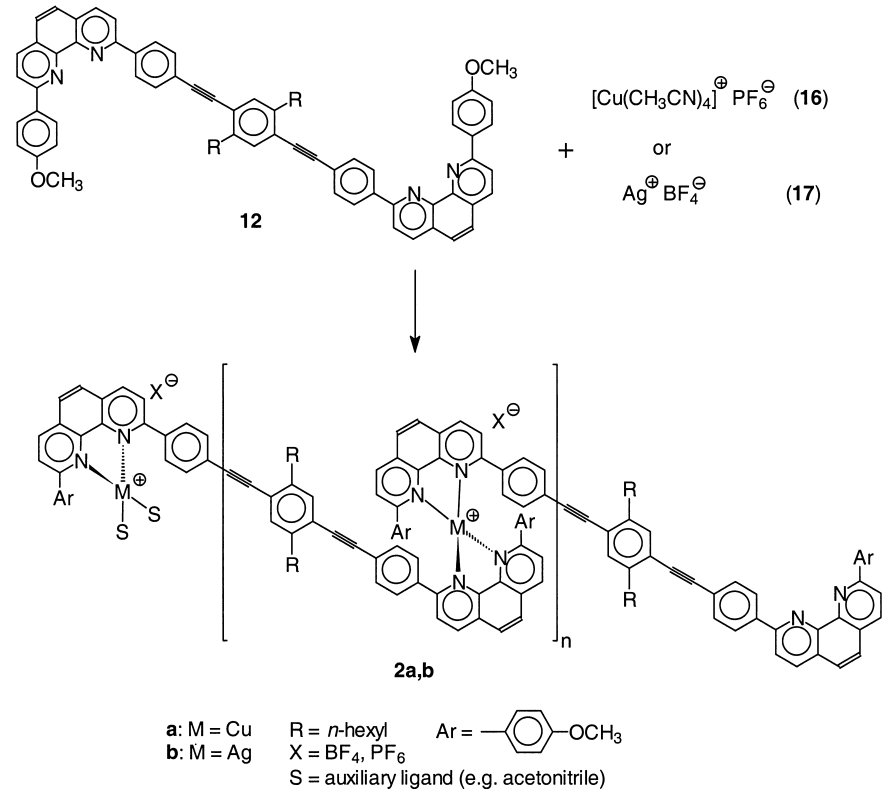


The molecular constitution of ligand monomers **12** and **15** as well as of all isolated intermediates was verified using ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The purity of the ligand monomers **12** and **15** was estimated to be > 98% (^{1}H NMR).

Polymer synthesis

Most of the subsequent conversions of ligand monomers **12** and **15** into the copper(I) and silver(I) coordination compounds **2a,b** and **3a,b**, respectively, were carried out in NMR tubes, using the same procedure as described recently for the synthesis of **1a,b**[4]. We started our studies by preparing the copper(I) system **2a** (Scheme 5): 1.0 equiv. (approx. 50 mg) of **12**, 0.8 equiv. of $[Cu(CH_3CN)_4]PF_6$ **16**, and approx. 1 mL of an 4:1 (v/v) mixture of TCE-d_2 and acetonitrile-d_3 were weighed into an NMR tube[a]: The mixture was slightly heated and subsequently, a ^1H NMR spectrum was recorded of the resulting homogeneous solution.

Scheme 5



[a] This solvent mixture was found to be well-appropriate for these conversions: TCE is a good solvent for the ligand monomers as well as for the resulting coordination polymers. Acetonitrile, on the other hand, readily dissolves the metal monomers like **16** and **17**. Moreover, it catalyzes the formation of the desired $[M(phen)_2]^+$ motifs.

Afterwards, further small quantities of **16** were added to the solution in steps of approx. 0.05 equiv. Each time, a ^{1}H NMR spectrum was recorded after complete conversion. As an example, Figure 2B shows the spectrum of an oligomeric complex **2a** prepared from 1.0 equiv. of **12** and 0.8 equiv of **16**. Figure 2A, on the other hand, displays the spectrum of ligand monomer **12**. Comparison of these two spectra makes evident that the desired (pseudo)tetrahedral $[Cu(phen)_2]^+$ motifs and hence the multinuclear complexes **2a** were formed: the characteristic upfield shift of most of the intense absorptions in spectrum B represents a clear proof of the desired catenation of ligand monomers **12** via copper(I) complexes[b]. In addition to the intense absorptions of the inner-chain repeating units of **2a** there are observable signals of minor intensity (assigned by asterisks in Figure 2B). We assign these absorptions to the chain-termini of **2a** which were expected because of the 1.0 : 0.8 molar ratio of the comonomers used here. Moreover, the ratio of the signal intensities of inner-chain repeating units and well-defined endgroups [in particular those of the OCH_3 protons at $\delta \approx 4.0$ ppm (terminal methoxy groups) and $\delta \approx 3.5$ ppm (inner-chain methoxy groups)] resulted in an average degree of polymerization of $P_n \approx 6$-8. This estimate is in good agreement with the comonomer ratio applied here.

When the 1 : 1 equivalence of the comonomers was finally adjusted, all the small absorptions disappear completely, and only the intense signals of the inner-chain repeating units remain. The spectrum does not change any more even if the formed product **2a** is isolated via precipitation in *n*-hexane and redissolved in pure TCE-d_2 (Figure 2C): the lack of endgroup absorptions and of absorptions that might correspond to structural defects proves both, the homogeneous constitution and the considerable chain length of **2a**. This conclusion was additionally supported by the ^{13}C NMR spectra: there as well, a full signal assignment could be done. To conclude, **2a** is stable also in the solid state and has — (*i*) due to the lack of endgroup absorptions, (*ii*) considering the limits of accuracy of the ^{1}H NMR method, and (*iii*) assuming that cyclic oligomers are not present here[c] — a value of $P_n \geq 20$.

A quite different behavior was observed when the corresponding silver(I) polymer **2b** was prepared. In order to illustrate this difference, Figure 2D shows the ^{1}H NMR spectrum of a reaction mixture obtained via conversion of 1.0 equiv. of ligand monomer **12** and 0.8 equiv. of $AgBF_4$ **17** in TCE-d_2 / acetonitrile-d_3 (4:1, v/v). The intense absorptions of the inner-chain

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[b] This upfield shift is due to magnetic shielding effects caused by the ring currents of the aromatic units of the neighboring ligand monomers: in polymers like **2a**, the succeding ligand monomers are spatially arranged in a way that their protons are placed "above" (or "below") the *o*-phenanthroline rings of the neighboring ligand monomers.

repeating units of **2b** are readily detectable and support the formation of the desired multinuclear complex **2b**. But surprisingly, no endgroup absorptions can be observed in this spectrum, despite of the fact that **12** is present in a 20% excess. This is in clear contrast to the corresponding spectrum of **2a** (Fig. 2B) and might be due to a very fast ligand-exchange occurring in the silver(I) complexes, smearing out the endgroup absorptions. To verify this hypothesis, the oligomeric product **2b** was precipitated in *n*-hexane, carefully dried, redissolved in pure TCE-d_2, and studied again by NMR. This was done because the rate of ligand exchange should strongly depend on the concentration of acetonitrile. Supposed our initial hypothesis is valid, i.e. the coordinating co-solvent acetonitrile supports the ligand-exchange, endgroup absorptions should appear as soon as acetonitrile is absent. In fact, the missing absorptions are observable in the latter ^{1}H NMR spectrum (signals assigned by asterisks in Figure 2E). Now, by means of these absorptions, the precise 1:1 equivalence of the comonomers could be adjusted easily, and high-molecular-weight samples of **2b** could be obtained which do not show any endgroup signals even in pure TCE-d_2 (Figure 2F). ^{1}H and ^{13}C NMR spectra moreover proved the constitutional homogeneity of the formed product. All together, it is important to emphasize that disappearence of endgroup absorptions for oligomers was not observed in the case of the silver(I) complexes **1b**. This is a strong evidence for the higher lability of the complexes incorporated in coordination compounds **2**. The less efficient shielding of the metal complexes of **2** due to their larger distance from the *n*-hexyl side chains might be responsible for this finding.

Now, we broadened our studies to systems **3** which do not bear aliphatic side chains at all. Here as well, we started the experiments by means of the copper(I) species, using TCE / acetonitrile as the solvent system. The ^{1}H NMR spectra recorded from reaction mixtures containing an excess of either **15** or **16** were dominated by the intense absorptions of the inner-chain repeating units of **3a**. Nevertheless, there were also detectable the absorptions of the chain termini. Therefore, it was possible to adjust the 1:1 equivalence of the comonomers **15** and **16** using ^{1}H NMR spectroscopy very precisely. Finally, the high chain length as well as the homogeneous constitution of **3a** could be proved by means of ^{13}C NMR spectroscopy as well. To conclude, the solution properties of **3a** are quite similar to those of **2a**. The only significant difference is the much higher solubility of **2a** due to its solubilizing *n*-hexyl side chains.

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[c] Cyclooligomerization would cause disappearence of the endgroup absorptions as well.

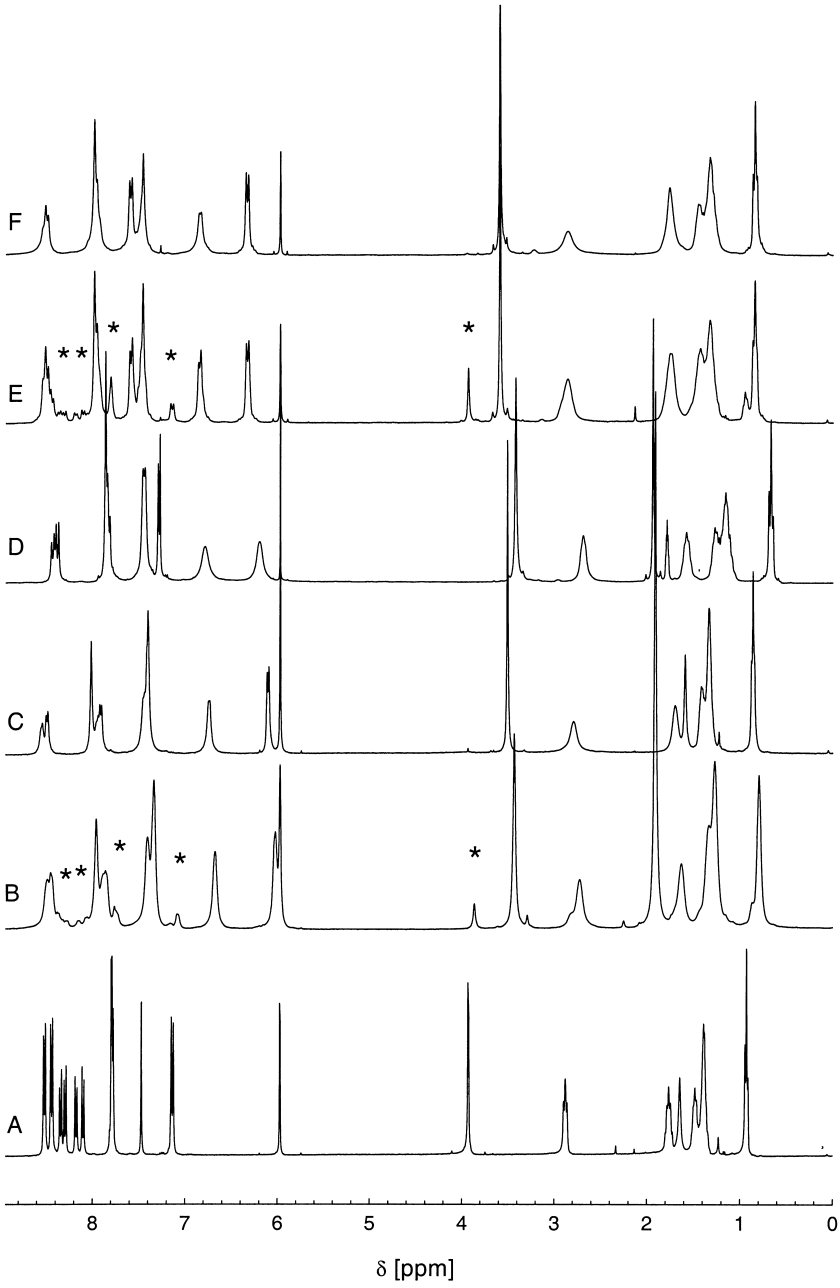


Fig. 2: ^{1}H NMR spectra of (A) ligand monomer **12** (TCE-d_2), (B) oligomeric complex **2a** (TCE-d_2/acetonitrile-d_3), (C) polymeric complex **2a** (TCE-d_2), (D) oligomeric complex **2b** (TCE-d_2/acetonitrile-d_3), (E) oligomeric complex **2b** (TCE-d_2), and (F) polymeric complex **2b** (TCE-d_2); see text for details.

Based on these results, the solution properties of the silver(I) compound **3b** were expected to be quite similar to those of **2b**. In full agreement with that, intense ^{1}H NMR absorptions were found for the inner-chain repeating units of **3b**, but endgroup absorptions could not be detected in the solvent system TCE / acetonitrile despite of an excess of **15** or **17** (20 % excess of **15** in the case of the spectrum shown in Figure 3B). After isolation of the formed oligomers and redissolution in pure TCE, however, the latter absorptions were detected as well (Figure 3C). Now, the precise 1:1 equivalence of the comonomers could be be adjusted (Figure 3D), and the homogeneous constitution as well as the considerable chain length of **3b** was proved using ^{1}H and ^{13}C NMR spectroscopy. To summarize, the above experiments show that — under otherwise identical conditions — the kinetic lability of the multinuclear silver(I) complexes **2b** and **3b** is higher than that of the corresponding copper(I) systems **2a** and **3a**. Moreover, it is evident that the lability of the polymeric complexes **2a** and **3a** as well as of **2b** and **3b** is quite similar. In other words, the aliphatic side chains of **2** are too far away from the metal centers and thus cannot cause a significant stabilization as was found for polymers **1**. Nevertheless, the *n*-hexyl side chains are of considerable benefit in polymers **2** because they increase the solubility considerably as one can see from the comparison with polymers **3**.

The quantities of **2** and **3** available via NMR titration are too small for a detailed analysis of their solution properties. Therefore, large-scale syntheses were performed, taking advantage of the elution time that the reaction mixture needs to pass a capillary to adjust the 1:1 equivalence of the comonomers. A three necked flask was equipped with a capillary viscosimeter, and we started the syntheses using 1.0 : 0.8 mixtures of the respective ligand- and metal monomers. After complete conversion, the elution time of the reaction mixture was determined. Subsequently, further quantities of metal monomer were added in steps of approx. 0.05 equiv. After each addition, the elution time was determined. A drastic increase was found until the 1:1 equivalence was reached. Then, if further metal monomer was added, the elution times dropped down again. In order to come back to the maximum elution time, the required quantity of ligand monomer was added. As an example, Figure 4 displays a characteristic plot recorded during the synthesis of **2a**. After isolation of the formed products as reddish-brown [copper(I) systems] or yellow [silver(I) systems] fibrous materials, it was possible to show by means of ^{1}H and ^{13}C NMR spectroscopy that really high-molecular-weight chain molecules of homogeneous constitution were formed under these conditions as well.

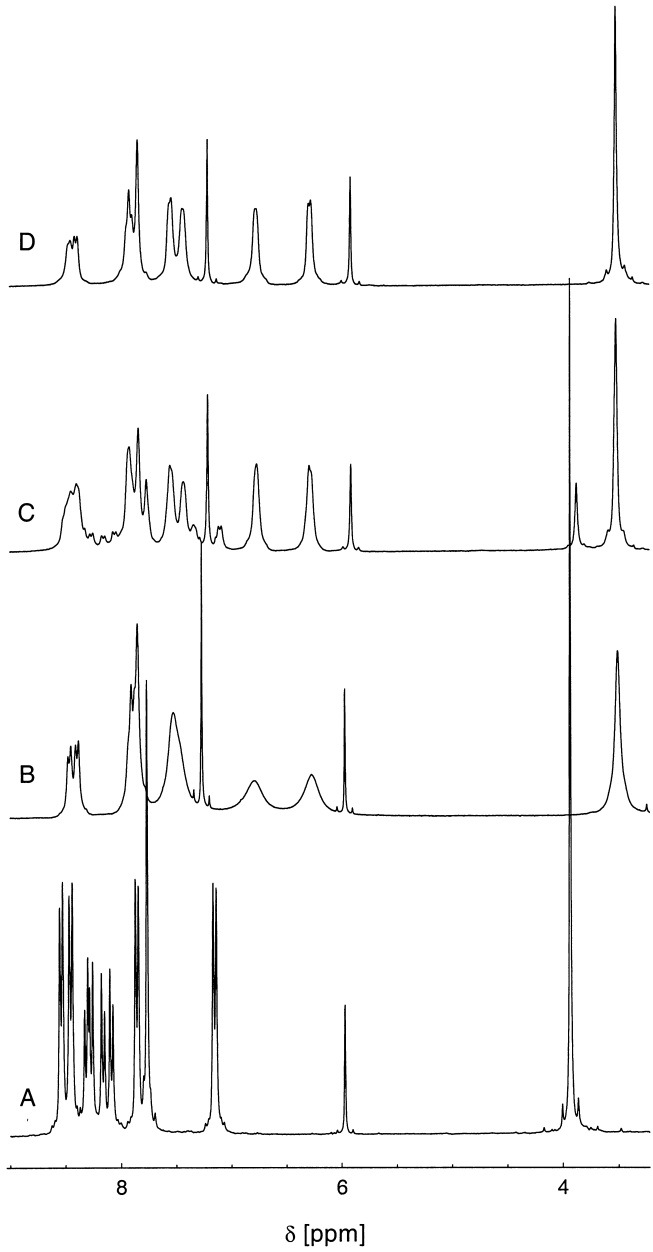


Fig. 3: ^{1}H NMR spectra of (A) ligand monomer **15** (TCE-d_2), (B) oligomeric complex **3b** (TCE-d_2/acetonitrile-d_3), (C) oligomeric complex **3b** (TCE-d_2), and (D) polymeric complex **3b** (TCE-d_2); see text for details.

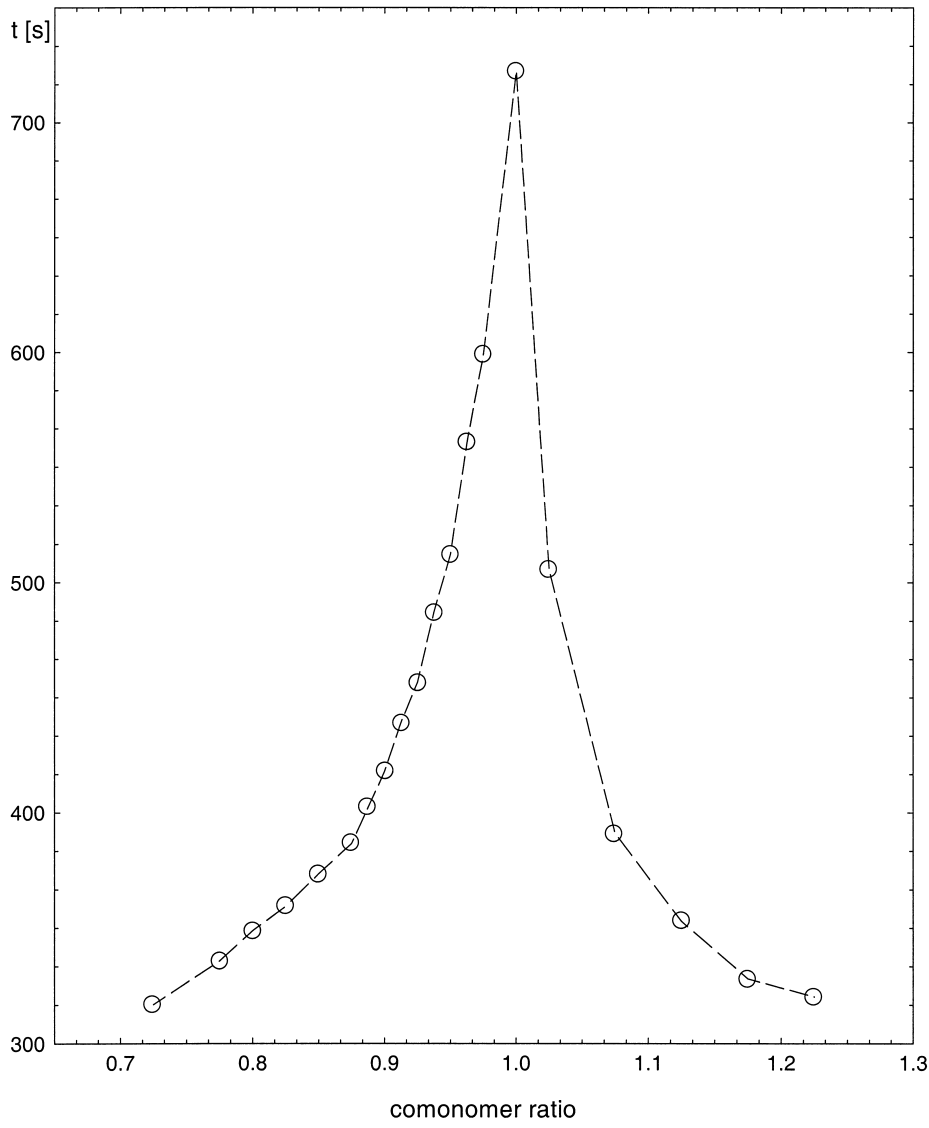
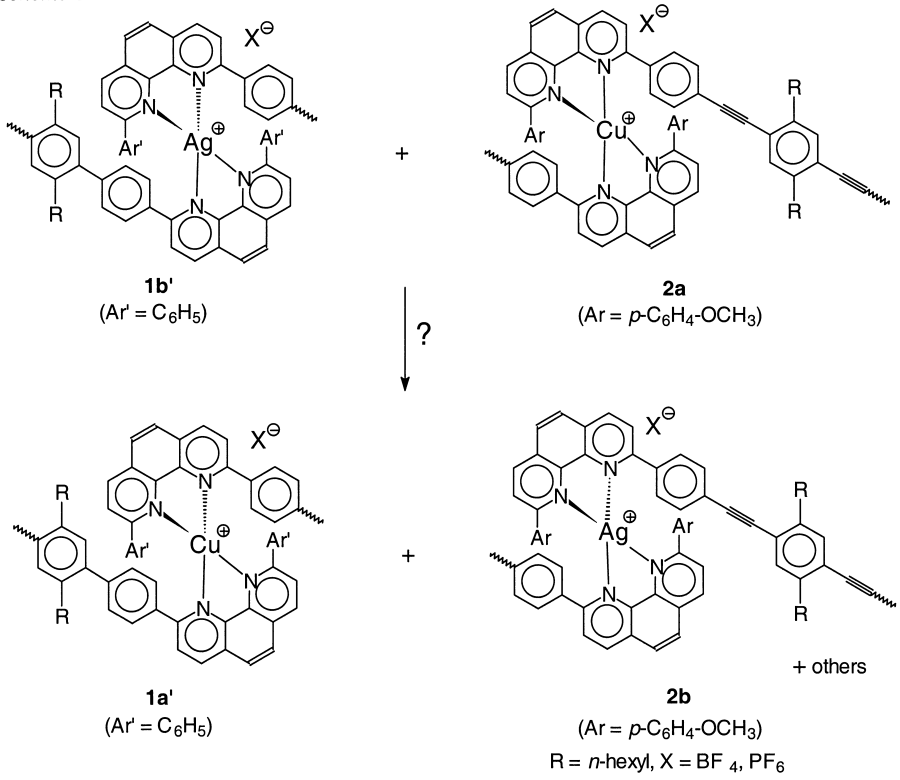


Fig. 4: Elution time of the reaction mixture vs. molar ratio of the comonomers **12** and **16**; the experiment was performed in acetone/acetonitrile. See text for details.

Properties in solution

The investigations described so far showed the multinuclear complexes **2a,b** and **3a,b** to undergo perpetual ligand exchange when dissolved in a coordinating solvent. Hence, under these conditions, the chains are dynamic (open) solution aggregates. On the other hand, ligand exchange is dramatically slowed down when no auxiliary ligands are available in the solution. So far, however, we did not show whether or not the ligand exchange is completely stopped in the latter media. Therefore, we carried out two further series of NMR studies in order to show under which conditions the multinuclear complexes are real macromolecules. First, a series of hybridization experiments was performed using various deuterated solvent systems (Scheme 6).

Scheme 6



In these experiments, we took advantage of the fact that the terminal methoxy groups of the ligand monomers absorb at slightly different chemical shifts depending on whether they are

attached to a copper(I) or a silver(I) complex. In practice, the solution of a copper(I) system (**2a** or **3a**) was mixed with a solution of the silver(I) polymer **1b'**. The latter does not bear methoxy groups at its phenyl substituents ("Ar" in Scheme 6). Vice versa, solutions of the silver(I) systems (**2b** or **3b**) were mixed with solutions of the respective copper(I) polymer **1a'**. After mixing, NMR spectra were recorded of the resulting solution at regular intervals in order to follow an eventual ligand-exchange according to Scheme 6. This is easily possible by analyzing in particular the singlet of the methoxy protons at $\delta \approx 3.5$ ppm. As an example, Figure 5 shows the spectra recorded in the course of such an experiment performed according to Scheme 6. Spectra A and B are those of the pure starting polymers **1b'** and **2a**, respectively, recorded in pure TCE-d_2. Immediately after mixing the solutions (spectrum C) as well as after 3 days (spectrum D), only one single absorption is observable at $\delta \approx 3.5$ ppm. This result proves the practically complete lack of ligand exchange in the absence of coordinating species. If, however, small amounts of a coordinating solvent such as acetonitrile (or water) are added, the ligand-exchange starts immediately. This process is clearly detectable by the appearence of a second singlet at $\delta \approx 3.7$ ppm as well as of further absorptions in the aromatic region (spectrum E).

In the second series of NMR experiments, we studied the behavior of the multinuclear complexes at very high dilution. By means of these investigations, we wanted to find out in which solvents the chain molecules either remain unchanged or decompose into small, presumably cyclic oligomers upon diluting. The concentration of the investigated solutions varied from $c_P \approx 20$ g·L^{-1} down to $c_P \approx 0.1$ g·L^{-1}, and non-coordinating as well as coordinating solvents were tested. In full agreement with the above results, no change was observed in the NMR spectra even at the lowest concentration when TCE was the solvent: only the well-known absorptions of the inner-chain repeating units were observed in all spectra (see Figure 6 for **2a**), proving the complete stop of ligand exchange in this non-coordinating solvent. When, on the other hand, the experiments were carried out in the presence of acetonitrile, or in slightly humid acetone, decomposition of the chain molecules into cyclic oligomers was observed: new absoptions appear in particular in the aromatic region, clearly not identical to those of the chain termini whose chemical shifts are well-known from the linear oligomeric systems discussed above. As an example, Figure 7 displays a series of ^{1}H NMR spectra of **2a**, recorded in acetone-d_6 at various concentrations.

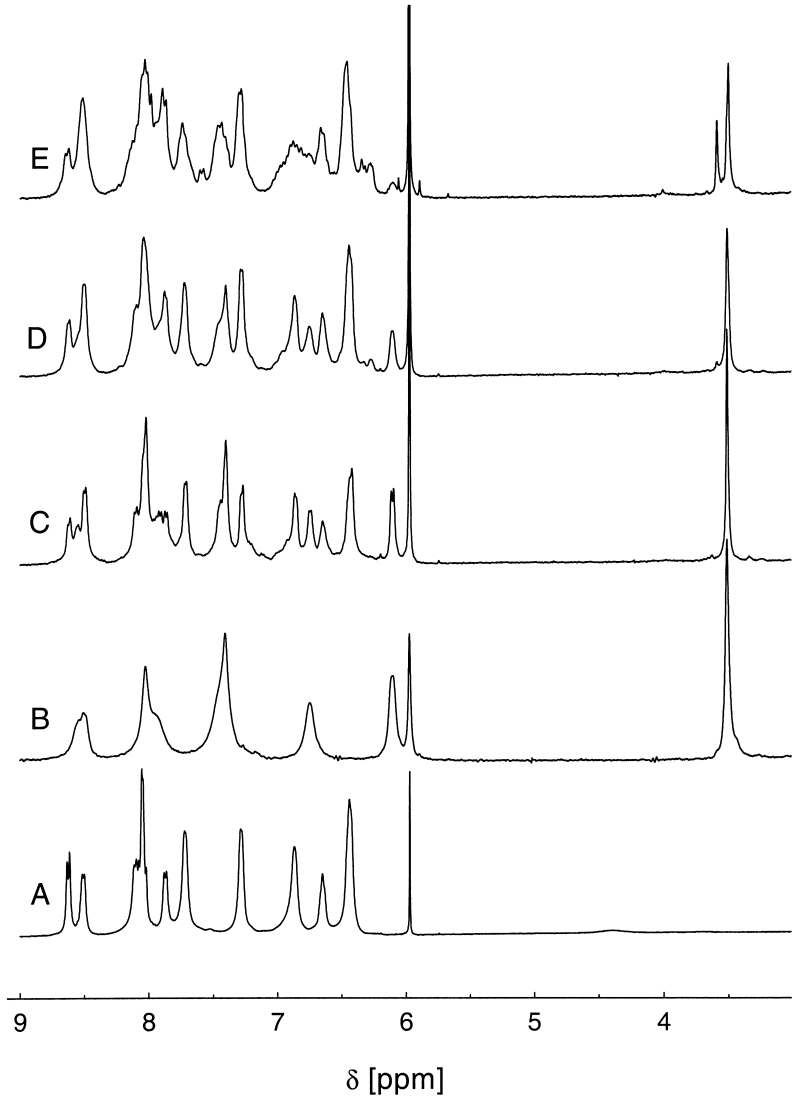


Fig. 5: ^{1}H NMR spectra of (A) polymeric complex **1b'** (TCE-d_2), (B) polymeric complex **2a** (TCE-d_2), (C) the mixture thereof after 5 min. (TCE-d_2), (D) the mixture thereof after 3 d (TCE-d_2), and (E) the mixture thereof after addition of acetonitrile; see text for details.

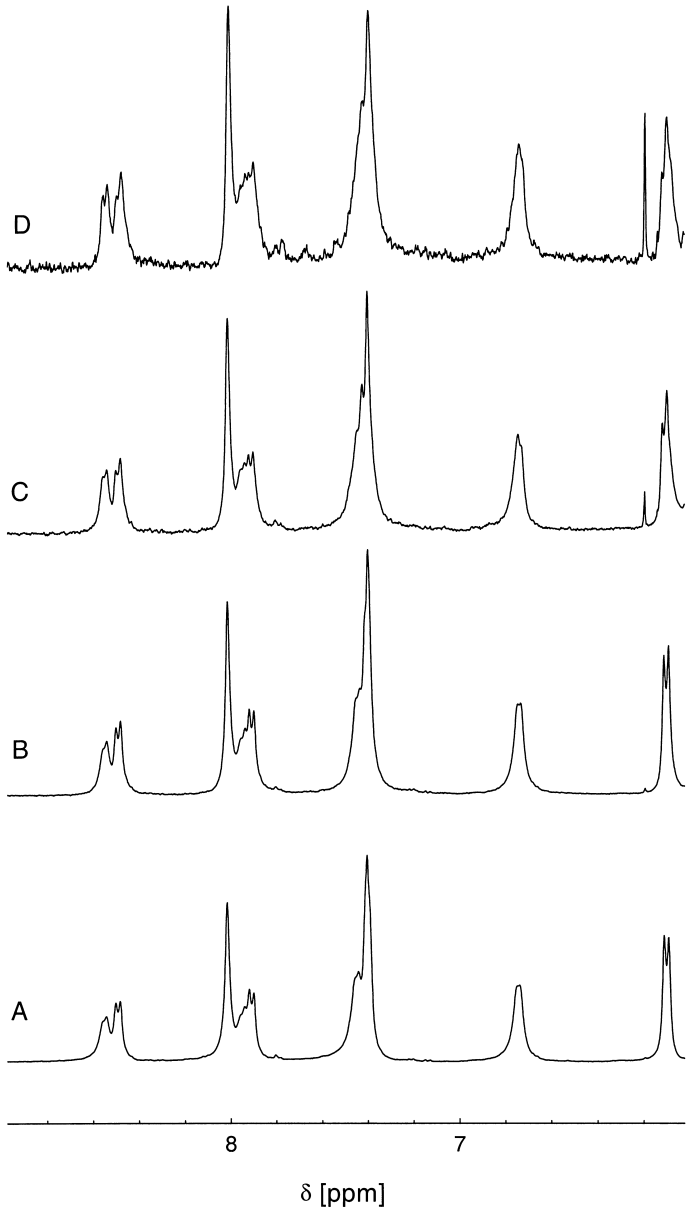


Fig. 6: ^{1}H NMR spectra of **2a** recorded at a concentration of c_P = (A) 10 g·L^{-1}, (B) 5 g·L^{-1}, (C) 1 g·L^{-1}, and (D) 0.1 g·L^{-1} (TCE-d_2). The sharp singlet at δ = 6.2 ppm is due to the solvent; see text for details.

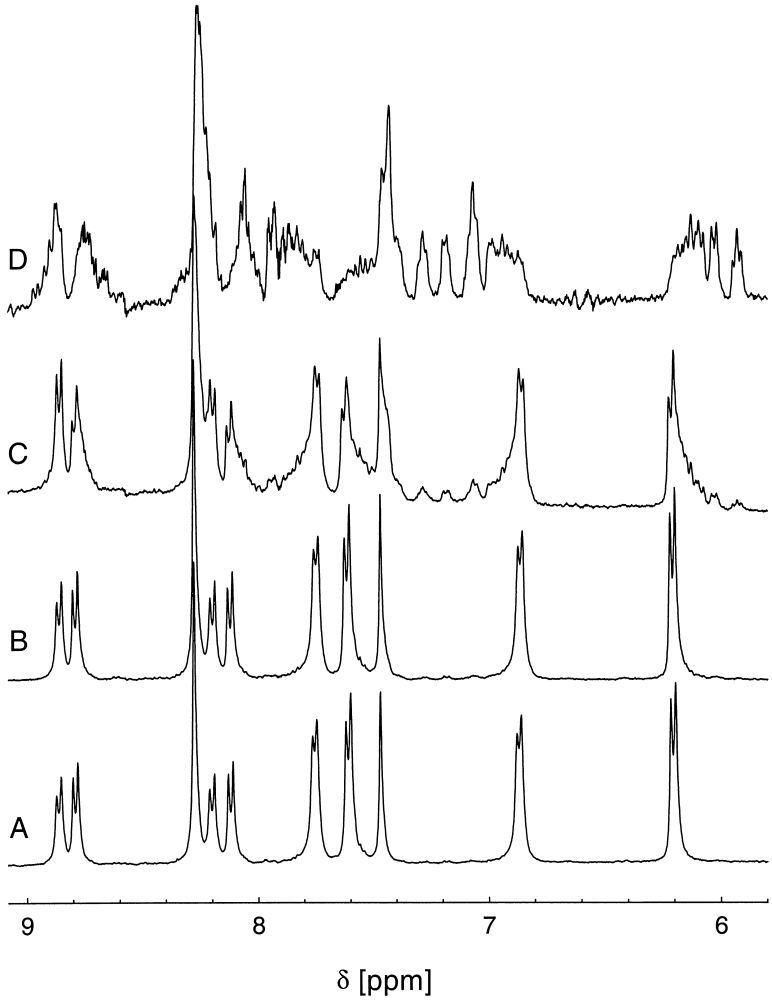


Fig 7: ^{1}H NMR spectra of **2a** recorded at a concentration of c_P = (A) 10 g·L^{-1}, (B) 5 g·L^{-1}, (C) 1 g·L^{-1}, and (D) 0.1 g·L^{-1} (acetone-d_6); see text for details.

While the solution leading to spectrum A ($c_P \approx 10$ g·L^{-1}) does not show any evidence of cyclization, there are observable new, well-defined absorptions at $c_P = 5$ g·L^{-1} (spectrum B). In particular the sequences of signals at $\delta \approx 6$ ppm and at $\delta \approx 7.2$ ppm are very significant in this regard. Their intensities increase further with decreasing c_P (spectra C, D). Since none of these absorptions is due to open chain termini, it is reliable to assume that the chain molecules change into well-defined cyclic oligomers (helicates seem to be rather unlikely due to the rodlike shape of the ligand monomers). This interpretation is supported by the above-mentioned series of new signals at $\delta \approx 6$ ppm and at $\delta \approx 7.2$ ppm which we believe correspond to cyclic oligomers of different ring sizes ("n" in Scheme 2). The obvious change of the linear macromolecules into low-molecular-weight species is additionally reconfirmed by viscosimetry which provides clear evidence of a systematic chain degradation upon dilution.

Conclusions and Outlook

Well-defined transition-metal coordination polymers **2a,b** and **3a,b** were prepared via conversion of ligand monomers **12** or **15** with metal monomers **16** or **17**. The homogeneous constitution and the high molecular weights ($P_{n,NMR} \geq 20$) of the products could be proved using ^{1}H and ^{13}C NMR spectroscopy. The polymers can be prepared in the gramm scale, are easily to handle, and are stable for months when stored as dry solids in the dark. The rate of ligand exchange is high in the presence of coordinating solvents and very low in non-coordinating solvents. This allows us to consider the systems as real polymers in the latter media but as open solution aggregates in the former. Moreover, ligand exchange is much more efficient in the silver(I) systems than in the analogous copper(I) species. Also, upon comparing polymers **2** and **3** with systems **1** recently reported, it is possible to conclude that the *n*-hexyl side chains do not only solubilize the coordination polymers but can additionally stabilize the metal complexes — provided their distance is not too large. A further key result of the present study is that it is possible to "trap" the macromolecules as long chains even at high dilution by using a strictly non-coordinating solvent. However, as soon as only traces of a coordinating solvent are added to these solutions, the chains degrade immediately, changing to presumably cyclic oligomers. Presently, we prepare more efficiently stabilized copper(I) and silver(I) coordination polymers to make feasible a full analysis of the solution properties also at very low concentration.

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