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Induction of liquid crystalline phases in linear polyamines by complexation of transition metal ions

Hartmut Fischer,[b] **Thomas Plesnivy,**[a] **Helmut Ringsdorf**[a] **and Markus Seitz***[,a,†]

[a]*Institut für Organische Chemie, J. J. Becherweg 18–20, Johannes Gutenberg-Universität,*
55099 Mainz, Germany
[b]*Technische Universiteit Eindhoven, Polymer Chemistry & Technology 5600 MB Eindhoven,*
Netherlands

In this paper, we describe the preparation and characterization of polyamine–copper complexes based on *N*-alkylated polyethyleneimines which were obtained by polymer analogous reduction of the corresponding *N*-acylated polymers. Liquid crystalline properties of the originating linear polyamides are lost in the resulting polyamines which show a higher conformational mobility. In analogy to low molecular mass azacrown derivatives, the complexation of transition metal ions, here copper(II), may reinduce liquid crystalline behavior. The structure formation in the liquid crystalline state is discussed based on X-ray investigations.

The generation of well-defined macroscopic structures by non-covalent interaction of two or more individual components is of great interest in liquid crystalline research, and more generally in the so-called field of 'supramolecular chemistry'.[1–3] For instance, two different molecular subunits that do not show any mesomorphic properties themselves may interact to form a liquid crystalline 'supramolecule'. The self-organization of such systems may take place either in solution, in the solid or even in the liquid crystalline state by various kinds of molecular interactions such as hydrogen bonding, donor–acceptor interactions or the complexation of transition metal ions.[4–9] The induction of liquid crystalline phases in polymeric materials by means of low molecular mass 'dopants', such as electron acceptor molecules or small cations that act as central units for a complex subunit is particularly interesting.[10–12]

Inorganic as well as organic amino compounds, especially multivalent ('polydentate') amino ligands such as linear and branched oligomers of the aminoethylene unit (dien and trien *etc.*), have played an outstanding role in the development of coordination chemistry.[13] In the context of the work presented here, macrocyclic amino ligands (azacrowns)[14] are of particular interest. Their principal ability to serve as a central unit of thermotropic liquid crystals was first recognized for a hexacyclene derivative peracylated with 4-dodecyloxybenzoyl chloride.[15]

In general, the use of suitable side groups—*e.g.* the 3,4-dialkoxybenzoyl unit[16]—provides the formation of columnar, especially discotic hexagonal mesophases (D_h) for a large number of substituted macrocyclic oligoamides. This was related to their discoidal molecular geometry, which in turn had been associated with the restricted conformational mobility of the central macrocycle by *N*-acylation with benzoic or cinnamoic acid derivatives.[17–19] As a consequence, discotic azacrown derivatives lose their mesomorphic properties by complete reduction to the *N*-alkylated macrocycle, due to the more flexible linkage of the side chains.[8] However, a conformational fixation of the *N*-alkylated core and thus the reinduction of a columnar mesophase may be achieved by coordination of the central core with transition metal ions,[8,17,20] as shown in Fig. 1 for tetrasubstituted cyclam derivatives. In a similar fashion, even the salts of protonated cyclic oligoamines may be enabled to form thermotropic mesophases.[21]

Considering azamacrocycles as cyclic oligomers of ethyleneimine, well-known principles relating structure and properties of *N*-substituted azacrowns can be applied to *N*-substituted polyethyleneimines. In particular, the formation of thermotropic hexagonal columnar mesophases by *N*-benzoylated as well as *N*-cinnamoylated azamacrocycles was also realized for the equivalent linear polymers.[22–24] The particular packing behavior of *N*-3,4-acylated ethyleneamine fragments results in a nearly identical thermotropic phase behavior for cyclic and linear oligomers as well as for linear polymers (Fig. 2).[24]

For the linear polyamide **3** (PEI-3,4), based on miscibility studies and entropic considerations it has been proposed that the columnar aggregates would consist of single helically folded polymer chains surrounded radially by the alkyl chains.[22,24] The polymer backbone of such a possible energetically favored conformation is shown in Fig. 3. One helix turn is formed by four to five repeat units resulting in a column center with a diameter of about 5 Å adopting a shape similar to the tetraazacycles; the pitch height in this model is 7.3 Å.‡

Based on the *N*-substituted alkyleneamine fragment one may think of a variety of different molecular architectures, such as branched or dendrimeric structures.[24–26] In this context, the phase separation in a hydrophilic central region surrounded by hydrophobic alkyl groups has been discussed as the main driving force for the hexagonal columnar mesomorphism observed in dendrimeric polymers of higher generation.[27]

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* E-mail: seitm@engineering.ucsb.edu
† *Present address*: Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA.

‡ The structure shown was obtained by first minimizing the steric energy of the decamer of *N*-dimethoxybenzoylethyleneimine starting both, from a 'prefolded' chain or a zig-zag conformation (2/1-helix). The final replacement of the methoxy substituents by decyloxy chains in the second step of the energy minimization gave rise to only gradual changes in the position of the atoms in the polymer main chain. However, this structure which was obtained using a standard software package (CSC Chem3D for Macintosh) should not be viewed as the result of an extensive modelling calculation. It rather provides a refined and reasonable model that we found very useful for the discussion of the packing requirements along the polymer main chain. Nevertheless, it is in good agreement with earlier molecular modeling calculations in which a 14/3-helical conformation has been proposed for polyoxazolines containing chiral centers in the main chain (*cf.* Y. S. Oh, T. Yamazaki and M. Goodman, *Macromolecules*, 1992, **25**, 6322). In this context, a discussion of the induction of a helical main chain conformation by the sterical requirements of tapered side groups has been presented recently (*cf.* V. Percec, D. Schlueter, J. C. Ronda, G. Johansson, G. Ungar and J. P. Zhou, *Macromolecules*, 1996, **29**, 1464).

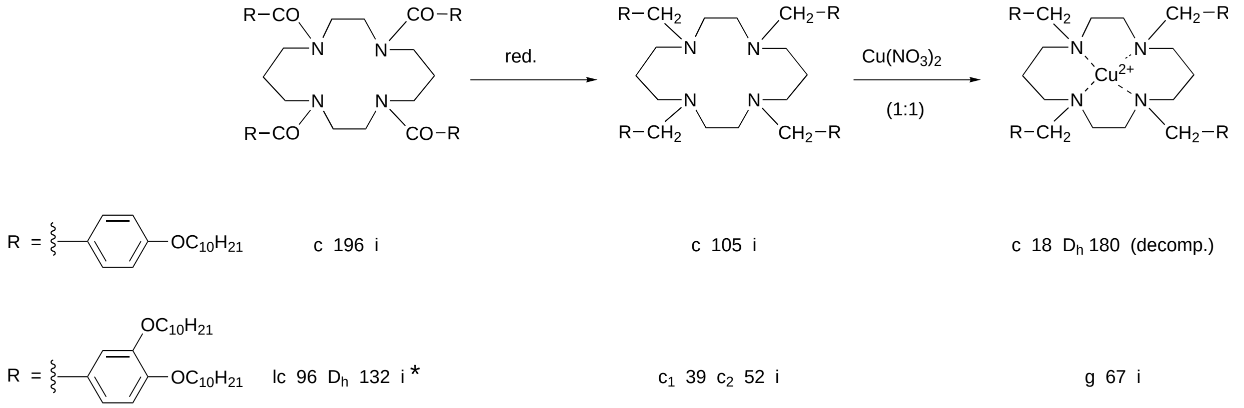


Fig. 1 Induction of columnar mesophases by transition metal ion complexation as observed for Cu^{II} complexes of *N*-alkylated cyclam derivatives (*cf.* refs. 8 and 17)

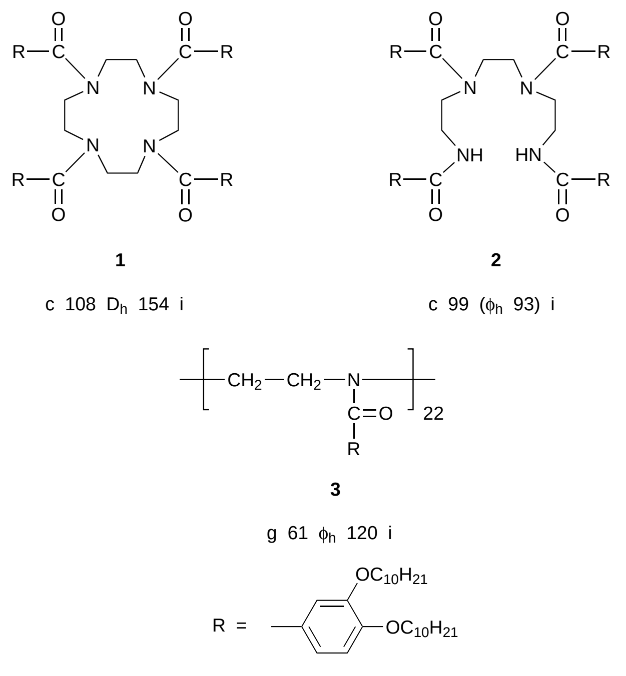


Fig. 2 Thermal phase behavior of cyclic and linear oligoamides as well as linear polymers based on the same *N*-benzoylated ethyleneimine unit (in °C, g = glassy; c = crystalline; ϕ_h = hexagonal columnar; i = isotropic)

It was supposed that further typical mesomorphic features of substituted macrocyclic oligoamides may be transferred to the analogous linear polymers.[24] In an earlier communication, we have already addressed this point and briefly described the induction of liquid crystalline phases in linear polyamines *via* complexation of transition metal ions.[28] Continuing this work, we now present a more detailed discussion of this concept in combination with the first structural studies by X-ray diffraction.

Experimental

Materials

The chemicals and solvents (p.a. grade) used for synthesis were purchased from Merck and were used as obtained without further purification unless explicitly stated. THF used for the polymer analogous reduction of linear polyamides was freshly distilled after refluxing over potassium in a nitrogen atmosphere for several hours.

Synthesis

The synthesis of *N*-acylated polyethyleneimine derivatives by polymer analogous conversion of linear polyethyleneimine has been extensively described elsewhere.[22,24] Also, the reduction of *N*-acylated polyethyleneimines to poly(*N*-alkylethyleneimines) has been investigated already by Saegusa and Kobayashi.[29] In general, the use of lithium aluminium hydride can lead to a decrease in the degree of substitution due to a C—N cleavage in the transition state of the reaction.[30] This side reaction had been attributed to a stabilization of the transition state by the lithium counterion,[31] and could thus be suppressed by using AlH_3 which was freshly prepared from $LiAlH_4$ with concentrated sulfuric acid in THF solution.[8,31,32] A C—N cleavage resulting in a degradation of the polymer main chain was not observed. During this work, the polyamides **3** (PEI-3,4) and **4** (PEI-4) could be completely reduced to the polyamines **6** (PA-3,4) and **5** (PA-4), respectively, using a five-fold excess of aluminium hydride (Scheme 1). The reaction was followed by IR spectroscopy, monitoring the disappearance of the C=O stretching band at *ca.* 1640 cm^{-1} as the reaction proceeded. In addition, ^{1}H NMR spectra of the polyamines in chloroform solution indicated their higher conformational mobility; the signals of the aromatic protons in the side group which could only be detected as single broad peaks for the polyamides were now split into doublets. Similar behavior has been observed for the corresponding azacrown derivatives.[19]

Poly(*N*-4-decyloxybenzylethyleneimine), 5 (PA-4). $LiAlH_4$ in THF (Aldrich) (1 M; 10 ml) was stirred under a dry stream of nitrogen at 0 °C. After dropwise addition of concentrated H_2SO_4 (0.26 ml) the mixture was stirred for an additional hour during which time the evolution of hydrogen could be observed, and a white precipitate was formed. This freshly prepared AlH_3 solution was filtered under argon. Then, 400 mg (1.32 mmol) of poly(*N*-4-decyloxybenzoylethyleneimine), **4** (PEI-4, $n = 85$), in dry THF was added slowly, and the resulting reaction mixture was stirred at room temp. overnight. The next day, excess of AlH_3 was destroyed by the addition of 3 ml THF–H_2O (1 : 1 v/v), the solvent was distilled off, and the white residue dissolved in a 1 : 1 mixture of 1 M NaOH and dichloromethane. The organic layer was washed with water, dried with sodium sulfate, and concentrated by evaporating most of the solvent. The white polymer was precipitated in cold acetone. Yield: 265 mg (69%); δ_H ($CDCl_3$, 200 MHz) 0.87 [t, 3H, $CH_3(CH_2)_9O$], 1.15–1.5 [br, 14H, $CH_3(CH_2)_7CH_2CH_2O$], 1.68 [t, 2H, $CH_3(CH_2)_7CH_2CH_2O$], 2.40 [br, 4H, CH_2NCH_2], 3.35 [br, 2H, NCH_2Ar], 3.81 [t, 2H, $CH_3(CH_2)_8CH_2O$], 6.70 (d, 2H, Ar H-3,5), 7.02 (d, 2H, Ar

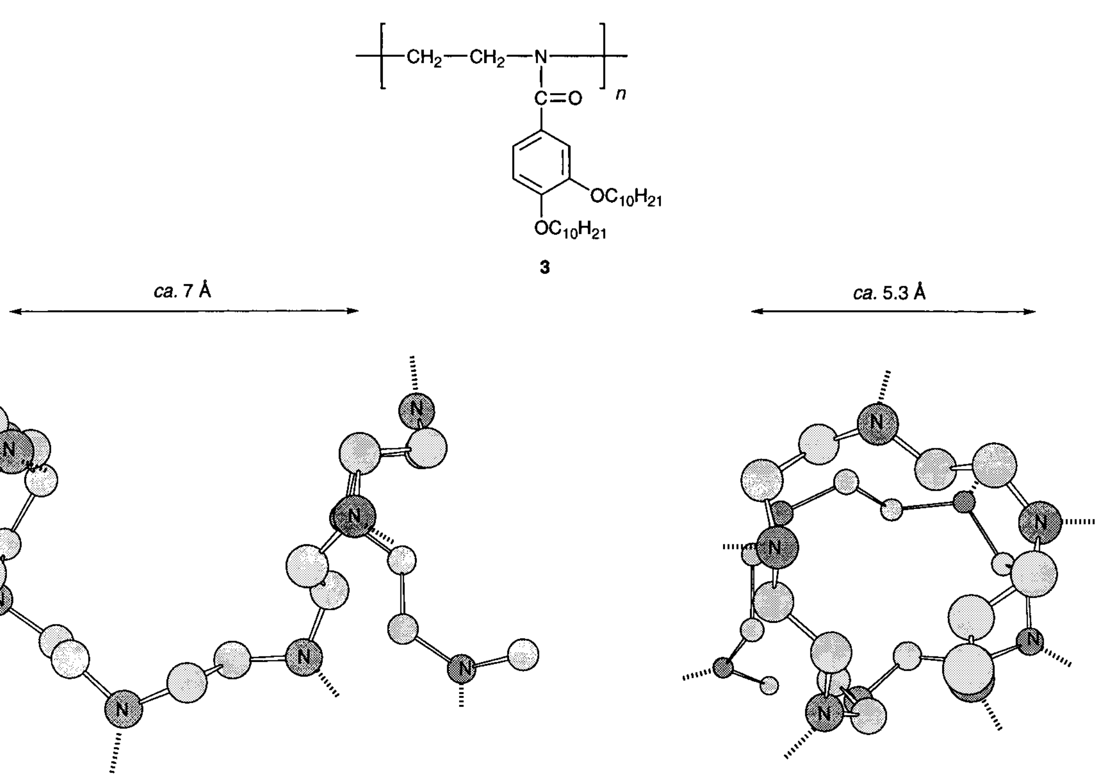
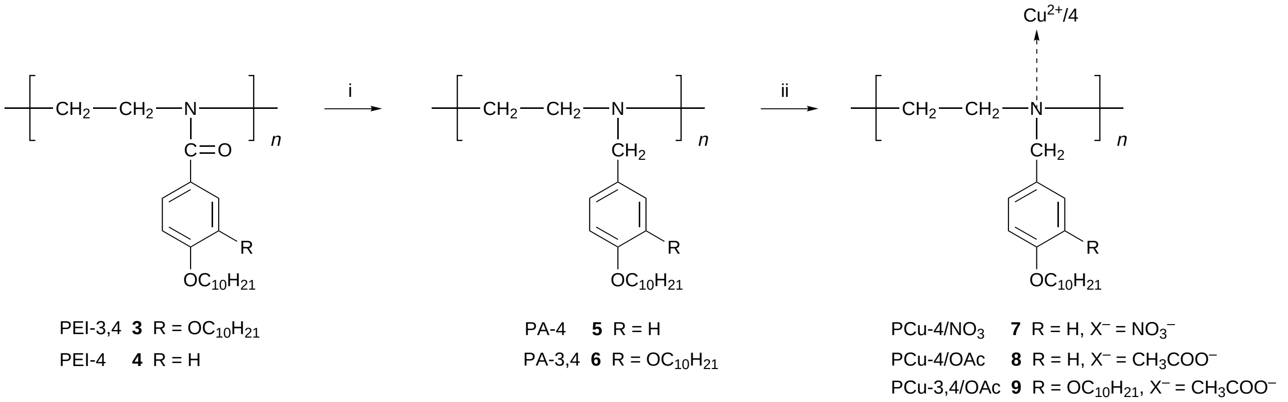


Fig. 3 Helical arrangement of the *N*-acylated polyethyleneimine **3** (PEI-3,4) in a possible energetically favored conformation (for matters of simplification only the atoms of the polymer backbone are shown; thus note that most of the apparent free volume in the center of the column is actually filled with hydrogen atoms)



Scheme 1 *Reagents and conditions*: i, AlH_3, THF, 0 °C, 16 h; ii, copper(II) nitrate (**7**) or copper(II) acetate (**8**, **9**), THF or CH_2Cl_2–H_2O, room temp., 1–3 d

H-2,6); ν_{max} (KBr)/cm^{-1} 2956, 2923, 2852, 2826 (CH_2), 1617, 1511, 1464 (C=C), 1246 (C—O) [Calc. for $C_{19}H_{31}NO$: C, 78.84; H, 10.79; N, 4.84 (C/N = 16.29). Found: C, 78.11; H, 10.93; N, 5.07% (C/N = 15.41); degree of substitution calculated from C/N ratio: *ca.* 93%].

Poly[*N*-3,4-bis(decyloxy)benzylethyleneimine], 6 (PA-3,4). The reaction proceeded in the same way as described for **5** (PA-4), starting from 1.0 g (2.2 mmol) of poly[*N*-3,4-bis(decyloxy)benzoylethyleneimine], **3** (PEI-3,4, *n* = 85), 15 ml (15 mmol) of 1 M $LiAlH_4$-solution in THF and 0.25 ml of concentrated H_2SO_4. Yield: 620 mg (63%); δ_H ($CDCl_3$, 200 MHz) 0.85 [t, 6H, $CH_3(CH_2)_9O$], 1.15–1.5 [br, 28H, $CH_3(CH_2)_7CH_2CH_2O$], 1.70 [m, 2H, $CH_3(CH_2)_7CH_2CH_2O$], 2.35 (br, 4H, CH_2NCH_2), 3.30 (br, 2H, NCH_2Ar), 3.80 [m, 4H, $CH_3(CH_2)_8CH_2O$], 6.5–6.65 (m, 2H, Ar H-2,5), 6.7 (br, 1H, Ar H-6); ν_{max} (KBr)/cm^{-1} 2935, 2849 (CH_2); 1525, 1469 (C=C); 1260 (C—O) [Calc. for $C_{29}H_{51}NO_2$: C, 78.15; H, 11.53; N, 3.14 (C/N = 24.89). Found: C, 76.18; H, 11.10; N, 2.84% (C/N = 26.82); degree of substitution calculated from C/N ratio >95%].

Preparation of polyamine–copper complexes

The binding of Cu^{2+} and Ni^{2+} to branched polyethyleneimine, resulting in the first known polyamine–metal complexes, was described in 1963[33] and has recently been reviewed.[34] In the work presented here, the complexes were prepared as described earlier for *N*-benzylated azamacrocycles,[8] by adding a solution of the polyamine in THF or dichloromethane to an excess of the metal salt (Scheme 1). The latter was either dissolved in water or used as a solid (which for the cases of nitrates and acetates, which are partially soluble in THF, yielded a homogeneous reaction mixture). The resulting mixtures were stirred for one to several days, although in most cases the complexation was indicated by a dark blueish or greenish color of the organic phase almost instantaneously. After removal of the solvent, the resulting residues were dissolved in dichloromethane and washed with water several times, and filtered through a 0.45 μm Teflon filter to remove traces of the metal salt. After distillation, the solid complexes were dissolved in benzene, filtered again and finally freeze-dried.

As an example, the analytical data of **7** (PCu-4/NO_3) obtained by reaction of polyamine **5** (PA-4) with copper(II) nitrate are as follows: blue–green powder; δ_H ($CDCl_3$, 200 MHz) 0.87 [t, 3H, $CH_3(CH_2)_9O$], 1.15–1.50 [br, 14H, $CH_3(CH_2)_7CH_2CH_2O$], 1.70 [t, 2H, $CH_3(CH_2)_7CH_2CH_2O$], 2.60–3.40 (br, 4H, CH_2NCH_2), 3.25–4.10 [br, 4H, NCH_2Ar and $CH_3(CH_2)_8CH_2O$], 6.70 (d, 2H, Ar H-3,5), 7.01 (d, 2H, Ar H-2,6); ν_{max} (KBr)/cm^{-1} 2953, 2923, 2850 (CH_2), 1612, 1514, 1468 (C=C), 1385 (N—O, nitrate counterion), 1305, 1252 (C—O), 1163, 1030, 818; λ (THF)/nm 665 (ε= 40 l mol^{-1} cm^{-1}) [Found: C, 67.44; H, 9.49; N, 6.30% (C/N= 10.71]. Assuming nitrate as the only counterion 21.7% copper(II) ions per repeating unit were calculated, resulting in an average composition of $CuL_{4.7}$ (L=amino ligand).§

For the complexation of different central ions (Ni^{2+}, Co^{2+}, $UO_2{}^{2+}$) and the use of other counterions ($SO_4{}^{2-}$, Cl^-, $BF_4{}^-$) during this work, the procedure as described above was used. However, it seems that this approach cannot be generalized: using copper chloride, copper sulfate or copper tetrafluoroborate which are not soluble in suitable organic solvents, the reaction had to be performed in heterogeneous media. Also, most complexation attempts with other metal cations (regardless of the counterion) failed so far, both in homogeneous as well as in heterogeneous reaction media. Only for the system **5** (PA-4)/$Ni(NO_3)_2$ was the preparation of a polymer–metal complex achieved in THF solution. The optimization of the experimental conditions to promote the polymer–metal complex formation has yet to be investigated.¶

Characterization

^1H NMR spectra were recorded with a 200 MHz FT–NMR Spectrometer AC-200 (Bruker). Infrared (IR) spectra were recorded from KBr pellets of the materials with an FT-IR spectrometer 5DXC (Nicolet). UV–VIS absorption spectra were measured in quartz cuvettes (Hellma) with a Lambda 5-spectrometer (Perkin-Elmer) using UVASOL grade solvents (Merck). For polarizing microscope investigations, thin films of the compounds prepared on microscopic slides were observed using an Ortholux II POL-BK (Leitz) microscope. For the photographs of the observed textures Olympus SC 35 (type 12) and Kodak-Ektachrome 400 ASA film material was used. Differential scanning calorimetry (DSC) measurements were performed with a DSC-7 (Perkin-Elmer) microcalorimeter using an Epson-PC and DSC-7 multitasking software (Perkin-Elmer) for data evaluation. Calibration standards were indium and lead. Prior to the measurements, 3–10 mg of the substances were sealed in aluminium pans. Observed peak maxima are given as the first order transition temperatures; the inflection points for the DSC traces are taken as the glass transitions. X-Ray structural investigations were performed with Cu-Kα-radiation (λ=0.1541 nm). The diffracted radiation was analyzed using a graphite monochromator and a Siemens X-1000 flat plate detector or a flat picture camera at different sample–detector distances. The temperature of the samples was controlled with an accuracy of 0.1 °C by a Linkam THM 600 heating stand.

Results and Discussion

Complexation of transition metal ions by *N*-alkylated polyethyleneimines

The complexation of the polyamines **5** (PA-4) and **6** (PA-3,4) was followed using different spectroscopic techniques, as will be discussed for the single-chain substituted polyamine–copper system **7** (PCu-4/NO_3). Fig. 4(*a*) shows the FT-IR spectra of the complex and of the pure polyamine ligand **5** (PA-4). As in the case of low molecular mass azacrown derivatives,[8] the CH-stretching band at $\nu = 2830\ cm^{-1}$ disappeared, which can be related to the methylene group next to the amino donor in the polymer main chain. The influence of the complexation was also seen in the ^1H NMR spectrum [Fig. 4(*b*)]. As compared to the relatively high mobility of the polyamine ligand, which in that case led to narrower peaks as well as to a doublet splitting of the aromatic signals, the bands were significantly broadened for the metal complex. This was particularly pronounced for the resonances of the amino methylene protons which, in addition, are shifted to lower field. For the pure polyamine ligand **5** (PA-4) they were detected at $\delta = 2.4$ (main chain) and $\delta = 3.4$ (side chain), whereas for the complex **7** (PCu-4/NO_3) two broad signals were found at $\delta = 2.6$–3.4 and $\delta = 3.4$–4.0.

Finally, the ligand–metal interaction could be observed by UV–VIS spectroscopy (spectra not shown here). A broad shoulder ($\lambda = 310$ nm) of the aromatic absorption band (λ_{max}= 275 nm) as well as a very weak d–d band of the central atom at $\lambda = 665$ nm ($\varepsilon = 40\ l^{-1}\ mol^{-1}\ cm^{-1}$) were detected. Because an exact determination of the coordination number of the central ions could not be achieved in all cases,§ it should be mentioned that several remarks on the complexation of transition metal cations with branched and linear polyethyleneimine have been given in the literature.[33–35] Based on this, the low molar extinction coefficient may be explained by the polymeric nature of the ligand resulting in a less defined complexation of the Cu^{II} ions, since in addition to the expected four-coordination, a possible five-coordination has to be taken into account as well.[34,36,37]

Characterization of thermal phase behavior

In analogy to the cyclic low molecular mass derivatives,[8] the corresponding polyamines **5** (PA-4) and **6** (PA-3,4) obtained by polymer analogous reduction from the polyamides **4** (PEI-4) and **3** (PEI-3,4), respectively, are partially crystalline materials that do not form liquid crystalline phases before melting into an isotropic liquid (Fig. 5). As in the case of the cyclic oligomers, this can be attributed to the higher conformational flexibility of the *N*-alkylated polymers as compared to the *N*-acylated compounds.

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§ The authors wish to apologize for an error in the elemental analysis data given for complex **7** (PCu-4/NO_3) in ref. 28. By mistake, the calculated data for the ligand **5** (PA-4) instead of the experimental data for the complex were reported there. This error has been corrected here. Also note that, although found useful for the determination of the average copper–ligand ratio in the complexes with nitrate counterion, the same calculation for the compounds obtained with copper(II) acetate did not yield meaningful values. From the analytical data of **8** (PCu-4/OAc) an average composition CuL_2 was calculated. Despite repeated filtration the complex seemingly still contains traces of copper(II) acetate. This also resulted in two sharp reflections in the wide angle region of the X-ray diffraction pattern as well as in a very weak first order transition at 116 °C in the DSC scans corresponding to the melting point of the copper salt. However, for **9** (PCu-3,4/OAc) which evidently does not contain inorganic impurities an even higher value for the copper content was evaluated. Obviously, the basic assumption for the calculation, accounting for only one counterion species, does not hold for the complexes obtained from copper acetate.

¶ Interestingly, the extraordinary stability of complexes formed by copper and branched polyethyleneimine even in acidic solution has been reported in this context (*cf.* B. L. Rivas and K. E. Geckeler, *Adv. Polym. Sci.*, 1992, **102**, 173), which even served for the separation of Cu^{2+} from other metal ions (*cf.* K. E. Geckeler, E. Bayer, G. A. Vorob'eva and B. Y. Spivakov, *Anal. Chim. Acta*, 1990, **230**, 171). As in general, metal complexes of branched polyethyleneimine are considerably more stable than those of the linear polymer (*cf.* S. Kobayashi, K. Hiroishi, M. Tokunoh and T. Saegusa, *Macromolecules*, 1987, **20**, 1496), the observed problems for most metal ions may be explained and thus also point to the stability of the copper–polyethyleneimine coordination compounds.

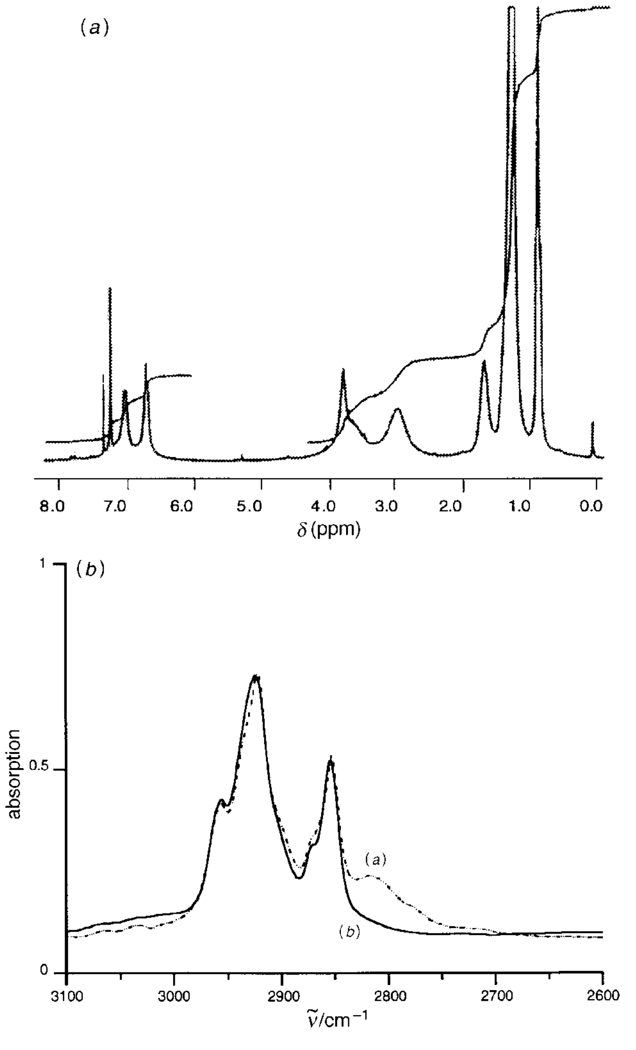


Fig. 4 Complexation of copper(II) ions by *N*-alkylated polyethyleneimines as followed by spectroscopic investigations on **7** (PCu-4/NO_3); (*a*) ^1H NMR spectrum (200 MHz, $CDCl_3$, room temp.); (*b*) FT-IR spectrum (KBr pellet)

Based on the results for the low molecular mass derivatives (Fig. 1) where a columnar mesophase was found for complexes formed from the macrocyclic ligand bearing a single-chained 4-alkoxybenzoyl substituent and copper nitrate,[8] the investigation of the polymeric complex **7** (PCu-4/NO_3) appeared most promising. Indeed, thermotropic liquid crystalline behavior was observed for this complex as described in an earlier communication.[28] Under the polarizing microscope, a rather unspecific, but shearable texture was observed above the determined glass transition at 53 °C. However, decomposition of the material was observed above 160 °C, and the observed texture completely disappeared at 173 °C. A more detailed analysis of the phase behavior by microscopic investigation was thus not possible.

By X-ray diffraction, the existence of a thermotropic liquid crystalline phase for **7** (PCu-4/NO_3) now could be ultimately proven. However, the exact determination of the phase type still remains unclear. In the diffraction pattern, next to a broad halo at ~4.6 Å which corresponds to the disordered alkyl side chains, only a first order Bragg peak was found which allowed calculation of the lattice parameter as d_{001} ~35.5 Å. For this material, the absence of mixed or higher order reflections still prevents the experimental distinction between a lamellar mesophase structure [Fig. 6(*b*)] and a cylindrical complex structure, as resulting for instance from a helical arrangement of the polyamine main chain around the central copper ions [Fig. 6(*c*)].

The latter model resembles the proposed structure for the observed hexagonal columnar mesophase of the corresponding linear polyamides,[22,24] and would be comparable with the helical crystal structures of metal complexes formed, *e.g.* by oligopyridine ligands.[38,39] On the other hand, a lamellar layered structure would be in agreement with smectic mesophases observed for different organometal complexes of Cu^{II}.[40]

Due to the observed decomposition of the complex nitrate at elevated temperatures, the introduction of the acetate ion was investigated. Although the thermal stability of the obtained compound **8** (PCu-4/OAc) was only slightly improved, this approach proved successful in so far as the simultaneous decrease of the clearing point below the decomposition temperature now allowed the heating of the material to the isotropic state. On first heating under the polarizing microscope (by 10 °C min^{-1}), the complex formed an unspecific texture which slowly cleared at *ca.* 94 °C (last anisotropic domains disappeared at ~105 °C). On decreasing the temperature, the sample showed a considerable supercooling of the clearing point to 72 °C. The growth of typical bâtonets[41] which eventually resulted in the formation of a fan-shaped texture (Fig. 7) at that temperature points to the existence of a smectic mesophase. In addition, the sample could be sheared easily even after cooling down to 40 °C, until at room temperature a marked increase of the viscosity of the material was observed. The behavior was reversible in the following heating and cooling cycles.

The copper complex **9** (PCu-3,4/OAc) obtained from the double side chain polyamine **6** (PA-3,4) and copper(II) acetate was obtained as a highly viscous and sticky material. Under the polarizing microscope, a Schlieren texture indicating a nematic mesophase was observed [Fig. 8(*a*)] at room temperature. On cooling from the isotropic liquid phase (*T ca.* 75 °C), typical 'Maltese crosses' were formed within an almost completely homotropically oriented sample [Fig. 8(*b*)].

In DSC measurements, **8** (PCu-4/OAc) showed a glass transition at *ca.* 10 °C and two first order transitions at 67 and 98 °C [in addition, a very weak signal at 116 °C was detected which can be related to residual traces of copper(II) acetate]. Whereas the latter corresponds to the microscopically determined transition to the isotropic melt, the nature of the first transition could not be completely clarified. As the material could be easily sheared in the microscopic investigations at 40 °C, the first peak may be related to a transition between two liquid crystalline mesophases. On cooling however, only one peak at 70 °C was detected next to the glass transition. Considering the higher cooling rate used in the DSC measurements (10 °C min^{-1}), this is in good agreement with the observations under the polarizing microscope, where a supercooling of the clearing point and the growth of a fan-shaped texture at *ca.* 72 °C were seen. Thus, the anisotropic domains observed on heating above 72 °C could also be related to a biphasic behavior of the material above that temperature. The curves of **9** (PCu-3,4/OAc) showed a first order melting transition in the same temperature region in which the glass transition of **8** (PCu-4/OAc) was detected. The clearing temperature of 68 °C agreed with the microscopic observations. The transition temperatures of the copper(II) complexes **7** (PCu-4/NO_3), **8** (PCu-4/OAc), and **9** (PCu-3,4/OAc) as determined from DSC are listed in Table 1.

X-Ray investigations on a powder sample of **8** (PCu-4/OAc) cooled from the isotropic phase to room temperature proved the liquid crystalline character of the material. Next to the first order Bragg reflection with a corresponding lattice parameter $d_{001} = 34.9$ Å, two very weak signals were detected in the low angle region of the flat camera picture [Fig. 9(*b*)]. Their corresponding spacings of 17.5 Å (*ca.* $d_{001}/2$) and *ca.* 11.5 Å (*ca.* $d_{001}/3$) identify them as the (002) and (003) reflections of a lamellar structure in which the copper ions are complexed by the amino head groups of polyamine bilayers. In the wide

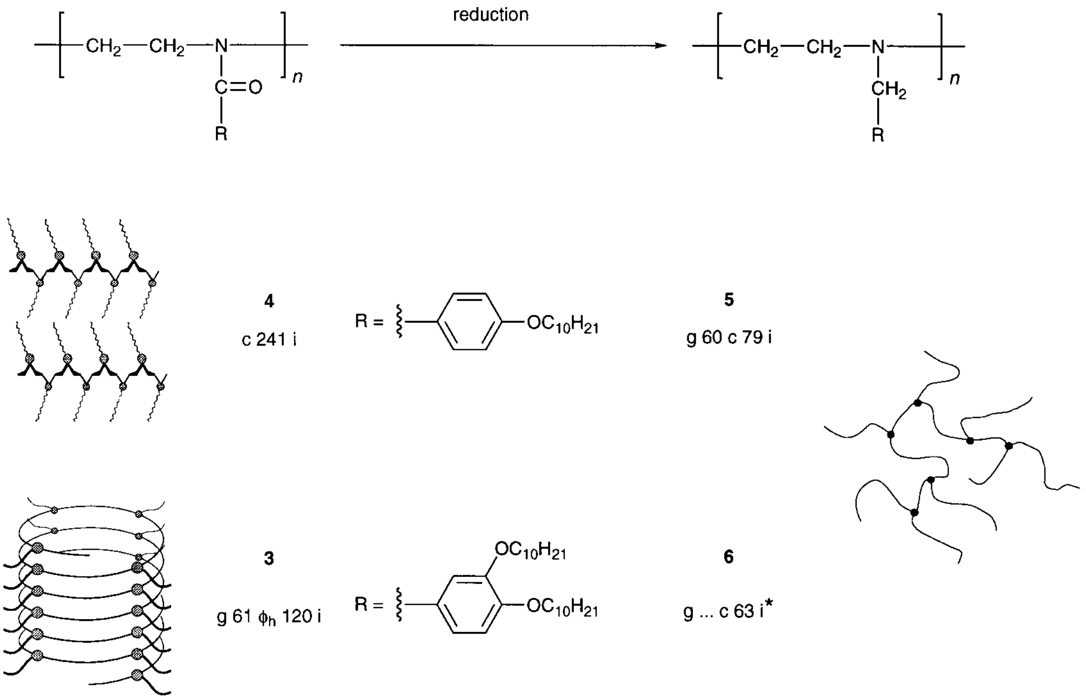
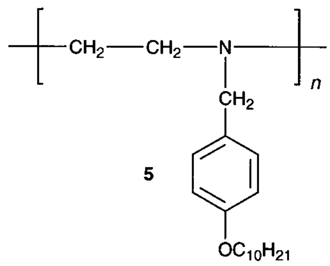


Fig. 5 Thermotropic phase behavior of *N*-alkylated polyethyleneimines **5** (PA-4) and **6** (PA-3,4) (in °C, taken from second DSC heating scan, scan rate: 10 °C min^{-1}); g = glassy; c = crystalline; i = isotropic. * The sample could be sheared under the polarizing microscope below the detected first order transition, proving the semicrystalline nature of the polymer, so that a glass transition has to be assumed below 40 °C (not unambiguously detected in the DSC scans).



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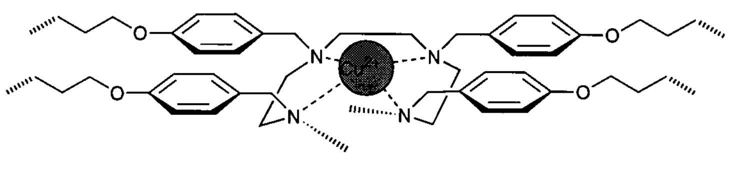

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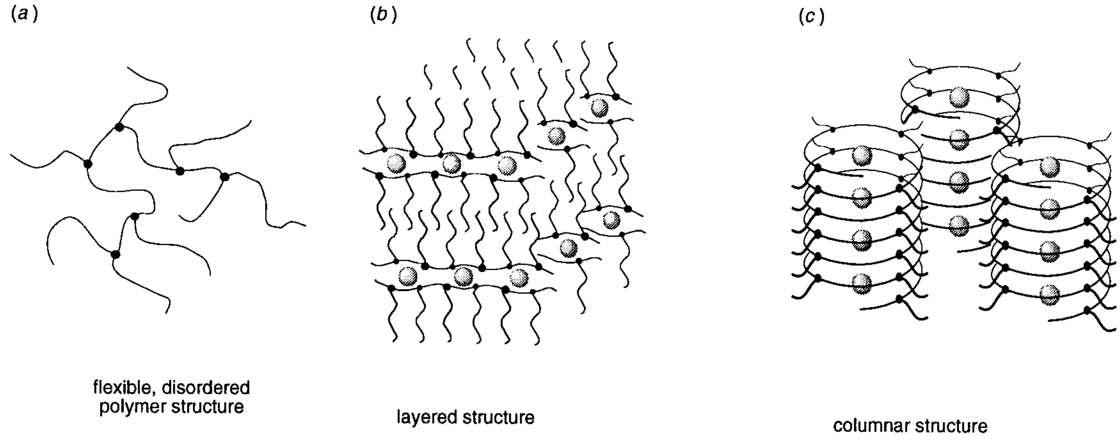

flexible, disordered polymer structure

layered structure

columnar structure

Fig. 6 Schematic representation of possible structures of the polyamine–copper complex **7** (PCu-4/NO_3) within the thermotropic mesophase; (*a*) layered structure; (*b*) columnar structure.

angle region [Fig. 9(*a*)], a broad halo of the alkyl chains with a maximum at *ca.* 4.8 Å was found. In addition, **8** (PCu-4/OAc) showed two additional sharp reflections at 2*θ* *ca.* 29° and *ca.* 44° (*ca.* 3.0 and *ca.* 2.0 Å, respectively) which can be attributed to residual traces of copper acetate (compare discussion of DSC results).

Contrary to expectations which were based on the nematic texture observed in polarizing microscopy, the X-ray diffractogram of the polyamine–copper complex **9** (PCu-3,4/OAc) measured at room temperature [Fig. 10(*a*)] exhibited a rather broad, but pronounced Bragg peak in the small angle region at 2*θ* *ca.* 2.7° from which a spacing of *ca.* 32.8 Å was calculated; mixed or higher order reflections were not found. In the flat camera picture shown in Fig. 10(*b*), next to the Bragg peak (from which a slightly higher value of *ca.* 34 Å was determined) and the halo related to the alkyl chains at

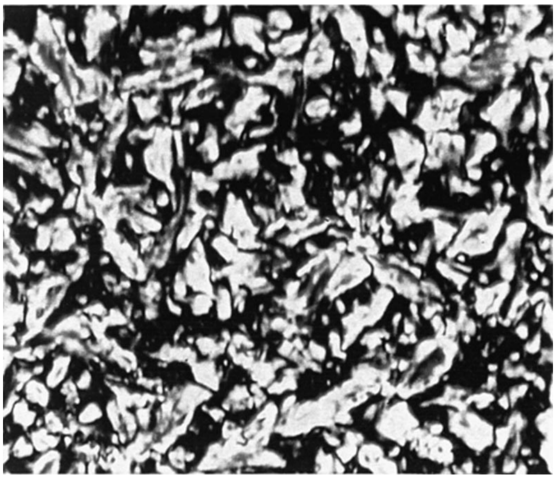

Fig. 7 Microscopic texture of **8** (PCu-4/OAc) after cooling to 70 °C from the isotropic phase with 1 °C min^{-1}

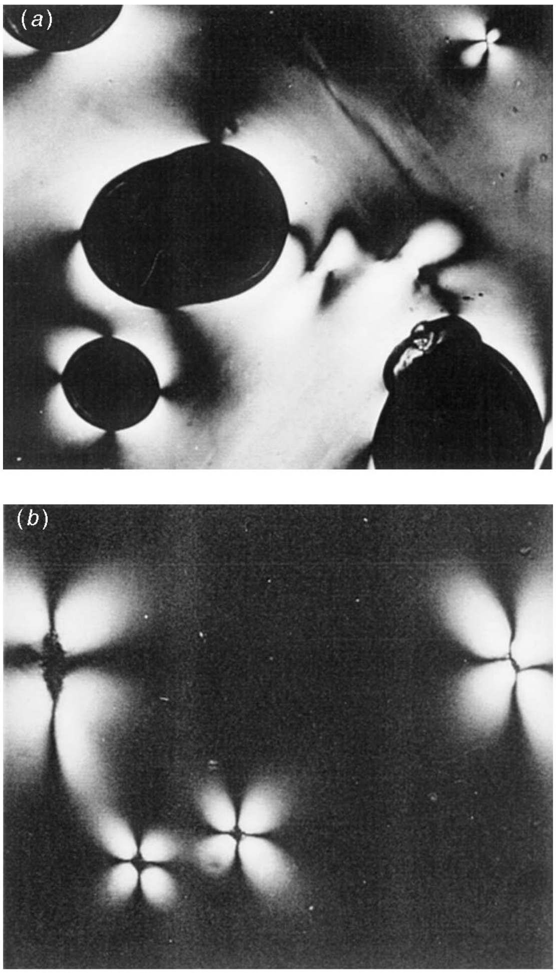

Fig. 8 Microscopic textures of **9** (PCu-3,4/OAc): (*a*) room temperature, directly after preparation; (*b*) after cooling to 42 °C from the isotropic phase with 1 °C min^{-1}

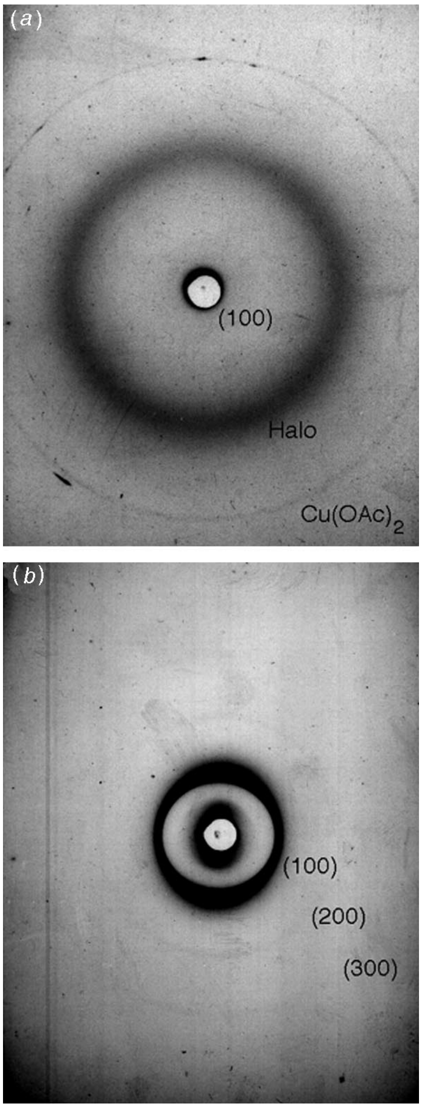

Fig. 9 X-Ray flat camera picture of **8** (PCu-4/OAc) after cooling from the isotropic phase to the liquid crystalline state: (*a*) complete picture; (*b*) low angle region

4.4 Å (halo 2), an additional weak halo at *ca.* 7.3 Å (halo 1) was measured. This is particularly interesting as this distance coincides with the proposed pitch height of a helically wound polymer main chain in the model shown in Fig. 2 for the mesomorphic linear polyamide **3** (PEI-3,4).

Based on the X-ray data, a layered structure also seems possible for **9** (PCu-3,4/OAc). However, considering the comparably high width of the Bragg peak and the microscopic textures observed, the results point to a nematic columnar phase. This assumption appears reasonable since in comparison with the complexes **7** (PCu-4/NO_3) and **8** (PCu-4/OAc) of the polyamine ligand **5** (PA-4) which bear only one side chain per polymer repeating unit, and which both form layered structures [Fig. 11(*a*)], a higher number of side chains have to be incorporated in the aggregates of the double chain derivative

Table 1 Phase transition temperatures of copper(II)-polyamine complexes **7**(PCu-4/NO_3), **8**(PCu-4/OAc), and **9**(PCu-3,4/OAc) given in °C (taken from the second DSC heating scan measured with a scan rate of 10 °C min^{-1}, for **8**(PCu-4/OAc) the thermal transitions in the first cooling curve are also shown): g, glassy; c, crystalline; S_X, unidentified smectic/lamellar structure; S_A, smectic A/lamellar; N_C, nematic columnar; i, isotropic

		DSC scan	T/°C
7	from **5** (PA-4) and $Cu(NO_3)_2$	2nd heating	g 53 lc 173 (decomp.)
8	from **5** (PA-4) and $Cu(OAc)_2$	2nd heating	g 11 c/S_X 67 S_A 98 i
		1st cooling	g 10 S_A 70 i
9	from **6** (PA-3,4) and $Cu(OAc)_2$	2nd heating	c 12 N_C 68 i

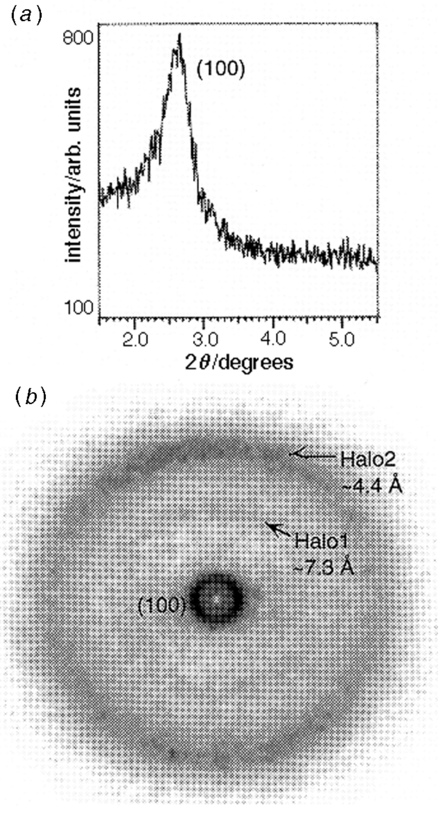

Fig. 10 X-Ray diffraction patterns of **9** (PCu-3,4/OAc) at room temperature: (*a*) goniometer scan; (*b*) flat camera picture

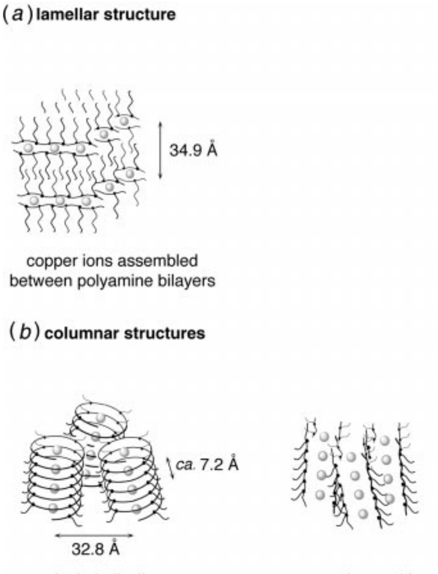

Fig. 11 Schematic representation of the possible structures of polyamine–copper(II) complexes within their thermotropic mesophases: (*a*) smectic mesophase of **8** (PCu-4/OAc); (*b*) nematic columnar mesophase of **9** (PCu-3,4/OAc)

9 (PCu-3,4/OAc). This is in agreement with the findings for the corresponding *N*-acylated polyethyleneimines where lamellar crystals or hexagonal columnar mesophases were observed for mono- or bis-decyloxysubstituted side groups, respectively.[24]

As has been discussed before for the original mesomorphic polyamides,[24] the formation of the complex columnar aggregates may be explained by several different structural models [Fig. 11(*b*)]. For instance, a single polymer main chain may be wound helically around the central copper ions. On the other hand, more than one polymer chain may constitute the columnar packing which may even result in a crosslinked structure, in which single polymer chains may participate in more than one column. However, based on the observed low viscosity of the material within the mesophase the latter model appears least likely. On the other hand, the packing of several polymer chains in the second model would afford a much higher order than a single more or less helically folded chain. In addition, although in each model the additional halo found at 7.3 Å in the flat camera picture could correspond to an average distance of copper atoms in the center of complex sub-units along such columns, the obvious similarity of this distance with the pitch height in the helical model discussed for *N*-substituted linear polyethyleneimines (Fig. 3) lets us favor the first structural model.

Conclusions

By polymer analogous reduction of the benzamide group in linear polyamides, *N*-alkylated polyethyleneimines were obtained which, due to their high conformational mobility cannot form liquid crystalline mesophases. As in the case of azamacrocycles, a mesophase is formed by the materials after the coordination of the polyamine to Cu^{II}. Whereas the discoid molecular structure of cyclic oligomers only allows discotic phases, based on the higher flexibility of the polyamine main chain, the polymeric complexes may also adopt layered structures. In addition, even for a higher side chain density for which a loss of mesomorphic features was observed in the case of macrocyclic complexes, now a presumably nematic columnar mesophase is found. Although detailed information about the conformation of the polymeric ligands in the liquid crystalline complexes has yet to be elucidated, the general principle of mesophase induction by metal ion complexation could be proven for the materials discussed. The results described again show the analogy between low molecular mass cyclic derivatives and linear polymers composed of the same basic monomer unit and are therefore of general interest in polymer liquid crystal research. In addition, based on their complex nature, numerous interesting possibilities for tailoring the physical properties of mesomorphous polymer systems appear. For instance, by simple variation of structural features such as the metal ion, the side chain density or by the introduction of chiral centers into the polyamine ligand, physical parameters such as thermotropic phase behavior and also the optical properties of the materials could be tuned.

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