

Induction of Liquid Crystalline Phases in *N*-alkylated Poly(ethyleneimine)s by Transition Metal Complexation

Hartmut Fischer,^a Thomas Plesnivý,^b Helmut Ringsdorf*^b and Markus Seitz^b

^a Technische Universiteit Eindhoven, Polymer Chemistry and Technology, 5600 MB Eindhoven, Netherlands

^b Institut für Organische Chemie der Universität Mainz, J.J. Becher-Weg 18-22, 55099 Mainz, Germany

A liquid crystalline mesophase is induced by complexation of copper(II)nitrate with an *N*-alkylated poly(ethyleneimine) obtained by reduction of the corresponding polyamide, in analogy to low molecular mass azacrown derivatives.

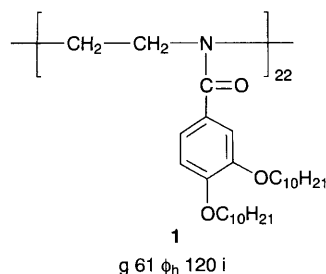
The generation of well-defined superstructures by non-covalent interactions between two or more individual components is one of the major topics of supramolecular chemistry. The self-organization of such systems may be induced either in solution, the liquid crystalline or the solid state by different types of interactions, *e.g.* hydrogen bonding, electrostatic or donor-acceptor interactions and metal-ion complexation.¹

Recently, we described the formation of a hexagonal columnar mesophase by an *N*-acylated linear poly(ethyleneimine) **1** which was explained by a more or less helical arrangement of the polymer backbone.²

This polyamide can be seen as a linear analogue of *N*-acylated azacrown derivatives which form hexagonal columnar mesophases by stacking the discoid molecules.^{2,3} On the other hand, *N*-alkylated azacrowns obtained by complete reduction from the acylated compounds in general do not show liquid crystalline behaviour due to the high ring flexibility. However, it is known that self-organization into columnar mesophases can be induced by complexation of transition metal salts which was in part attributed to a stiffening of the highly flexible amine macrocycles.^{4,5} Motivated by the intriguing similarity of linear polyamides and cyclic oligoamides (*N*-acylated azacrowns) found for various substituents,⁶ a metal complexation induced mesophase formation was expected even for linear polymeric amines.

By *N*-acylation of linear poly(ethyleneimine) **2** the highly crystalline single chain substituted polymer **3** was obtained which was, subsequently, converted into polyamine **4** by polymer analogous reduction using freshly prepared AlH₃ solution, as described already for azacrowns⁴ and polyoxazolines.^{7,†}

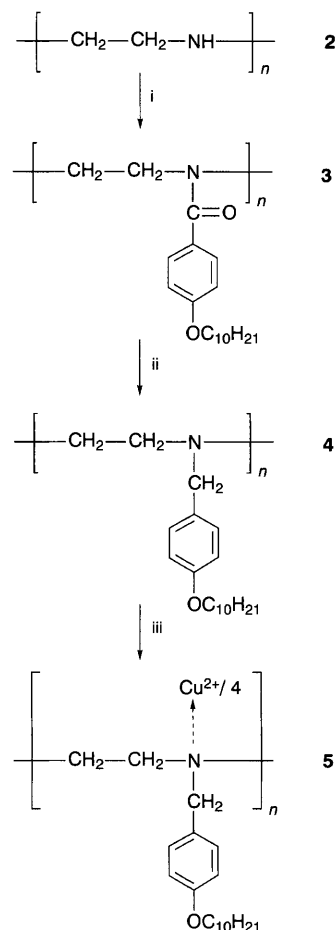
Compared to the polyamide **3** ($T_m = 241\text{ °C}$), the polyamine **4** is a partially crystalline material with a melting point of only $T = 79\text{ °C}$ ($T_g = ca. 60\text{ °C}$) reflecting the higher mobility of the polyamine backbone. Complexation of Cu(NO₃)₂ by linear polyamine **4** was carried out in heterogeneous medium‡ and controlled by spectroscopic methods. In the IR spectra, the shoulder at $\nu = 2830\text{ cm}^{-1}$ related to the CH-stretching vibration of the methylene groups neighbouring the donor centres disappears which indicates a complete complexation as discussed for the cyclic low molecular mass analogues.⁴ The same influence can be seen in the ¹H NMR: the signals of the aminomethylene groups are significantly broadened and shifted towards lower field.†,‡ In the UV-VIS spectra, a broad



Scheme 1 Linear polyamide **1**: phase transition temperatures given in °C (g: glassy, ϕ_h : hexagonal columnar, i: isotropic)

shoulder ($\lambda_{max} = 310\text{ nm}$) of the aromatic absorption at $\lambda = 275\text{ nm}$ may be attributed to the ligand-metal interaction. In addition, a weak d-d band of the central atom was detected at $\lambda = 665\text{ nm}$ ($\epsilon = 40\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) in agreement with the UV-VIS spectra of corresponding four-coordinated macrocycles ($\lambda = ca. 670\text{ nm}$, $\epsilon = 350\text{--}380\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).§ The polyamine-copper complex **5** exhibits a broad mesophase between the glass transition at 53 °C (as determined by DSC) and its decomposition at *ca.* 170 °C . The texture obtained under the polarizing microscope on heating is rather unspecific (Fig. 1).

Due to the decomposition of the complex at the clearing point it was not possible to observe defined and characteristic textures by slowly cooling down the samples from the isotropic state. Therefore, at the moment, we can not distinguish between a layered mesophase structure and a possible helical arrangement of the polymer backbone around the central Cu^{II} atoms which would result in a cylindrical complex structure (Fig. 2). The latter model would be comparable to the crystal structures found



Scheme 2 Reagents and conditions: i, 4-decyloxybenzoylchloride, DMAP, DMF, 70 °C , 3 d; ii, AlH₃, THF, 0 °C , 16 h; iii, Cu(NO₃)₂·2H₂O, CH₂Cl₂-H₂O, room temp., 16 h.

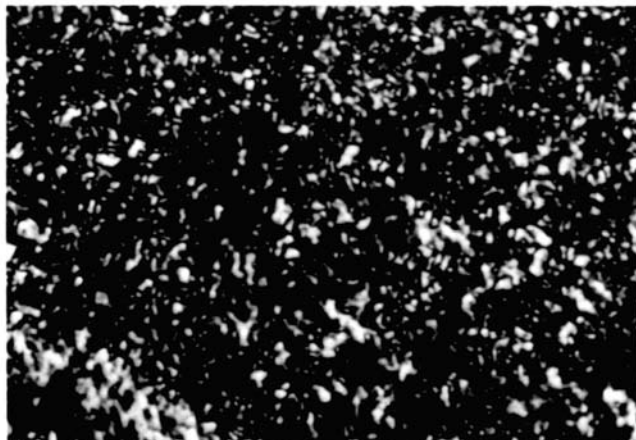


Fig. 1 Polarizing microscope texture of polyamine-copper complex **5** observed at $T = 120\text{ }^{\circ}\text{C}$ (on first heating)

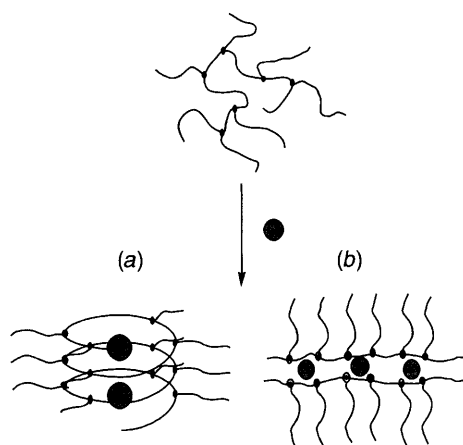


Fig. 2 Schematic representation of possible mesophase structures formed by polyamine-copper(II) complex **5**: (a) columnar structure (b) layered structure

for Cu^{I} and Ni^{II} complexes of oligobipyridine ligands for which the complexation induced generation of a double-⁸ and triple-helix⁹ was described, respectively. On the other hand, a lamellar structure would be in agreement with the smectic mesophases found for Cu^{II} complexes of *N*-alkylated poly(ethyleneimine)s with pendant mesogenic side groups¹⁰ and other polymeric organometallic complexes of copper^{II}.¹¹

Our results again show the analogy between linear polymers and oligomeric macrocycles based on the same structural unit. As in the case of the macrocyclic compounds, the mobility of the flexible polyamine backbone is reduced and the amphiphilicity of the polymer is enhanced by coordination to the transition metal ion, thus inducing a mesophase for the polyamine-copper complex **5**.

Received, 10th May 1995; Com. 5/02977E

Footnotes

† Linear poly(ethyleneimine) was synthesized by cationic polymerization of 2-phenyloxazoline in bulk (initiator: $\text{CF}_3\text{SO}_3\text{Et}$, $[\text{I}]/[\text{M}] = 1:80$, $110\text{ }^{\circ}\text{C}$, 4 d) followed by acid hydrolysis of the poly(2-phenyloxazoline) using 8

mol dm^{-3} HCl (reflux, 10 d, cf. R. Tanaka, I. Ueoka, Y. Takaki, K. Kataoka and S. Saito, *Macromolecules*, 1983, **16**, 849). According to the ^1H NMR, approximately 97% of the benzoyl groups were removed. Poly(*N*-4'-decyloxybenzoyl-ethyleneimine) **3** was synthesized by polymer analogous acylation of linear poly(ethyleneimine) as described for the two chain polyamide **1** (cf. ref. 2). According to elemental analysis (degree of hydration water) and ^1H NMR, a degree of substitution of 93% was reached. GPC analysis: $M_n = 24000$ ($M_w/M_n = 1.57$); $P_n = ca. 85$ ($M_{\text{rep. unit}} = 283.6$). Spectroscopic data for poly(*N*-4'-decyloxybenzyl-ethyleneimine) **4**. ^1H NMR (200 MHz, CDCl_3) δ 0.9 (t, 3 H, CH_3), 1.15–1.5 [br, 14 H, $(\text{CH}_2)_7$], 1.7 (t, 2 H, CH_2), 2.3–2.6 (br, 4 H, CH_2NCH_2), 3.25–3.5 (br, 2 H, NCH_2Ar), 3.8 (t, 2 H, OCH_2), 6.7 (d, 2 H, ArH) and 7.0 (d, 2 H, ArH). It should be noted that first attempts to use the $\text{BH}_3\cdot\text{THF}$ complex for the reduction of the polyamide backbone were rather unsatisfying. Long reaction times and higher temperatures were needed to guarantee a complete reduction in this case and resulted in partial cleavage of the amide bond and formation of 4-decyloxytoluene (as established by ^1H NMR, elemental analysis and FD mass spectroscopy).

‡ To prepare the copper complex **5**, polyamine **4** was dissolved in dichloromethane and stirred with an aqueous solution of the copper salt overnight. The organic layer was separated, filtered and the solvent was removed to yield a green complex. ^1H NMR (200MHz, CDCl_3) δ 0.9 (t, 3 H, CH_3), 1.15–1.5 [br, 14 H, $(\text{CH}_2)_7$], 1.7 (t, 2 H, CH_2), 2.6–3.4 (br, 4 H, CH_2NCH_2), 3.25–4.1 (br, 4 H, NCH_2Ar and OCH_2), 6.7 (d, 2 H, ArH) and 7.0 (d, 2 H, ArH); IR ν /1384 cm^{-1} (NO_3^- stretching mode); UV-VIS (THF) λ 665 nm ($\epsilon = 40\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). Assuming only NO_3^- as the counterion, 21% Cu^{II} per repeating unit are calculated from elemental analysis (C, 78.83; H, 10.80; N, 4.84) corresponding to a statistical composition of $\text{CuL}_{4.7}$.

§ The lower absorption coefficient may be due to the polymeric nature of the ligand and a less defined complexation since a possible five-coordination of Cu^{II} has to be considered as well (cf. A. von Zelewsky, L. Barbasa and C. W. Schl pfer, *Coord. Chem. Rev.*, 1993, **123**, 229; J. Arag o, A. Bencini, A. Bianchi, E. Garcia-Esp a a, M. Micheloni, P. Paoletti, J. A. Ramirez and P. Paoli, *Inorg. Chem.*, 1991, **30**, 1843).

¶ Note that as in the case of azacrown-transition metal complexes the formation of columns could lead to both, nematic and hexagonal mesophases (cf. ref. 4).

References

- J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304
- H. Fischer, S. S. Ghosh, P. A. Heiney, N. C. Maliszewskyj, T. Plesniviy, H. Ringsdorf and M. Seitz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 795
- J. M. Lehn, J. Malth te and A. M. Levelut, *J. Chem. Soc., Chem. Commun.*, 1985, 1794; C. Mertesdorf and H. Ringsdorf, *Liq. Cryst.*, 1989, **5**, 1757; G. Lattermann, *Liq. Cryst.*, 1989, **6**, 619
- A. Liebmann, C. Mertesdorf, T. Plesniviy, H. Ringsdorf and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1375
- G. Lattermann, S. Schmidt, R. Kleppinger and J. H. Wendorff, *Adv. Mater.*, 1992, **4**, 30
- H. Fischer, S. Kobayashi, W. Paulus, M. Edelmann, T. Plesniviy, H. Ringsdorf and M. Seitz, *Macromolecules*, submitted.
- T. Saegusa, A. Yamada, H. Taoda and S. Kobayashi, *Macromolecules*, 1978, **11**, 435
- J. M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565; J. M. Lehn and A. M. Rigault, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095; U. Koert, M. M. Harding and J. M. Lehn, *Nature*, 1990, **346**, 339; C. D. Eisenbach, U. S. Schubert, G. R. Baker and G. R. Newkome, *J. Chem. Soc., Chem. Commun.*, 1995, 69.
- R. Kr mer, J. M. Lehn, A. DeCian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.
- R. Festag, H. Ringsdorf, M. Seitz and J. H. Wendorff, *15th International Conference on Liquid Crystals*, Budapest July 3–8, 1994, *Abstracts Vol. I*, 78.
- C. Carfagna, U. Caruso, A. Roviello and A. Sirigu, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 345; U. Caruso, A. Roviello and A. Sirigu, *Macromolecules*, 1991, **24**, 2606; K. Hanabusa, J. Higashi, T. Koyama, H. Shirai, N. Hojo and A. Kurose, *Makromol. Chem.*, 1989, **190**, 1.