

# Synthesis and Chain Extension of Bipyridine-Terminated Polyethers with Copper(I) Ions

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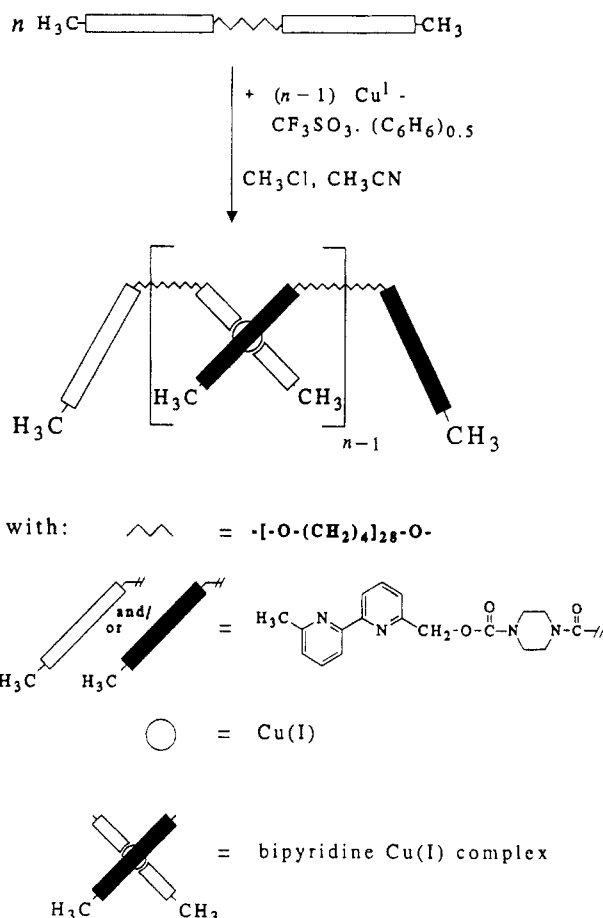
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**Introduction.** Well-defined supramolecular structures similar to those formed by spontaneous and recognition-directed self-assembly in biopolymeric systems have not as yet been realized in synthetic macromolecules. However, there are several approaches to obtain highly ordered polymeric systems both by specific interactions between functional groups and/or by taking advantage of segregation phenomena.<sup>1</sup>

It is known from supramolecular chemistry that bipyridine oligomers exhibit spontaneous self-organization in the presence of Cu(I) ions to form a double-stranded helical complex, which possesses characteristic features reminiscent of the DNA double helix.<sup>2</sup> Here we report on the application of the concepts of organic supramolecular chemistry to the formation of a "linear polymeric supramolecular material" (cf. ref 3) by bipyridine (bpy) metal coordination of telechelic polyethers with 6,6'-disubstituted 2,2'-bipyridine terminal unit containing end blocks (Figure 1). This work extends our previous studies of the control of segregation and chain folding of monodisperse segments in multiblock copolymers to specific superstructures and morphologies<sup>1e-h</sup> in that constitutive units capable of double-helix formation by metal complexation have been employed; the study addresses one aspect of the problem of how the conformation and packing of macromolecules are influenced by segments of different constitution and to which extent self-assembly and self-organization phenomena of lower molar mass compounds can be transferred to macromolecular systems. The results of the first measurements by UV spectra, viscosimetry, gel permeation chromatography (GPC), and torsion pendulum of the formation of a mononuclear complex consisting of a Cu(I) ion coordinated to the four nitrogens of two bpy units are reported.

**Experimental Section.** The synthesis of the monofunctional 6,6'-disubstituted 2,2'-bipyridine 5 starting from 2-bromo-6-picoline (1)<sup>4</sup> was modified as compared to the literature<sup>5</sup> in order to improve the yield at the various reaction steps (Scheme 1); details will be published later.<sup>6</sup> For example, 1 can be prepared in about 400 g/day quantities by a semicontinuous procedure; 2 is obtained in 70-g quantities (68% yield) per experiment after two distillation steps for purification. Starting from 2, the synthesis of 5 proceeds without further purification of the intermediates 3 and 4; pure 5 is obtained in 50-g quantities (overall yield 68%) after distillation.

**6-[[[(Chlorocarbonyl)oxy]methyl]-6'-methyl-2,2'-bipyridine (6).** The alcohol 5 (6.07 g, 30.4 mmol) was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the resulting solution was treated with 12 mL of 12 N HCl, concentrated, and freeze-dried with 50 mL of benzene. The hydrochloride was dissolved in 250 mL of acetonitrile, and the resulting solution was dropwise added to a solution of 30 mL of phosgene at -15 °C. After stirring for 6 h, the phosgene was removed. Yield: 9.01 g (99%). IR (KBr):  $\nu$  = 1770 cm<sup>-1</sup> (C=O).

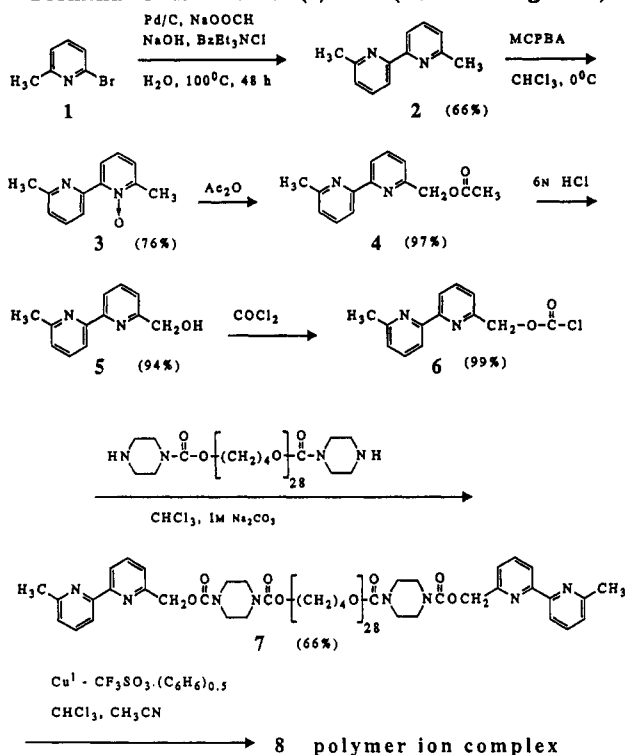


**Figure 1.** Schematic of the bipyridine/Cu(I) complex<sup>2</sup> in the chain extension of telechelic polyethers with bipyridine terminal units.

**Telechelic Polyether (7).** A total of 3.48 g (1.56 mmol) of  $\alpha$ -[(piperazinylcarbonyl)oxy]- $\omega$ -(piperazinylcarbonyl)-poly(oxytetramethylene) with an average of 28 oxytetramethylene repeat units<sup>7</sup> in 10 mL of destabilized CHCl<sub>3</sub> was slowly added to a vigorously stirred suspension of 1.00 g (3.36 mmol) of 6 in 10 mL of destabilized CHCl<sub>3</sub> followed by addition of 15 mL of a 1 M Na<sub>2</sub>CO<sub>3</sub> solution. After stirring for 20 h, the water layer was separated and the organic layer was extracted with water (3  $\times$  100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo, and precipitated in CH<sub>3</sub>OH (800 mL, -78 °C). The white solid was filtered off and freeze-dried out of 50 mL of benzene. Yield: 2.8 g (65%). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, 25 °C): 1.55–1.72 (m, 4 H, H5,6,9), 2.56 (s, 3 H, H7''), 3.36–3.46 (m, 4  $\times$  8 H, H2,7,8), 4.10 (t, 4 H, H4), 4.73 (s, 2 H, H7'), 7.10 (d,  $J$  = 7.6 Hz, 1 H, H-5''), 7.26 (d,  $J$  = 7.6 Hz, 1 H, H5'), 7.43 (t,  $J$  = 7.6 Hz, 1 H, H4''), 7.59 (t,  $J$  = 7.6 Hz, 1 H, H4), 8.12 (d,  $J$  = 7.7 Hz, 1 H, H3''), 8.26 (d,  $J$  = 7.6 Hz, 1 H, H3'). <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C): 23.8 (C7''), 25.4 (C5,6), 26.0 (C9), 43.4 (C2), 43.7 (C1), 65.2 (C4,7'), 70.1 (C7,8), 118.0 (C3'), 119.1 (C3''), 120.9 (C5'), 123.4 (C5''), 136.0 (C4'), 136.7 (C4''), 146.7 (C6'), 149.1 (C2''), 155.0 (C3,2'), 157.5 (C6'').

**Complexed Telechelic Polymer (8).** A solution of 0.036 00 g (0.1430 mmol) of a copper(I) trifluoromethanesulfonate/benzene complex in 10 mL of acetonitrile was added slowly to a solution of 0.3508 g (0.1391 mmol) of 7 in 10 mL of CHCl<sub>3</sub>. After stirring for 6 h, the solvent was removed and the red solid was extracted with acetonitrile (2  $\times$  5 mL) and dried. Yield: 0.387 g (99%). UV/vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$ ( $\epsilon$ ) = 305 nm (22 000 M<sup>-1</sup> cm<sup>-1</sup>), 405 (2300).

**Scheme 1. Synthesis of 6-[[[(Chlorocarbonyl)oxy]methyl]-6'-methyl-2,2'-bipyridine (6) via the N-Oxide Route: Synthesis of the Cu(I)-Complexed Polymer with Two Bipyridine End Blocks via Condensation and Complexation of the Terminal Units with Cu(I) Ions (See Also Figure 1)**

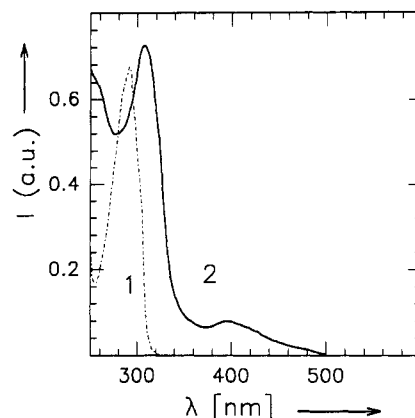


**Characterization.** Gel permeation chromatography (GPC), differential scanning calorimetry (DSC), dynamic mechanical measurements, and transmission electron microscopy investigations were carried out as already described elsewhere.<sup>1f-h</sup> The UV/vis spectra were recorded with a Perkin-Elmer Lambda 15 spectrophotometer.

**Results and Discussion.** The synthesis route to the 6-[[[(chlorocarbonyl)oxy]methyl]-6'-methyl-2,2'-bipyridine (6) is illustrated in Scheme 1. Compared to the low-yield procedures previously described in connection with disubstituted bpy and oligo(bpy) synthesis,<sup>2,8,9</sup> the synthesis of the chloroformate precursor 5 has been considerably improved by the route via bipyridine *N*-oxide (cf. refs 4 and 5). The chloroformate 6 was readily obtained in almost quantitative yield by reacting 5 with excess phosgene. It has to be emphasized that all reactions depicted in Scheme 1 can be carried out in a 50–100-g scale, thus providing enough of the pivotal bipyridine starting material 5 for polymer synthesis in sufficient quantities for material testing. The conversion of 6 with  $\alpha$ -[(piperazinylcarbonyl)oxy]- $\omega$ -(piperazinylcarbonyl)poly-(oxytetramethylene) (that is, piperazinyl-terminated POTM<sup>7</sup>) gave the segmented three-block copolymer 7 with a polyether centerblock and the bpy terminal units (Scheme 1).

The chain extension reaction of the telechelic polymer with Cu(I) ions is schematically shown in Figure 1. This reaction is a type of step-growth polymerization reaction in that the chain extension occurs by the linkage of chain ends through formation of a mononuclear copper(I) complex involving the bpy functional group of the terminal units as bidentate ligands.

The Cu(I) complex of bpy end groups was immediately formed after addition of the copper(I) trifluoromethanesulfonate solution to the three-block copolymer solution in chloroform/acetonitrile (see Scheme 1). This was

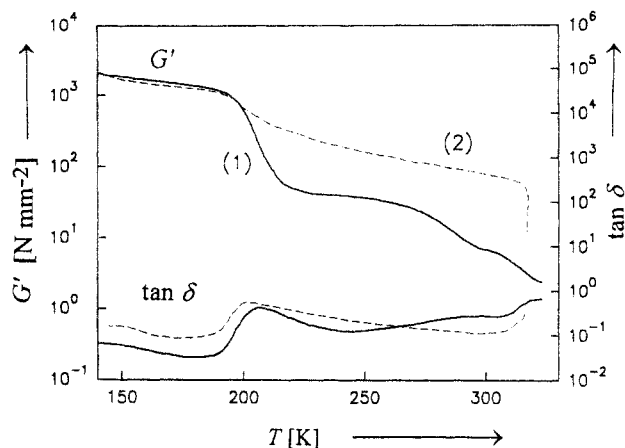


**Figure 2.** UV/vis spectra of the uncomplexed telechelic polymer 7 (---, curve 1) and of the Cu(I)-complexed polymer 8 (—, curve 2) in CHCl<sub>3</sub> (7, *c* = 0.076 g/L; 8, *c* = 0.107 g/L).

indicated by the deep orange-red coloring of the solution. The UV spectra of the triblock copolymer before and after complexation with Cu(I) are depicted in Figure 2. In view of the pseudotetrahedral coordination of the Cu(I) complexes of 6,6'-dimethyl-2,2'-bipyridine<sup>10</sup> and similar structures of oligo(bpy)/Cu(I) complexes,<sup>2</sup> it can be inferred that this Cu(I) complex with two [[[(6'-methyl-2,2'-bipyridin-6-yl)methylene]oxy]carbonyl]piperazinyl]-carbonyl end segments had a corresponding structure.

Besides the UV spectroscopic evidence of the mononuclear copper(I) complex, both viscosity measurements and gel permeation chromatography (GPC) indicated that the chain extension of **7** to the polymer ion complex **8** occurred. The intrinsic viscosity in a  $\text{CHCl}_3$  solution at  $25^\circ\text{C}$  changed from  $[\eta] = 26.0 \text{ L/g}$  of **7** to  $[\eta] = 41.8 \text{ L/g}$  for **8** (stoichiometric quantities of **7** and copper(I) trifluoromethanesulfonate). Similarly, the peak maximum elution volume in GPC decreased significantly and corresponded to a 3-fold increase of the molar mass upon complex formation. In this context the equilibrium dynamics in the Cu(I) complex formation in solution have to be considered, because the reversibility in complex formation will result in apparently lower molar masses (polymer ion complex **8**;  $M_w = 16\,100$ ;  $M_w/M_n = 2.04$ ) than would be expected for quantitative complex formation (see Figure 2).

The stress-strain and dynamic mechanical properties of the polymer ion complex **8** were typical for elastomers. For example, the temperature dependence of the storage modulus  $G'$  and  $\tan \delta$  was characteristic of a two-phase thermoplastic elastomer (Figure 3) and distinctively different from the waxy properties of **7** or its POTM precursor, as well as from those of a high molecular weight POTM thermoplast (curve 2, Figure 3). The sharp drop in the modulus at low temperature was related to the glass transition of the polyether soft segments. The elastomeric plateau region extended to about 310 K; and the shoulder seen at about 260–290 K is assigned to recrystallization and subsequent melting of soft segment crystallites. The softening of the elastomer which was associated with the destruction of hard segment Cu(I) complex domains starts at about 310 K and was followed by a yielding of the material. Similar properties were found for corresponding multiblock copolymers with polyether soft segments and Cu(I)-complexed bpy containing hard segments.<sup>6</sup> The two-phase structure (that is, the existence of domains of Cu(I) complex end units) is backed by results obtained from transmission electron microscopy and by using the element spectroscopy imaging (ESI) technique: The bright-field image showed randomly distributed nanoscopic domains.



**Figure 3.** Dynamic mechanical properties of the Cu(I)-complexed polymer 8, (curve 1) and of high molecular weight poly(oxytetramethylene) (curve 2;  $M_n = 63\,000$ ):  $G'$  = storage modulus;  $\tan \delta$  = loss factor.

This was complemented by the imaging of the copper and nitrogen elements, which are both specific for the complexed end blocks; almost identical element distribution pictures characteristic of nanoscopic domains were obtained, thus visualizing the phase-separated system.<sup>11</sup>

**Conclusion.** In conclusion it can be stated that this terminal-complexed, telechelic polyether system exhibited all of the features typical for the controlled self-organization of bpy units in the presence of Cu(I) ions. The basic features of the distorted tetrahedral coordinations of bpy around the copper atom were maintained when going from the mononuclear to di-, ..., pentanuclear complexes, resulting in double-stranded helices (cf. refs 2 and 10). It can be assumed that segmented triblock copolymers and multiblock copolymers with oligo(bpy) segments exhibit recognition-directed self-assembly with high cooperativity to yield supramolecular polymers. This is the subject of ongoing work.

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## References and Notes

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