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ORIGINAL CONTRIBUTION

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Supramolecular structures of macromolecules containing bipyridine–copper(I) complexes as revealed from transmission electron microscopy studies

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Abstract Transmission electron microscopy (TEM) studies on bipyridine (bpy) containing block copolymer systems showed the formation of nanoscopic polymer–ion complexes through complexation with copper(I) ions which segregated to highly ordered columnar domains of mesoscopic dimensions. The domains, i.e. stacks of $[(bpy)_2Cu(I)]$ complex moieties could be visualized by complementary TEM techniques. First, electron energy loss spectra (EELS) showed the absorption edges of copper and nitrogen, which are specific for the bipyridine copper complexes. The element spectroscopic imaging (ESI) technique allowed the imaging of the net copper and net nitrogen distribution, and the coinciding pictures exhibited a microphase separated system in the case of a 3-block copolymer with complexed end segments. High resolution elastic bright field images showed interference lines with a line to line distance of about 8 Å which could be related to the Cu–Cu distance in staggered Cu(I)–bipyridine complexes.

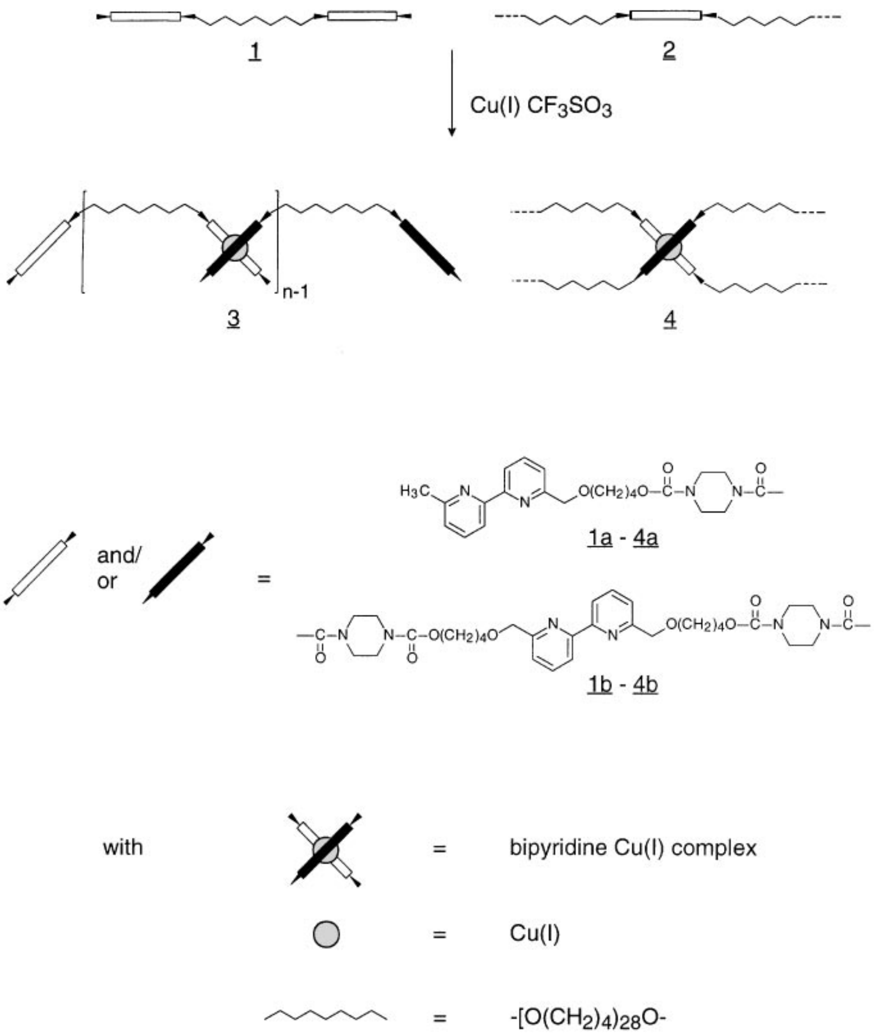
Key words Transmission electron microscopy – supramolecular structures – bipyridine–copper(I)-complexes – microphase separation – thermoplastic elastomers

Introduction

One challenge in material science is the design of organic or inorganic molecular compounds with the ability to form well-defined supramolecular macromolecular architectures by specific recognition-directed self-assembly processes and thus leading to materials with novel properties [1–5]. Oligo(bipyridine) metal cation systems are well known from organic supramolecular chemistry for their self-organization and spontaneous formation of helical metal complexes of bipyridines (bpy) in the presence of e.g. Ag^I or Cu^I cations [6–13]: two oligo(bipyridine) strands wrap around the metal cations to form structures similar to the Watson and Crick double-helix in nucleic acids [14].

In order to mimic recognition-directed self-organization and self-assembly in synthetic polymers with regard to the building of highly ordered structures, segmented macromolecules containing bipyridine (bpy) and polyether building blocks have been synthesized [15–20]. Besides the spectroscopical proof of the formation of the mononuclear $[Cu(I)(bpy)_2]$ complex, the thermal and mechanical properties of the bulk material proved the novel superstructure of the polymer ion complex as revealed by the elastomer properties [15–20]. In this paper we report on transmission electron microscopy (TEM) studies to visualize the structure and morphology of the

Fig. 1 Schematic of the formation of the [Cu(I)(bpy)$_2$] complexes of bipyridine (bpy) units containing 3-block (**1**) and multiblock (**2**) copolymers under chain extension (**3**) and crosslinking (**4**), respectively



uncomplexed and Cu(I) complexed segmented block copolymers (Fig. 1). The electron spectroscopic imaging (ESI) TEM which has been shown to be a powerful technique in the analysis of microphase separated polymer systems [21–25] complemented and further elucidated the ordered structure on a mesoscopic scale.

Experimental part

Sample preparation

The synthesis and characterization of segmented 3-block and multiblock copolymers consisting of 6,6′-disubstituted-2,2′-bipyridine containing segments and poly(oxytetramethylene) ($M_n = 2000$) segments, and the polymer ion complexation with Cu(I) have been described in previous papers [15, 16, 18–20]. The structure of the copolymers are shown in Fig. 1.

Electron microscopy

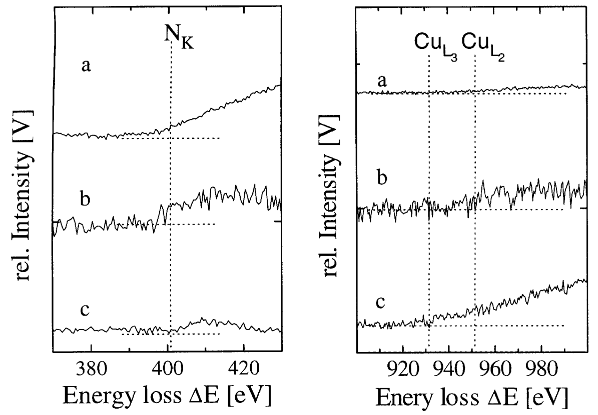
The ultrathin polymer films of 30–50 nm thickness required for ESI-TEM in order to prevent multi scattering of the electrons were obtained by cryo-ultramicrotom cutting (−130 °C) using a Reichert-Jung-Ultracut E equipped with a diomond knife; the samples employed for ultramicrotomy were taken from test specimen for dynamic mechanical experiments that had been obtained by casting from $CHCl_3$ solution [15, 16]. The ultrathin polymer films were put onto a copper grid with an one hair brush and were transported via a transfer unit directly to the microscope and then investigated at −160 °C.

The transmission electron micrographs were obtained by a Zeiss CEM 902 electron microscope equipped with an energy filter system (prism–mirror–prism-system). High resolution elastic bright field images were recorded up to a magnification of 1 : 250 000 by an integrated plan film camera on Kodak SO-163 films. The element distribution pictures were taken with a Dage SIT 66 video camera which is directly attached to the microscope, stored in a computer, and the image processing was performed from the digitized images with the Kontron IBAS 1.3 processing software. The generally, and especially at the copper absorption edge, unfavourable signal to noise ratio was improved by a multi window technique which has been discussed in detail elsewhere [26]. In comparison to the conventional three windows technique, this technique used four reference pictures just above the element absorption edge and six element pictures below the edge. The electron energy loss spectra (EELS) were obtained at a magnification of 1 : 85 000 by measuring the intensity distribution in dependence of the enengy loss of inelastically scattered electrons via a photomultiplier attached to the microscope. The obtained spectra were background corrected by an exponential fit [26].

Results and discussion

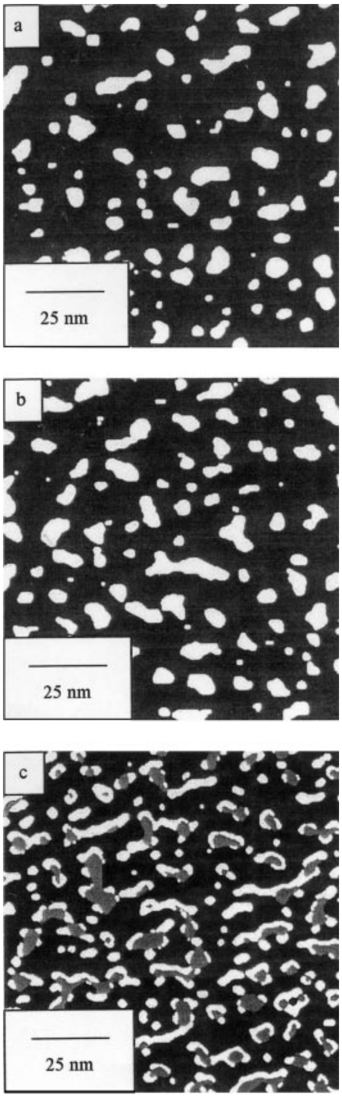
Electron energy loss (EEL) spectra were recorded in order to identify the copper and/or nitrogen in the polymer system. Copper was detected by its absorption edges at an energy loss of $\Delta E = -931$ eV (L_3 edge) and -951 eV (L_2 edge), and nitrogen was detected by the absorption edge at $\Delta E = -401$ eV (K edge). Figure 2 shows the EEL spectra of the Cu(I) complexed 3-block copolymers **3a** and **3b** without and with spacer unit. Similar spectra were obtained for the multiblock copolymer systems **4b**. The occurrence of the copper absorption edges in the EEL spectra indicated the presence of copper and thus the copper ion complex formation which is in agreement with the UV-spectroscopical data [15, 16, 18–20]. Insights in the morphology, i.e. if microphase separation has occured in the complexed bulk polymer, could be obtained from element distribution pictures and elastic bright field images of the polymer films. The uncomplexed block copolymeres could not be investigated because of their waxy consistency.

Fig. 2 Electron energy loss spectra of Cu(I)-complexed 3-block copolymer **3a** without spacer between the bpy and piperazinyl unit (a), Cu(I)-complexed 3-block copolymer **3b** with spacer between the bpy and piperazinyl unit (b) and of **4b** with tetramethylene spacer (c); N_k: nitrogen absorption edge; $Cu_{L2,3}$: copper absorption edges



Both the nitrogen and the copper net element distibution pictures (Fig. 3a and b) of the Cu(I) complexed 3-block copolymer showed that microphase separation had occured in the polymer ion-complexes. This was evident from the bright areas representing nitrogen and copper rich domains in the matrix (dark background). As it was

Fig. 3 Net element distribution pictures of Cu(I) complexed 3-block copolymer **3a** (magnification: 1 : 85 000); (a) nitrogen distribution; (b) copper distribution; (c) nitrogen/copper superposition of bisbipyridine 3-block copolymer Cu(I) ion complex [26]



demonstrated for the complexed 3-block copolymer with bis(bipyridine) endgroups, a superimposing of the nitrogen and copper net element distribution pictures taken from the same sample region showed that both nitrogen and copper were located at the same place (Fig. 3c). This proves the existence of domains of bipyridine–Cu(I)-complexes in the bulk polymer. However, it was not possible to image the counter-ions of the polymer ion complex domains. Neither the recording of electron energy loss spectra nor the application of the element spectroscopic imaging technique gave some indication about fluorine or the sulphur of the trifluorosulphonate counter ions or any information about an agglomeration of counter-ions in the polymer matrix. This infers that the counter-ions are not clustered around the copper-bipyridine complexes but are distributed in the polymer matrix. As far as the not detected fluorine absorption edge is concerned, it is known from literature that there are difficulties in imaging the fluorine absorption edge and the fluorine distribution (e.g. of BF_4^- counter-ions) in polymeric systems [27]; the same holds true for samples with low sulphur content where it was demonstrated for sulphur containing rubber that the detection limit is about 1 wt% [28]. Thus the question remains open whether the counter-ions are homogeneously distributed in the sample, or if they are located near the bipyridine–Cu(I) complexes in defined places like in the [Cu(I)(bpy)$_2$] model systems [6, 13].

The elastic bright field images of the polymer ion complex **3a** (or **3b**) of the triblock copolymer **1a, b** with bpy end blocks showed a microphase separated system as well (Fig. 4a), whereas the corresponding picture (Fig. 4b) of the polymer ion complex **4b** of the multiblock copolymer **2** was completely featureless. In the latter system, microphase separation was prevented by the topology of the network formed by complex formation, whereas in the case of the linear segmented polymer ion complex phase separation is not impeded [16].

High resolution elastic bright field images showed regular structures in Ångstöm-scopic to nanoscopic dimensions (interference lines) (Fig. 5). These structures could only be explained by very regular, i.e., periodic arrangements of the Cu(I)–bipyridine complexes in the polymer system itself. The line-to-line distance was measured to about 8 Å, which is in good agreement to the Cu–Cu distance in bipyridine–Cu(I)-complex model systems as determined from single crystal X-ray analysis [6, 13]. The regular stacking of the [Cu(I)(bpy)$_2$] complexes in microdomains as visualized from the high resolution electron micrograph (Fig. 5) was further confirmed by electron diffraction studies, which were done in detail for the corresponding Cu(I) complexed triblock copolymers with bisbipyridine units in the hard block [26]. A typical electron diffraction pattern is depicted in Fig. 6, together with radial intensity distribution curve. The reflex at or around 8 Å is characteristic for the packing of the Cu(I) bipyridine complexes, and the intensity of this reflex increased upon annealing which is indicative for the perfecting of the packing order. Due to the decomposition of the sample by the electron beam it was not possible to take a focus series. However, the astigmatism was always corrected by taking a picture at high magnification with the digital SIT camera; a fourier transformation of that picture was calculated and corrected for the astigmatism until a radial symmetric fourier picture had been obtained [29, 30].

The above results could only be explained by microphase separation of the complexed 3-block copolymer

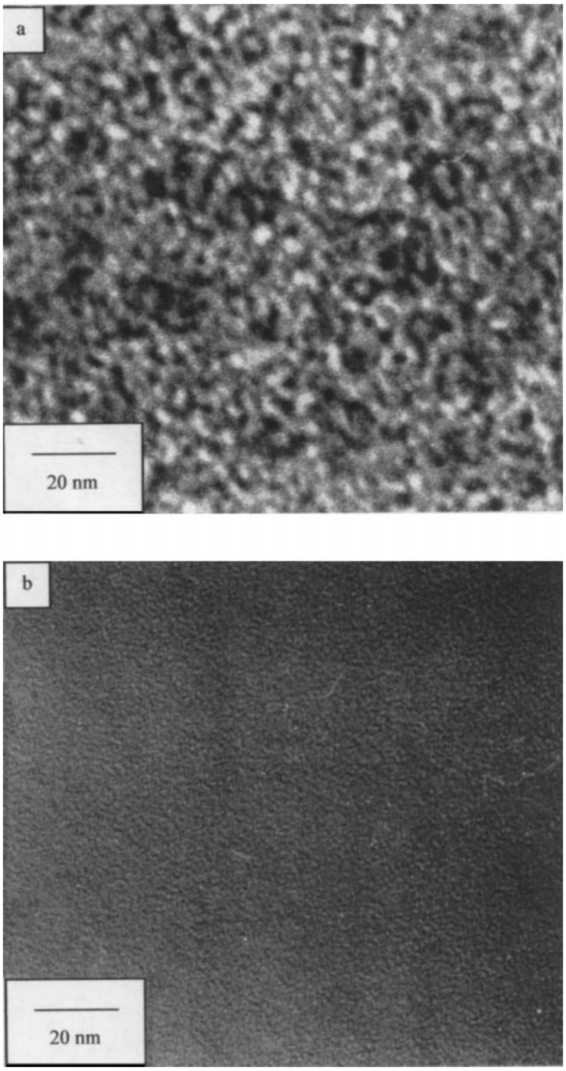


Fig. 4 Elastic bright field images of Cu(I) complexed 3-block copolymer (**3a**) (a) and multiblock copolymer **4b** (b): (magnification: 1 : 250 000)

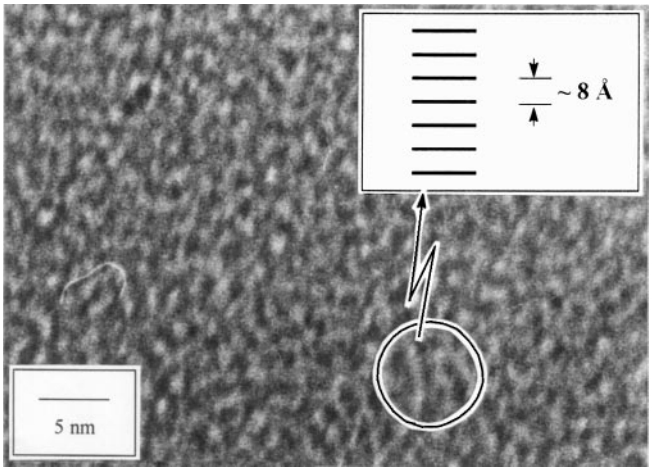


Fig. 5 High resolution elastic bright field image of the complexed 3-block copolymer showing highly ordered domains (interference lines). Close up: schematic model of bipyridin Cu(I) complex stack

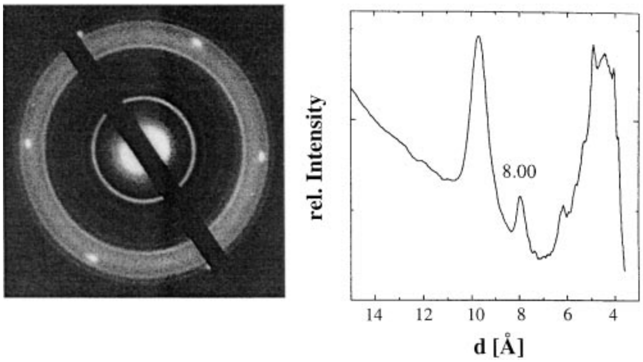


Fig. 6 Electron diffraction pattern (left) and radial intensity distribution (right) of a Cu(I) complexed bisbipyridine-containing block copolymer (after annealing at 110 °C for 30 min) [16]

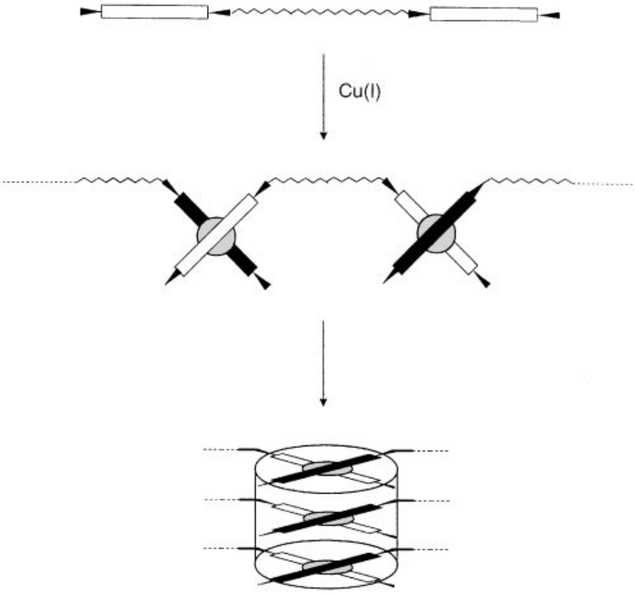


Fig. 7 Schematic model of the segregation and packing of the bipyridine (bpy) Cu(I) complexes in 3-block copolymer **3a** to columnar aggregates

resulting in aggregates of [Cu(I)(bpy)$_2$] complex end blocks in a polyether center block matrix: complexation of Cu(I) ions by the bpy unit of the end blocks meant a chain extension reaction [15, 16], and the newly formed [Cu(I)(bpy)$_2$] constitutional units (segments) in the resulting linear macromolecules **3a** and **3b** (see Fig. 1) segregated to domains like in conventional multiblock copolymers such as segmented polyurethanes; this explained the thermoplastic elastomer properties of the complexed 3-block copolymer [15, 16]. Furthermore, the bipyridine–Cu(I)-complexes of **3a, b** had formed highly ordered aggregates, i.e. stacks of Cu(I)-complexes in an almost crystal-like fashion as schematially shown in Fig. 7. This effect caused the interference lines in high resolution bright field images. Contrary to this, in the case of the segmented multiblock copolymer **2b,** complexation of the bpy units in the polymer chain with the equivalent amount of Cu(I) meant crosslinking: obviously the topology of the resulting network characterized by tetrafunctional [(Cu(I)(bpy)$_2$] net points (see Fig. 1) and exhibiting elastomeric properties of a network [16] did not allow further clustering of the ion complex netpoints.

Conclusion

The 3-block and multiblock copolymer systems with bipyridine containing segments showed features typical for the self-organization of low molecular weight (oligo)bpy molecules in the presence of Cu(I) ions under formation of copper-ion-complexes. Results obtained from transmission electron microscopy (TEM) exhibited an ordered superstructure in the case of the chain extended 3-block copolymers **3a** and **3b**. Using element spectroscopic imaging (ESI) TEM, a microphase separation under formation of domains composed of bipyridine Cu(I) complexes could be visualized: identical and superimposable net element distribution pictures of the elements copper and nitrogen, which are both specific for the bipyridine copper complex, were obtained; the location of the counter-ions could not be identified by electron loss spectroscopy or element spectroscopic imaging because of insufficient contrast of the fluorine and sulphur elements of the counter ions in the given concentration. High resolution elastic bright field images demonstrated the existence of quasi crystalline domains of nanoscopic to mesoscopic dimensions consisting of stacks of [Cu(I)(bpy)$_2$] complex units. To the best of our knowledge, these findings are the first examples of a direct visualization of highly ordered structures obtained in synthetic macromolecule systems by applying the principle of complex formation from supramolecular chemistry (see e.g. [31] for TEM investigations of other supramolecular systems).

Further insights into the potential of helix formation through bipyridine copper complexes and creation of highly ordered supramolecular structures should be obtained by systems containing oligo(bipyridine) units capable to form real double-stranded helical sequences with a high cooperativity; this is subject of ongoing work [32, 33].

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