Redox-active liquid-crystalline ionomers: 1. Synthesis and rheology

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Liquid-crystalline (LC) copolymers with redox-active groups were prepared by copolymerization of mesogenic and ferrocene-containing monomers (up to 10%). In these copolymers the ferrocene groups can be oxidized reversibly to prepare ionomers, while retaining the LC phase. It is thus possible to vary the amount of ionic groups in the ionomers by a redox reaction. The oxidized (charged) polymers show a strong excess X-ray scattering at small angles. This is typical for ionomers and is assigned to the scattering of ionic aggregates. Dynamic mechanical measurements show that these aggregates are effective as crosslinking points. Thus an oxidation–reduction reaction can be used to transfer an uncrosslinked polymer (reduced ferrocene groups, uncharged) reversibly into an oxidized polymer that acts like a weakly crosslinked gel.

(Keywords: liquid-crystalline polymers; ionomers; redox polymers; synthesis; rheology; ionic aggregation)

INTRODUCTION

Liquid-crystalline (LC) polymers[1–4] and especially LC elastomers[5,6] have received a lot of interest during recent years, owing to their special optical, mechanical and piezoelectric properties. The polymer network structure of the LC elastomers studied so far has been prepared by covalent crosslinking of polymer chains[5–8]. Physical crosslinking (as in ionomers[9–11]) has not yet been tried. In ionomers, the gelation of the polymer chains is caused by cluster formation of ionic groups that belong to different polymer chains. This leads to the formation of a temporary network structure.

It was the aim of this work to bring together the topics of liquid crystals and ionomers by preparation of LC polymers that are functionalized with redox-active groups[12]. We chose ferrocene derivatives[13] for this purpose, because they are chemically stable in both the reduced and the oxidized states. In this case the positively charged groups (ferrocenium ions) can be introduced reversibly by a redox reaction[14], whereas in most ionomers the electrically charged groups are introduced by neutralization (salt formation) of polymeric acids[15].

The advantage of this concept (redox polymers) may be that no specific interaction of the functional groups is to be expected for neutral polymers, which act as reference polymers to determine the influence of ionic groups. In classical ionomers, on the contrary, strong hydrogen bonding of the polymeric acids is already present prior to salt formation.

In this paper we describe the synthesis and characterization of LC polymers functionalized with redox-active groups and the influence of the redox-active groups in the reduced and oxidized state on the LC phase transitions. Furthermore we give the first evidence for cluster formation of the ferrocenium ions, which leads to a gelation of the LC ionomers.

RESULTS AND DISCUSSION

Preparation and characterization of the polymers

For the preparation of redox-active LC ionomers, we synthesized 2-ferrocenylethyl acrylate (**2**) as redox-active component, and as liquid-crystalline part the two mesogenic phenyl benzoates, 4-(cyanophenyl-4-(6-acryloyloxy)hexyloxy)benzoate (monomer **1a**) and 4-(methoxyphenyl-4-(6-acryloyloxy)hexyloxy)benzoate (monomer **1b**). LC polymers with different contents of ferrocene component (0–9.93%) were prepared by a radical-initiated copolymerization in toluene. The preparative oxidation of the redox-active group was carried out in a mixture of methylene chloride and acetonitrile (volume ratio 1/1) with copper(II) perchlorate hexahydrate (see *Scheme 1*). All experimental details are given in the experimental part.

Copolymer composition of the ferrocene-containing polymers (see *Table 1*) was investigated by ^{1}H n.m.r. spectroscopy and potentiometric titration with copper(II) perchlorate hexahydrate as oxidizing reagent[16]. The results are compiled in *Table 1.*

The values of ferrocene content derived from both methods are in good accordance with the monomer ratios used (see *Table 1*). In combination with the copolymerization parameters determined for monomers with a similar electronic structure[17] (monomer **2** and methyl

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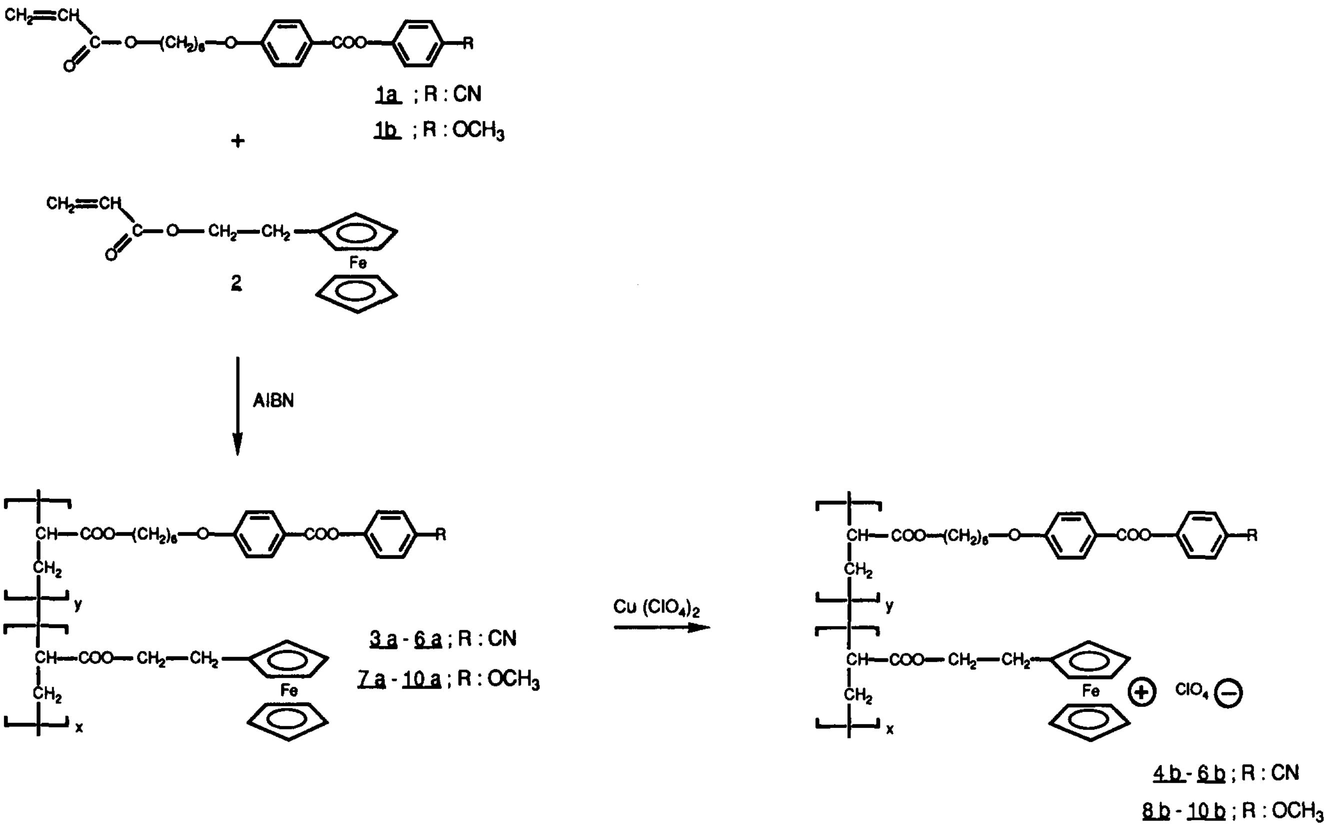

Scheme 1 Synthesis of ferrocene-containing side-group polymers and oxidation of the ferrocene units

Table 1 Molecular weights and compositions of copolymers 3–10

No.	R	Molecular weight[a], M_w (g mol^{-1})	Composition according to ^1H n.m.r. spect. (% ferrocene)	Composition according to redox titration (% ferrocene)	Monomer composition of the react. mixt. (% ferrocene)
3a	-CN	14 100	0	0	0
4a	-CN	20 000	2.3	3.0	3.36
5a	-CN	15 500	7.5	7.0	6.69
6a	-CN	17 700	8.3	9.43	9.95
7a	$-OCH_3$	28 500	0	0	0
8a	$-OCH_3$	43 800	2.3	2.82	2.30
9a	$-OCH_3$	24 900	4.3	4.43	5.90
10a	$-OCH_3$	18 900	9.5	10.36	13.80

[a] Determined from g.p.c. in $CHCl_3$, calibrated against polystyrene standards

acrylate, $r_1 = 0.76$ and $r_2 = 0.69$), this points to a copolymerization under nearly ideal conditions.

In order to introduce a reversible change of properties by changing the amount of ionic groups in the LC network, the redox process ferrocene/ferrocenium must be chemically reversible. To prove this, we performed cyclic voltammetric measurements on the polymers synthesized. As an example the cyclic voltammogram of polymer **9a** is shown in *Figure 1*.

At a potential of +450 mV the oxidizing peak of the ferrocene units occurs and at +200 mV the corresponding reduction peak occurs. The cyclic voltammogram shows a large hysteresis, and it was found that the amount of charges of both electrode reactions is identical. This behaviour is characteristic for quasi-reversible electrode reactions[18] and show the chemical reversibility of the

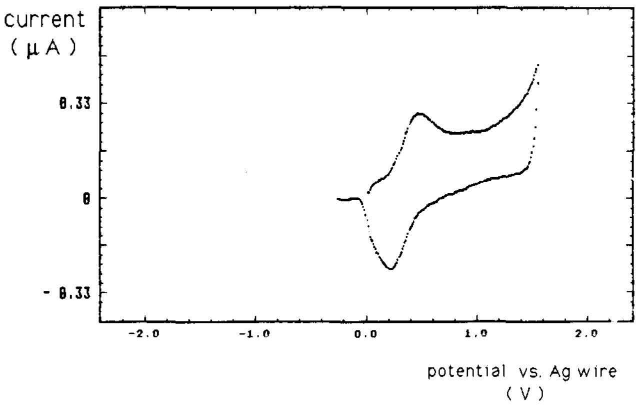

Figure 1 Cyclicvoltammogram of polymer **9a**; sweep, 70 mV s^{-1}

Table 2 LC phase behaviour[a] of ferrocene-containing side-group polymers

No.	R	Ferrocene content (%)	Reduced state (K)	No.	Oxidized state (K)
3a	-CN	0	g 297 n 386 i	-	-
4a	-CN	2.65	g 303 n 388 i	**4b**	g 305 n 359 i, dec
5a	-CN	7.25	g 299 n 379 i	**5b**	g 306 n 379 i, dec
6a	-CN	8.87	g 303 n 367 i	**6b**	g 310 n 368 i, dec
7a	$-OCH_3$	0	g 306 s_A 370 n 393 i	-	-
8a	$-OCH_3$	2.56	g 304 s_A 363 n 389 i	**8b**	g 304 s_A 363 n, dec
9a	$-OCH_3$	4.37	g 301 s_A 355 n 381 i	**9b**	g 305 s_A 357 n, dec
10a	$-OCH_3$	9.93	g 299 s_A 339 n 369 i	**10b**	g 309 n 370 i, dec

[a] g, glassy; n, nematic; s_A, smectic A; i. isotropic; dec, decomposition a few degrees above the transition into the isotropic phase (i, dec) or nematic phase (n, dec)

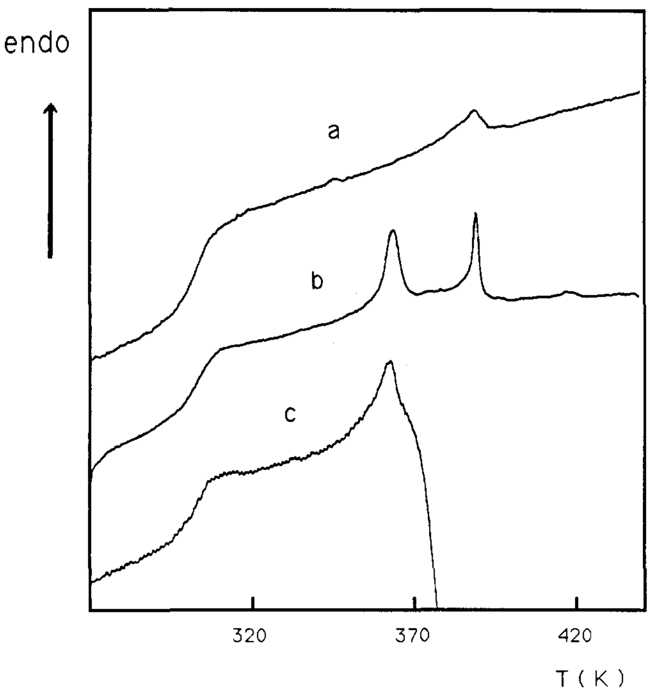

Figure 2 D.s.c. thermogram of polymers **4a** (R = CN) (a), **8a** ($R = OCH_3$) (b) and **8b** ($R = OCH_3$) (c)

redox process ferrocene/ferrocenium also for the polymers.

Because of the low ferrocene content of the polymers and the slow diffusion rate of the polymer-bound ferrocene groups, low peak currents (0.3 μA) were measured. Therefore, it was not possible to suppress all currents caused by electroactive impurities of solvent. However, measurements performed on all side-group polymers showed peaks at the same potentials.

Liquid-crystalline behaviour

The liquid-crystalline behaviour (LC phases and their transition temperatures) of the polymers **3**–**10** was determined by polarization microscopy, differential scanning calorimetry (d.s.c.) and X-ray measurements. The results are collected in *Table 2*. *Figure 2* shows the d.s.c. thermograms of copolymers **4a**, **8a** and **8b**.

It follows from the results of *Table 2* that the reduced ferrocene comonomer has only a minor influence on the formation of the LC phases. The LC phases are unchanged compared to the corresponding homopolymers[19] and only a slight decrease of the phase width with increasing comonomer ratio is observed.

Analysis of the data leads to a linear dependence between mesophase width (nematic and smectic A phase) and ferrocene content. The nematic mesophase width of polymers **3a**–**6a** and the smectic mesophase width of polymers **7a**–**10a** decreases, whereas the nematic mesophase width of polymers **7a**–**10a** increases slightly. A linear extrapolation of the decreasing phase widths to a value at 0 K (full suppression of liquid-crystalline phases) leads to ferrocene contents of 48% for polymers **3a**–**6a** and 26% for polymers **7a**–**10a**. The X-ray fibre patterns of copolymers were identical to those of the homopolymers[20].

In the oxidized state the phase transitions glassy–nematic (polymers **4b**–**6b**) and glassy–smectic A (polymers **8b**–**10b**) are shifted to higher temperatures. The transition to the isotropic phase is unchanged for polymers **5b** and **6b** (see *Table 2*).

In polymer **10b** (highest ferrocene content) the smectic A phase is suppressed and only a nematic phase is found. This could be confirmed by X-ray measurements of fibres of polymers **10a** and **10b**.

In all cases, the oxidized polymers decomposed a few degrees above the first transition temperature, so that the phase transition from the nematic to the isotropic phase could not be observed for the polymers **8b** and **9b**.

To clarify the reason for the decomposition, thermogravimetric measurements were carried out on copolymer **4** in the reduced and oxidized states and on a mixture of homopolymer **3a** and copper(II) perchlorate hexahydrate. A comparison of these results shows an analogous thermal behaviour of the oxidized polymer and the mixture. This result leads to the conclusion that decomposition of the oxidized copolymers is caused by the incorporated perchlorate counterion. The incorporation of a non-oxidative counterion would therefore be desirable.

Small-angle X-ray scattering (SAXS) measurements

During X-ray measurements to identify the LC phase structure of the polymers, it turned out that the reduced polymers show the same X-ray patterns as the liquid-crystalline homopolymers. But for the oxidized polymers an additional diffuse scattering at small scattering angles was found.

To get more information on the intensity distribution of the diffuse scattering, we investigated the small-angle scattering behaviour of polymers **6a** (reduced form) and **6b** (oxidized form) (see *Figure 3*) with a Kratky camera.

The strong excess scattering of the oxidized polymer **6b** shows that areas of different electron densities are present. Analysis of the data leads to a linear dependence between the normalized and desmeared X-ray intensity $I(q)$ and q^{-4} in the region of 0.15 to 0.36 nm^{-1}. This intensity profile is typical for systems of randomly dispersed particles in a medium of different electron density[21]. Such scattering behaviour is similar to the behaviour of block copolymers with ionic head-groups[22]. For these microphase-separated systems, dispersed spherical domains with domain sizes up to 20 μm were detected by optical microscopy.

We calculated the size of the dispersed domains by Guinier analysis using the equation:

$$\ln I(q) = -(q^2 R_G/3) + A$$

where I is the normalized X-ray intensity, q is the scattering vector ($q = 4\pi \sin \vartheta/\lambda$), R_G is the radius of gyration and A is a constant. From the slope of the graph of $\ln I(q)$ *versus* q^2 in the region of small q values (see *Figure 4*), a mean radius of gyration of 15.4 nm was calculated. The existence of excess scattering with the reported intensity distribution leads to the conclusion that large ionic aggregates (clusters) are formed in the liquid-crystalline matrix of the oxidized copolymers with high ferrocene content. Since nothing is known about the geometry of these clusters and their internal structure (amount of uncharged polymer within the cluster), it is not possible to determine the number of ferrocenium units per cluster.

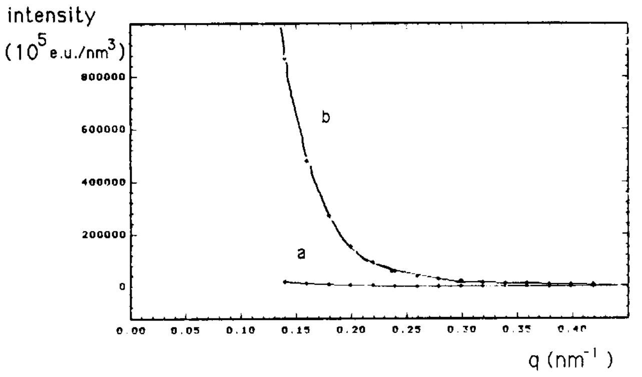

Figure 3 SAXS measurement of side-group polymer **6a** (reduced form) (a) and **6b** (oxidized form) (b). Data points were taken between q values of 0.14 and 2.8. Only the values at small scattering angles are presented

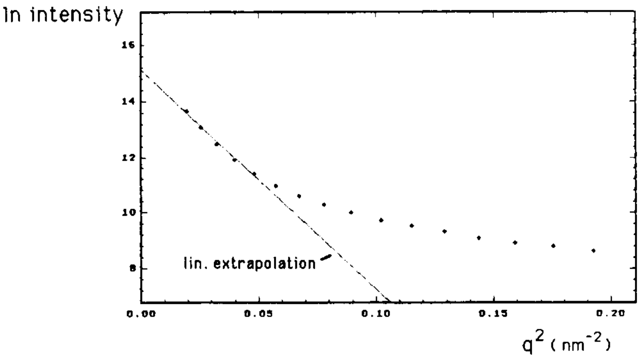

Figure 4 Guinier plots of SAXS data of polymer **6b**. Only the data points at very low scattering angles (see *Figure 3*) were used for the evaluation

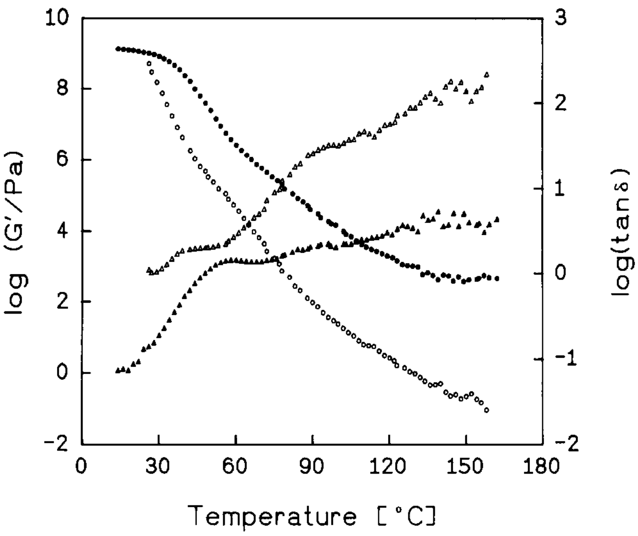

Figure 5 Dynamic mechanical behaviour of polymer **5a** (reduced form) ((○) G', (△) tan δ) and polymer **5b** (oxidized form) ((●) G', (▲) tan δ); frequency, 10 Hz; temperature dependence of tan $\delta = G''/G'$, with G'' = loss modulus and G' = storage modulus

Dynamic mechanical measurements

In order to test whether cluster formation is effective for dynamic crosslinking of the LC ionomers, the temperature dependences of dynamic mechanical properties were measured for both the reduced and the oxidized polymers. The results representing the elastic component G' of the complex shear modulus and the loss factor tan δ (describing the ratio of dissipative and elastic components) are shown in *Figure 5*.

For the reduced polymer a continuous increase of tan δ with increasing temperature above the glass transition is observed. This means that the ratio of dissipated to elastically stored energy is increasing, which is typical for the flow behaviour of a non-crosslinked polymer. However, the corresponding oxidized polymer shows a much smaller increase of tan δ and the values are two magnitudes smaller at high temperatures (150°C). In this case the ratio of loss modulus G'' and storage modulus G' is nearly independent of temperature. Such behaviour is typical for slightly crosslinked polymers[23] (elastomers) and proves indirectly the formation of ionic aggregates (X-ray) of ferrocenium and perchlorate counterions. So the formed clusters act as temporary ionic crosslink points in the LC matrix of oxidized polymers however, since the number of ferrocenium units per cluster and the number of clusters cannot be calculated, mechanical and X-ray data cannot be related rigorously.

EXPERIMENTAL

Synthesis of monomers 1a and 1b

The mesogenic acrylates **1a** and **1b** were synthesized according to the procedures described in ref. 19.

Synthesis of monomer 2

The first three steps in the synthesis of the ferrocene-containing monomer reported in refs. 24–27 have been modified to get more reproducible yields.

Ferrocenylaceto thiomorpholide

First, 84 g acetylferrocene (0.37 mol, recrystallized from n-hexane) was dissolved in 200 ml of freshly distilled morpholine (2.3 mol). The solution was stirred at a temperature of 100°C in an argon atmosphere. After a reaction time of 4 h, 42 g sulphur (1.31 mol, recrystallized from toluene) was added and the reaction mixture was stirred for 14 h at 100°C. After cooling and repeated extraction of the black mass with petroleum ether (b.p. 40–60°C) the solvent was removed and the crude product was purified by column chromatography with petroleum ether/ethyl acetate (volume ratio 5/1) on silica gel. The solvent was removed and the obtained yellow oil was recrystallized twice from n-hexane. Yield, 51.1 g ferrocenylaceto thiomorpholide (43.0%); m.p. 121°C.

Ferrocenylacetic acid

A mixture of 50 g ferrocenylaceto thiomorpholide (0.156 mol), 40 g potassium hydroxide (0.71 mol), 400 ml water and 200 ml ethanol was heated for 8 h under reflux. After cooling, concentrated hydrochloric acid was added dropwise to the stirred mixture (pH value of 5.5 to 6.5). The precipitated product was filtered and purified by chromatography with petroleum ether/ethyl acetate (volume ratio 1/1) on silica gel. Yield, 30.0 g ferrocenylacetic acid (79.0%); sintered at 130–140°C.

2-Ferrocenylethanol

A solution of 1 g of ferrocenylacetic acid (4.1 mmol) in dry diethyl ether was added dropwise to a stirred suspension of 0.2 g lithium aluminium hydride (5.3 mmol) in 50 ml dry diethyl ether at room temperature. Thereafter the reaction mixture was refluxed for 1 h. Then 20 ml water and 20 ml hydrochloric acid (20%) was added to the stirred and cooled mixture. The organic layer was separated, washed three times with 5% aqueous sodium hydroxide, washed with water and was then dried over sodium sulphate. After removal of the diethyl ether a yellow oil was obtained, which was recrystallized from petroleum ether (b.p. 40–60°C). Yield, 0.69 g 2-ferrocenylethanol (73%); m.p. 38°C.

2-Ferrocenylethyl acrylate was synthesized according to the procedure reported in ref. 27.

*Synthesis of the homo- and copolymers **3–10***

*Homo- and copolymers **3a–10a**.* One gram of the desired mixture of monomer **1a** or **1b**, monomer **2** and 2 mol% azobisisobutyronitrile (AIBN) was dissolved in 10 ml toluene. Dry nitrogen was bubbled through the solution for 30 min, which was thereafter polymerized for 12 h at 60°C. If some of the copolymers precipitated, they were dissolved by addition of 10 ml of chloroform. Then the polymers were precipitated twice into cold methanol (0°C) and once into cold diethyl ether (0°C). The polymers were dried at 40°C under reduced pressure. Yields, 50–82%.

*Oxidized copolymers **4b–6b** and **8b–10b**.* As an example of the general procedure, the oxidation of polymer **5a** is described. First, 0.216 g of polymer **5a** (4.5×10^{-5} mol ferrocene equivalents) are dissolved in 10 ml methylene chloride and poured into a mixture of 22 mg copper(II) perchlorate hexahydrate (6×10^{-5} mol), 0.1 g conc. $HClO_4$ and 0.1 g water in methylene chloride/acetonitrile (volume ratio 1/1). The polymer solution changes colour from yellow to deep blue. Most of the solvent was removed rapidly and 2 ml acetone was added. Then the polymer was reprecipitated twice into cold diethyl ether (0°C) and dried at 40°C under reduced pressure. Yield, 80%.

Potentiometric titration of the ferrocene-containing polymers was performed with a titration stand E 436 D and a Potentiograph E 436 (Metrohm, Herisau). Potentials were measured on a platinum electrode against the saturated Ag/AgCl reference electrode. Some 0.4–1.3 mg of polymers ($1–2 \times 10^{-7}$ mol ferrocene units) were dissolved in a mixture of 5 ml of methylene chloride and 5 ml acetonitrile and titrated with a solution of 23.1 mg copper(II) perchlorate hexahydrate in 249 ml methylene chloride, 249 ml acetonitrile, 1 ml H_2O and 1 ml $HClO_4$ (72%). The activity of titrator was calibrated by titration of pure acetylferrocene.

Cyclic voltammetric measurements were carried out with an Atari 1040 STF personal computer as control unit and a parallel input–output interface[28]. The measurements were performed in a typical three-electrode arrangement with platinum working (disc of a diameter of 1 mm) and counter-electrodes and a silver reference electrode. Before measuring, the solvent was purified by column chromatography with neutral Al_2O_3 at 0°C. To guarantee the conductivity of the solvent (CH_2Cl_2), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was added. The polymers were dissolved in 40 ml of CH_2Cl_2 (0.1 mol/l $TBAPF_6$) and a potential sweep was generated. The resulting current was amplified with a current amplifier type 427 (Keithley), digitized and the data were stored by the personal computer.

The liquid-crystalline behaviour and the transition temperatures of the polymers were investigated by differential scanning calorimetry (d.s.c.) and polarization microscopy. A Leitz model Ortholux 2 Pol-Bk microscope with a Mettler model FP 52 heating stage was used. The d.s.c. measurements were performed with Perkin–Elmer instrument DSC-2C.

The small-angle X-ray scattering behaviour was investigated with a Kratky camera with Ni-filtered K_α radiation. The normalized X-ray intensity was calculated from the raw X-ray data considering the background of radiation, the intensity of the X-ray beam, the geometry of the samples and the different absorption of polymers in the reduced and oxidized states. Samples were formed into a cuboid (1 mm × 2 mm × 10 mm) under pressure at 60°C and measurements were carried out at room temperature.

The mechanical properties were measured with a Rheometrics Mechanical Spectrometer model 800. The shear storage modulus G', loss modulus G'' and loss tangent ($\tan \delta$) of the polymers were obtained as a function of temperature at a constant frequency of 10 Hz and a heating rate of 1 K min^{-1}. The specimens in the form of small discs, 6 mm in diameter and 1 mm in height, were measured between parallel plates.

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