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Highly Ordered Structures of Amphiphilic Polythiophenes in Aqueous Media

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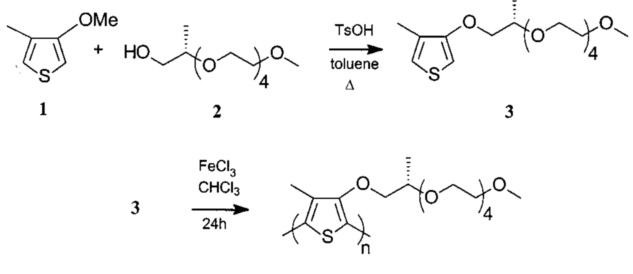
ABSTRACT: Aqueous dispersions of a regioregular polythiophene, bearing enantiomerically pure oligo(ethylene oxide) side chains, are obtained by injecting small volumes of a THF solution of the polymer into water. The interplay of hydrophilic and hydrophobic interactions accounts for the unprecedented formation of hexagonal platelets, as well as other aggregates. Electron microscopy and selected area electron diffraction revealed that the platelets show diffraction patterns typical for single crystals. The relative amount of these highly ordered structures reaches 30% of all aggregates, in case of dispersions containing 10% (v/v) of THF in water. The effect of the organic solvent in controlling the formation of highly ordered assemblies is also investigated by means of UV−vis spectroscopy, where the occurrence of main chain organization gives rise to a distinct red-shifted absorption band. In the fluorescence spectra, the same situation accounts for quenching of the emission located at higher wavelengths with respect to the one in pure THF. The chiral information in the side chain is expressed at the supramolecular level in the highly ordered states, as revealed by CD spectroscopy. Notably, the intensity of the bisignated Cotton effect reaches its maximum at 10% (v/v) of THF, which coincides with the highest amount of single crystals in TEM. Thermochromic experiments show high thermal stability of the chiral assemblies in water.

Introduction

Control over the molecular conformation and supramolecular organization of π-conjugated polymers provides the best opportunities to fine-tune their electrical and optical properties; an important issue in their applications as field effect transistors,[1a] electroluminescent devices,[1b] solar cells,[1c] chemical sensors,[1d] or biosensors.[1e] Aggregation in apolar organic solvents has been extensively studied for a variety of conjugated polymers.[2] Assemblies in solution, exhibiting properties that are similar to those observed in the solid state, can be formed in poor solvents or by cooling solutions in good solvents. These solution studies were used to obtain detailed insight into the mesoscopic order of the material as used in devices. The growing interest in the detection of substrates in biological media requires similar studies of water-soluble π-conjugated oligomers and polymers.

The self-organization of π-conjugated polymers in water has only been accomplished through the introduction of ionic substituents.[3] In all of these cases, the aggregation phenomena are exclusively controlled by side chain electrostatic interactions and not comparable with those found in oligomeric systems of defined molecular weight.[4] Although films of conducting polymers bearing crown ether or oligo(ethylene glycol) side chains have been extensively studied, in particular for sensor applications,[5] thus far no reports have appeared on the self-assembling properties of these polymers in water. Here we report on the generation of highly ordered structures through the self-assembly of poly{3-[(2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyloxy]-4-methylthiophene} (**PMPT**) in aqueous dispersion, analogous to those obtained by the aggregation of block copolymers.[6] The presence of a chiral perturbation in the substituent is known to induce preferred handedness in the supramolecular assembly provided regularity is present in the backbone.[7] Hence, CD spectroscopy can be used in this work as a powerful tool to investigate the organization of this new amphiphilic π-conjugated polymer.

Scheme 1



PMPT

Results and Discussion

Synthesis of PMPT. Thiophene derivative **3** was conveniently obtained (yield 69%) through the transetherification (Scheme 1) of 3-methoxy-4-methylthiophene (**1**)[8] with (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecanol (**2**)[9] using *p*-toluenesulfonic acid as the catalyst. Chemical polymerization of **3** using iron trichloride as the oxidizing agent yielded the polymer **PMPT** with a number average molecular weight of 41 000 and a polydispersity index (PDI) of 4.4 (determined by SEC). The head-to-tail coupling of the monomer resulted in a highly regioregular structure, as was evidenced by the presence of only four sharp peaks in the aromatic region of the ^{13}C NMR spectrum and the presence of a single peak at 2.3 ppm in the ^{1}H NMR spectrum, characteristic for the methyl group at the 4-position. The molecular weight, PDI, and high regioregularity (above 95%) are in agreement with what has been reported previously by Leclerc and co-workers.[10]

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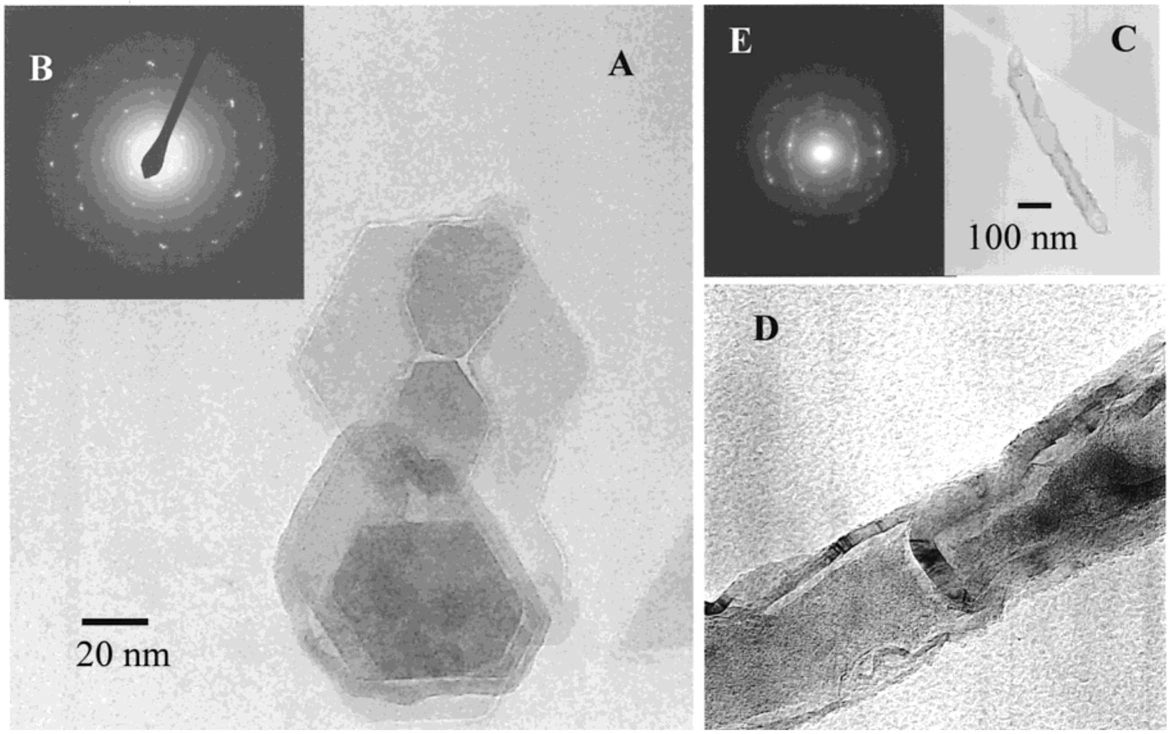

Figure 1. TEM images of hexagonal crystals (A) and elongated polycrystalline structures (C; magnification in D) obtained from a dispersion of **PMPT** in water containing 10% (v/v) THF. The corresponding selected area electron diffraction patterns are shown in parts B and E.

Aggregate Formation in Water. The polymer **PMPT** was soluble in aprotic solvents, such as chloroform, THF, and dichloromethane, and, upon heating, also in polar protic solvents such as methanol and ethanol, but was insoluble in water. A stable aqueous dispersion could be obtained, however, by injecting microliter amounts of a THF solution of the polymer **PMPT** (1 mg/mL) into an excess of water. Transmission electron microscopy (TEM) carried out on samples obtained from aqueous dispersions containing 1, 10, and 17% of THF (v/v), revealed the formation of platelets with an average dimension of 100 nm (Figure 1A), as well as elongated structures (Figure 1C,D) with lengths exceeding 500 nm. The sample containing 10% THF (v/v) was the richest in hexagonal platelets (approximately 30% of all the structures).

Selected area electron diffraction of the platelets showed diffraction patterns (along the [001] direction) typical for single crystals (Figure 1B), whereas all other aggregates were polycrystalline in nature (Figure 1E). The relative intensities of the reflections in the diffraction pattern suggest that several single crystal platelets were stacked on top of each other in a nonregular fashion. Analysis of the diffraction patterns indicated a hexagonal lattice; both the presence of single crystals and this shape feature were not previously described among examples of multiple crystal structures obtained from 3-substituted polythiophenes.[11] However, the mode of packing of the polymer chains cannot be elucidated from the electron diffraction data alone, and further investigation is therefore required. The formation of single crystals from such polydisperse macromolecules is highly unexpected; however, it should be noted that well-defined self-assembled structures have already been reported for copolymers with a PDI as high as 1.6.[6g]

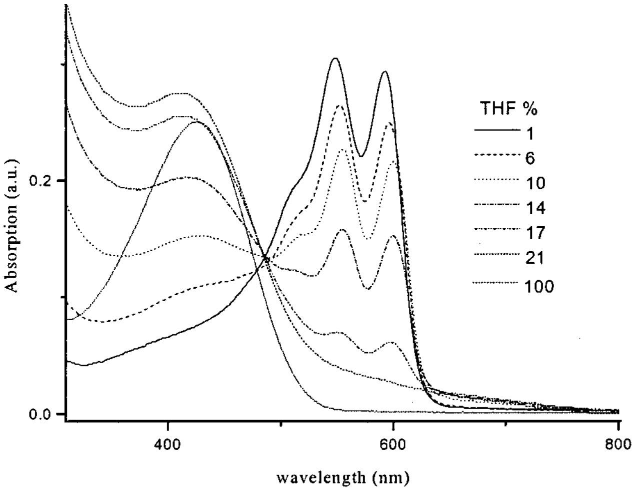

Figure 2. UV−vis spectra of **PMPT** in THF/water mixtures. UV spectra at different THF content are shown (percentages are shown in the inset). Polymer concentration is 0.01 mg/mL.

Solvatochromism. The aggregation behavior of **PMPT** in different THF−water mixtures was studied using UV−vis spectroscopy, monitoring the changes in the $\pi \rightarrow \pi^*$ transitions arising from conformational alterations in the polymer backbone. At high THF content, the spectrum strongly resembled the one in pure THF having a broad absorption band at $\lambda_{max} = 415$ nm (Figure 2). This band was tentatively attributed to a coil conformation. The presence of scattering for these water−THF mixtures suggests that aggregates are present, possibly due to the coagulation of the oligo(ethylene oxide) side chains.

At lower amounts of the organic solvent, another band at higher wavelengths appears, giving rise to a clear isosbestic point. The second band has a fine structure, with λ_{max} at 550 and 590 nm that was assigned to the vibronic progression of the $\pi \rightarrow \pi^*$ transition related to the C=C bond vibration[12] and was identical to the one

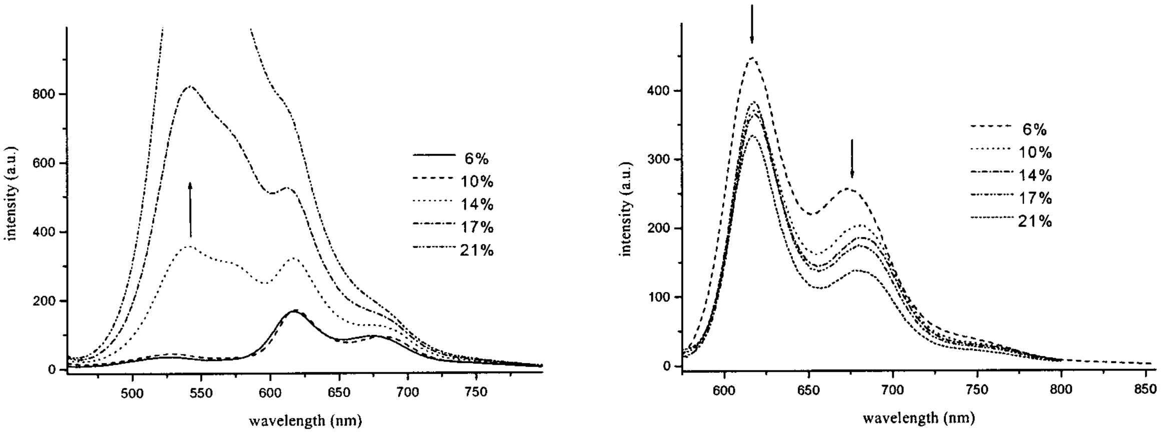

Figure 3. Fluorescence spectra of **PMPT** in THF/water mixtures. Spectra at different THF contents are shown (volume percentages are shown in the inset) for $\lambda_{ex} = 430$ nm (left) and $\lambda_{ex} = 550$ nm (right).

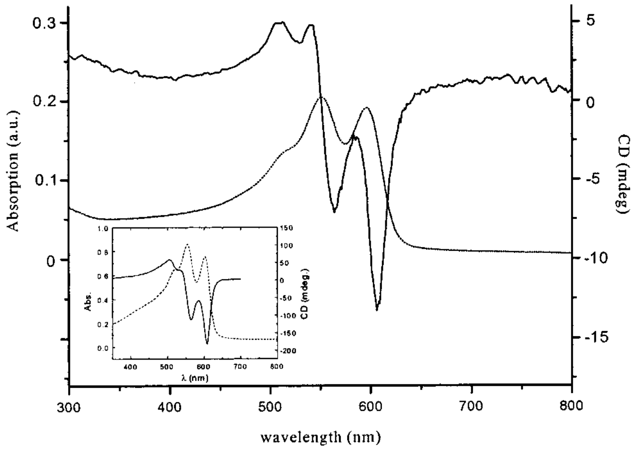

Figure 4. CD (solid line) and UV (dotted line) spectra of a dispersion of **PMPT** in water obtained from dialysis of a sample containing 1% THF. Inset: CD (solid line) and UV (dotted line) spectra of the polymer film.

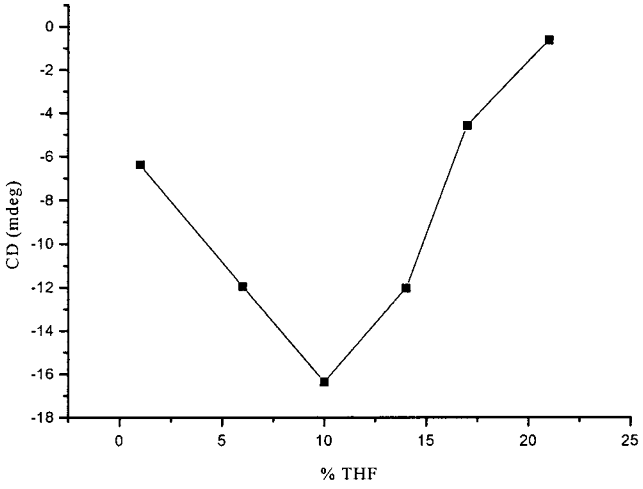

Figure 5. CD intensity at 600 nm as a function of the percentage of THF (v/v) in a aqueous dispersion of **PMPT**.

displayed by solid films obtained from the same aqueous dispersions. We propose that the red shift in the absorption is due to the formation of assemblies displaying main chain aggregation. This process is expected to be associated with conformational modifications of the backbone leading to a higher coplanarity and, therefore, to an increase in conjugation length.[13] In addition to the evident spectral changes, a small bathochromic shift was displayed by the low energy absorption upon increasing THF content; this effect reached its maximum at approximately 10% (v/v) of organic solvent and then leveled off.

Solvatochromism in the fluorescence emission spectrum (Figure 3) closely matched the phenomena observed in the UV–vis spectra, supporting the existence of two different forms of organization. The intensity of the two fluorescence bands at 617 and 680 nm ($\lambda_{ex} = 550$ nm) decreased upon addition of THF to the dispersion, concomitant with the disappearance of the structured absorption centered around $\lambda_{max} = 550$ nm. Notably, this emission was considerably less intense than the one appearing at $\lambda_{max} = 540$ nm ($\lambda_{ex} = 430$ nm), which resembled the strong emission in pure THF. This quenching was tentatively attributed to the aggregation of the conjugated main chains.

The introduction of chirality in the side chains allowed us to use CD spectroscopy to probe for conformational processes occurring in the formation of supramolecular structures.[4] **PMPT** dispersions at low THF content displayed a vibronically structured bisignated Cotton effect in the CD spectrum, attributed to an exciton coupling between the thiophene chromophores (Figure 4). Also in this case the Cotton effect is almost completely identical to the one typical for the solid state, characterized by a g value of -7.8×10^{-3} at 607 nm (Figure 4, inset). The intensity of the CD effect was found to be dependent on the concentration of the organic solvent, reaching a maximum at 10% THF (v/v) and then disappearing at approximately 20% (Figure 5). The disappearance of the Cotton effect suggests that although at high THF content aggregates may still be present, ordered assemblies of polythiophene backbones no longer exist under these conditions. Remarkably, the maximum of the CD intensity was obtained for the sample that, according to TEM, was characterized by the highest amount of highly ordered structures, namely the **PMPT** single crystals.

Thermochromism. The thermochromic behavior of dialyzed dispersions obtained from samples, which initially contained 10% and 1% of THF (v/v), was also investigated using UV–vis and CD spectroscopy. After dialysis, the UV–vis spectra of the two samples predominantly showed the vibronically structured absorptions centered around $\lambda_{max} = 550$ nm, indicating that in both cases the more ordered structures prevail in pure water. Upon increasing the temperature from 20 to 90 °C the appearance of a band at 413 nm was

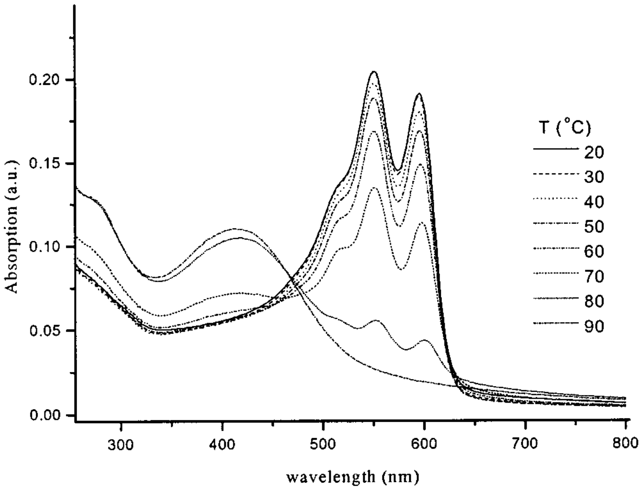

Figure 6. UV spectra as a function of temperature for a dispersion obtained from dialysis of a sample containing 1% (v/v) THF.

observed (Figure 6), indicating a deaggregation process in analogy with the solvatochromism experiment described above.

Variable-temperature CD spectra revealed a monotonic decrease in CD intensity with increasing temperature (Figure 7a). Upon cooling, the Cotton effect was recovered with some hysteresis (Figure 8), indicative of a slow aggregation process. When the anisotropy factor *g* was monitored at 600 nm (Figure 7a, inset), a maximum was registered at 80 °C. This behavior is attributed to a transition from an ensemble of aggregates characterized by different degrees of order to a single, highly ordered microcrystalline form, which is also the thermally most stable structure.

PMPT dissolved in methanol by heating the sample up to 40−50 °C. After cooling to room temperature, it displayed a bisignated CD signal with a *g* value of -3.3×10^{-3} at 607 nm. As the temperature of this solution was increased, a sharp transition was observed at 35 °C, as was indicated by the disappearance of the CD signal (Figure 9). Remarkable is the difference in transition temperature between the methanolic system and the aqueous dispersions reported above (Figure 7). The transition temperature of the former is situated approximately 40 °C lower than that of the latter, suggesting an increased stability of the aggregates in the presence of water, due to hydrophobic forces between the polymer main chains.

Conclusions

Water-based dispersions of a new regioregular polythiophene with chiral oligo(ethylene oxide) side chains were prepared through THF injection. The resulting dispersions contained different types of aggregates, most notably thin platelike single crystals, which are unprecedented in the literature. The spectroscopic and microscopic investigations showed that the aggregation process depends on the amount of THF used. At high THF content, the polymer backbones are in a coil conformation, while at lower THF contents, they are aggregated and have extended conformations, leading to longer conjugation lengths. The polythiophene chains in the crystalline platelets have a high degree of organization as was deduced from selected area electron diffraction patterns and a maximum in the CD effect. In methanol, aggregates were obtained which had spectroscopic properties similar to those in aqueous dispersion containing low amounts of THF. The former, however, showed a much lower stability upon heating compared to the latter, suggesting a key role for water in organizing the polymer by solvophobic interactions. All dispersions obtained proved to be stable, also after removal of THF via dialysis. This allows the generation of water-born electroactive coatings, e.g., for biosensor applications; investigations along those lines are in progress.

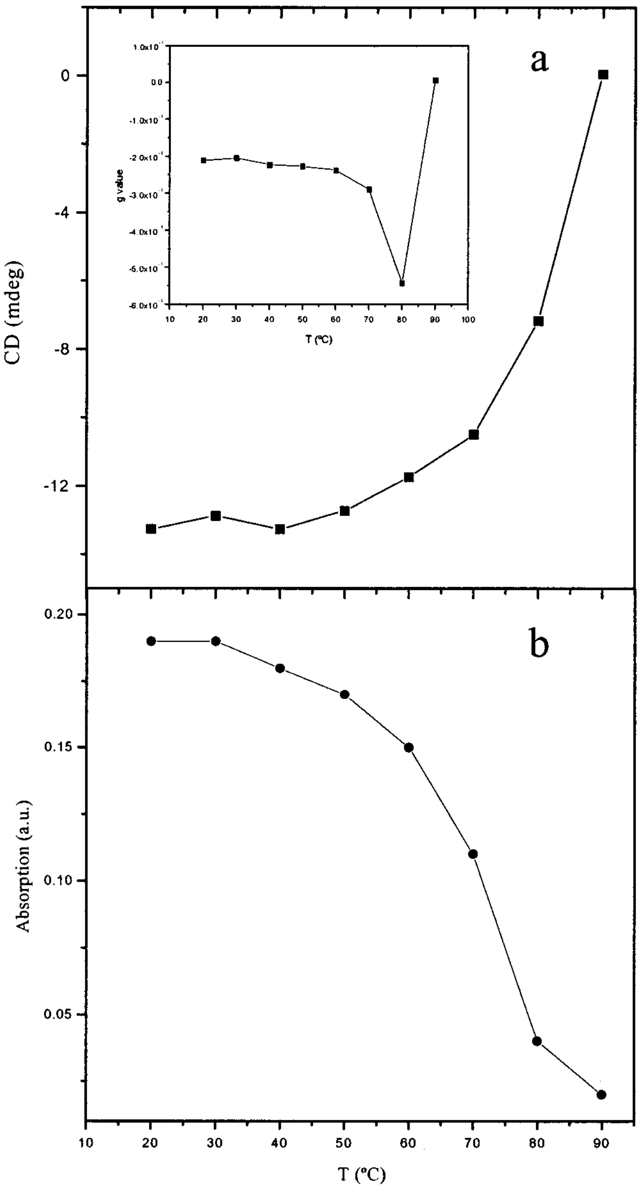

Figure 7. CD intensity (a) and UV absorbance (b) at 600 nm as a function of temperature for a dispersion obtained from dialysis of a sample containing 1% (v/v) THF. The inset in graph a shows the corresponding *g* values.

Experimental Section

General Methods. GPC measurements were performed on a Waters 590 GPC, using THF as solvent and a PL Gel column, calibrated with polystyrene standards. The ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.1 MHz. ^{13}C NMR spectra were measured on a Bruker AM-400 spectrometer at 100.6 MHz. Chemical shifts are reported in ppm downfield from TMS. Chemical shifts in D_2O are reported using as reference the signal at 4.78 ppm of HOD. The IR spectra were recorded as films on KBr disks, on a Perkin-Elmer 1600 series FT-IR spectrometer. The UV−vis spectra

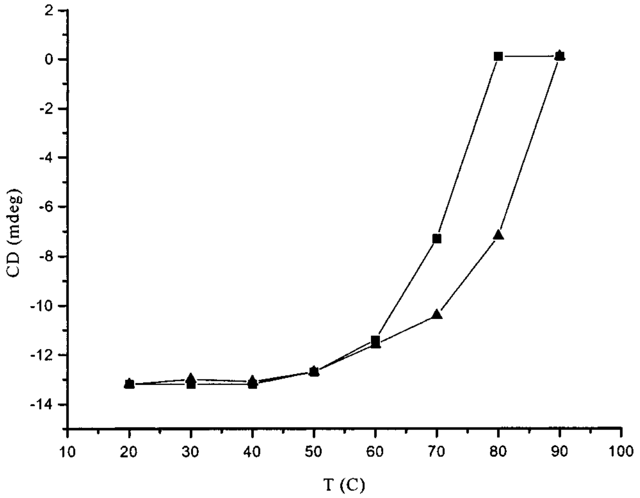

Figure 8. Hysteresis in temperature dependence of CD intensity. The heating run (▲) described in Figure 7a is reported together with the cooling run (■) for the same sample.

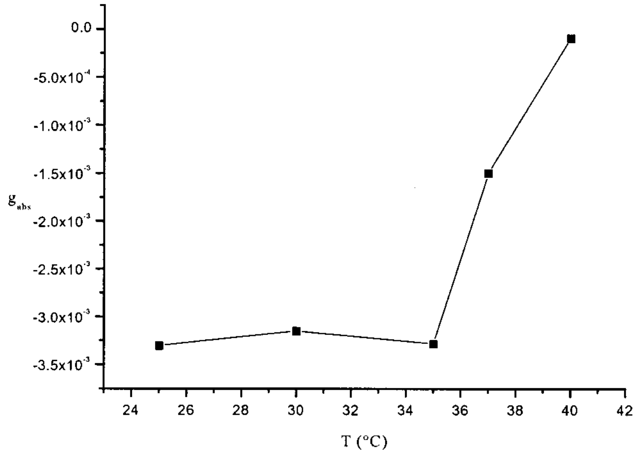

Figure 9. Temperature dependence of the *g* value for a methanol solution of **PMPT**.

were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. The fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer LS 50 B, solutions with an optical density of approximately 0.1 were used. The CD spectra were recorded on a Jasco J600 spectrophotometer. For temperature-dependent (20−90 °C) solution measurements the spectrophotometers were provided with a thermostated sample holder controlled by a water-ethylene glycol bath. Spectra are recorded after a period of 1 h in order to let the system stabilize to the desired temperature. A typical procedure for the preparation of the aqueous dispersions is the following: 20 μL of a THF solution of polymer **PMPT** (1 mg/mL) were injected in 2 mL of water. When required, dialysis of these samples was carried out against pure water using dialysis bags with an exclusion limit between 12 000 and 14 000 Da. For measurements on solid samples a few drops of the aqueous dispersion were spin-coated on a glass plate. Methanol solutions of **PMPT** were obtained by dissolution of the polymer via heating and allowing it to cool for 3 h. Transmission electron microscopy was carried out using a JEOL JEM (2000-FX) operating at 120 kV; a droplet of solution was placed on a Cu-grid (200 mesh, C covered, for TEM), and allowed to dry for a few seconds, after which the droplet was removed. GC/MS measurements were performed on a Shimadzu GCMS-QP5000.

Materials. Toluene was freshly distilled from sodium. 3-Methoxy-4-methylthiophene (**1**)[8] was prepared as previously reported. (2*S*)-2-Methyl-3,6,9,12,15-pentaoxahexadecanol (**2**)[9] was derived from (*L*)-ethyl lactate. All other solvents and reagents were commercial products and were used as received. Bio-Beads S-XI Beads were obtained from BioRad Laboratories.

3-[(2S)-2-Methyl-3,6,9,12,15-pentaoxahexadecyloxy]-4-methylthiophene (3). 3-Methoxy-4-methylthiophene (**1**) (2.00 g, 0.014 mol), *p*-toluenesulfonic acid (0.2 g, 1.2 mmol), (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecanol **2** (7.5 g, 0.047 mol), and toluene (20 mL) were stirred under a flow of nitrogen for 3 days at 110 °C. The reaction mixture was allowed to cool to room temperature and diluted with ether (50 mL). The organic layer was washed with water (50 mL), and the water phase was washed with ether (50 mL, twice) and discarded. The collected organic phases were dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by means of column chromatography (SiO_2, ethyl acetate) to give **3** (69% yield) as colorless oil that darkens upon prolonged standing under light at room temperature. ^{1}H NMR ($CDCl_3$): δ 6.79 (1H, d, *J* 3.2, H-5), 6.12 (1H, d, *J* 3.2, H-2), 3.96 and 3.83 (2H, m, $CH_2(\alpha)$), 3.83 (1H, m, CH), 3.73 (2H, m, CH_2), 3.63 (12H, m, CH_2), 3.52 (4H, m, CH_2), 3.35 (3H, s, $CH_3(\theta)$), 2.08 (3H, s, CH_3−Th), 1.24 (3H, d, $CH_3(\kappa)$). ^{13}C NMR ($CDCl_3$): δ 156.0 (1C, C-3), 129.2 (1C, C-4), 120.0 (1C, C-5), 96.4 (1C, C-2), 74.6 (1C, $CH_2(\alpha)$), 74.4 (1C, $CH_2(\kappa)$), 73.7 (1C, CH_2), 72.0 (1C, CH_2), 71.0 (1C, CH_2), 70.7 (3C, CH_2), 70.7 (1C, CH_2), 70.6 (1C, CH_2), 69.1 (1C, CH_2), 59.1 (1C, $CH_3(\lambda)$), 17.5 (1C, $CH_3(\mu)$), 12.7 (1C, CH_3−Th). IR ν_{max}/cm^{-1}: 3106, 2870, 1564, 1450, 1375, 1204, 1126, 1250, 1029, 852, 753.

Poly{3-[(2S)-2-methyl-3,6,9,12,15-pentaoxahexadecyloxy]-4-methylthiophene} (PMPT). A suspension of dry $FeCl_3$ (0.247 g, 1.52 mmol) in $CHCl_3$ (5 mL) was stirred for about 30 min at room temperature under argon. After this period $FeCl_3$ was only partially dissolved in chloroform giving a dark solution. To this suspension was added monomer **3** (0.200 g, 0.381 mmol) dissolved in $CHCl_3$ (5 mL) dropwise over a period of 5 min. Immediate formation of a black precipitate was observed. After 1 day of stirring under argon, the reaction was stopped by addition of NH_4OH_{aq} (10 mL). The aqueous layer was extracted with chloroform (2 × 50 mL) and discarded. The organic extracts were washed with water (25 mL) and separated. The organic solvent was removed by rotary evaporation, and the residue was purified by column chromatography (Bio-Beads, dichloromethane) to provide **PMPT** as a purple amorphous solid in 45% yield. ^{1}H NMR ($CDCl_3$): δ 3.86 and 3.78 (2H, broad, $CH_2(\alpha)$), 3.78 (1H, broad, CH), 3.70 (2H, broad, CH_2), 3.64 (12H, broad, CH_2), 3.52 (4H, broad, CH_2), 3.35 (3H, s, $CH_3(\lambda)$), 2.28 (s, 3H, CH_3−Th), 1.24 (d, 3H, $CH_3(\mu)$). ^{13}C NMR ($CDCl_3$): δ 152.3 (1C, C-3), 130.0 (1C, C-4), 126.9 (1C, C-5), 118.8 (1C, C-2), 76.6 (1C, $CH_2(\alpha)$), 75.1 (1C, $CH_2(\kappa)$ or $CH(\beta)$), 72.2 (1C, $CH_2(\kappa)$ or $CH(\beta)$), 71.1 (3C, CH_2), 70.9 (1C, CH_2), 70.85 (1C, CH_2), 70.8 (1C, CH_2), 69.1 (1C, CH_2), 59.3 (1C, $CH_3(\lambda)$), 17.6 (1C, $CH_3(\mu)$), 13.3 (1C, CH_3−Th). IR ν_{max}/cm^{-1}: 2868, 1451, 1352, 1260, 1077, 1028, 948, 849, 803. GPC: M_n = 41 000, M_w = 182 000.

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