Polymer-Bound Chiroptical Molecular Switches; Photochemical Modification of the Chirality of Thin Films

MICHIEL L.C.M. OOSTERLING, ANNE MARIE SCHOEVAARS, HENK J. HAITJEMA, AND BEN L. FERINGA*
Department of Organic and Molecular Inorganic Chemistry, Groningen Centre for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 9 June 1996)

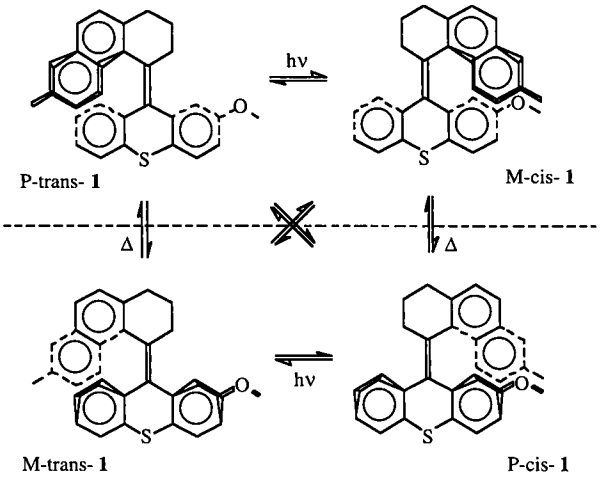
Abstract. Photobistable chiral polymers were obtained by covalent attachment of inherently dissymmetric 2-hydroxy-9-(7'methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene to methacrylate copolymers with appropriate spacers. Upon irradiation at 300 nm the optical activity of thin films of these polymers could be altered.

INTRODUCTION

Photochemical control of structures and functions of organic materials by means of molecular switches has seen rapid progress in recent years.[1] A large range of photochromic materials has been developed[2] and photomodulation of conductivity,[3] liquid crystalline phases,[4,5] gels,[6] and helicity of polypeptides,[7] as well as photoresponsive host–guest systems,[8] are illustrative for the effects that can be controlled. Major advances are furthermore seen in the photoregulation of structure and function of biomaterials.[9] The design of optical switches based on bistable organic molecules has particularly been stimulated by the challenge of molecular memory elements. Polymers are excellent supporting materials for practical application of photochromic compounds, as stability and easy processability are notable features. Azobenzenes, fulgides, and spiropyrans, either covalently attached to macromolecules or used as dopant in the polymeric matrix, have been employed to control, for instance, the macroscopic organization in liquid crystalline polymers,[10] the helicity of poly(benzyl)-l-glutamate,[11] and the permeability of membrane-mimetic systems.[12]

We have focused on the control of chirality by light[13] in bistable photoresponsive materials.

The chiroptical switches developed in our group[13–19] consist of chiral overcrowded ethylenes that adopt a helical shape. The photochemically bistable system **1** which is used in the present study is shown in Scheme 1.



Scheme 1. The four different chiral isomers of alkene **1**

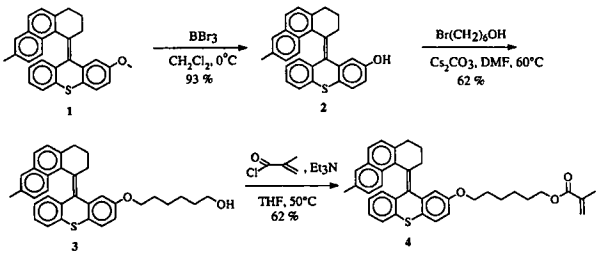
Compound 1 consists of four stereoisomers which are stable towards racemization (i.e., thermal P-trans ⇌ M-trans or M-cis ⇌ P-cis interconversions) under ambient conditions. Irradiating with UV light results in the rapid reversible interconversion of the two helical alkene diastereomers, P-trans ⇌ M-cis, with opposite helicity (pseudoenantiomers).[14] Irradiation of the switch in *n*-hexane at 300 nm leads to a cis:trans ratio of 64:36, whereas irradiating at 250 nm or 350 nm results in a

*Author to whom correspondence should be addressed.

cis:trans ratio of 68:32. The photostationary states can therefore be modulated by irradiating the chiroptical switch with UV light of different wavelengths. This change in chirality can be monitored by CD spectroscopy.

These materials are particularly interesting for possible use in optical data storage devices and the photomodulation of chiral surfaces and thin films. As a next step towards application we envisioned to incorporate the chiroptical switches into polymer films. This might be achieved by functional polymers in which the switching unit is attached to the polymer backbone through a spacer[20,21] or by mixing of the switches with polymers. The first method, which is reported here, is particularly attractive as aggregation of the switches is avoided. Major advantages of the overcrowded alkenes described here are that they can be switched back and forth using UV-Vis light, their photostationary states are stable without thermal isomerization, and nondestructive readout is possible by chiroptical methods. In azobenzene modified polymers, for instance, thermal instability of the cis form is often encountered.[22] In our current investigation we coupled 2-methoxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene (Scheme 1) to a polymer by a spacer. The methoxy group in **1**, which is easily converted to a phenol, enables us to attach switching unit **1** to a variety of spacers. Initially a methacrylate monomer **4** was synthesized with a photoactive chiral unit **1** attached to it via a spacer and subsequently copolymerization of **4** with methyl methacrylate (MMA) using a radical initiator was studied.

Random copolymerization is unlikely to occur this way however and furthermore it was shown that the overcrowded alkenes are not completely inert toward radical conditions of polymerization. The results of this approach, using monomer **4**, were not satisfactory.[23] Therefore it was decided to start with a copolymer with reactive side chains and attach the chiroptical switch at a later stage.



Scheme 2. Synthesis of MMA monomer with attached alkene **1**

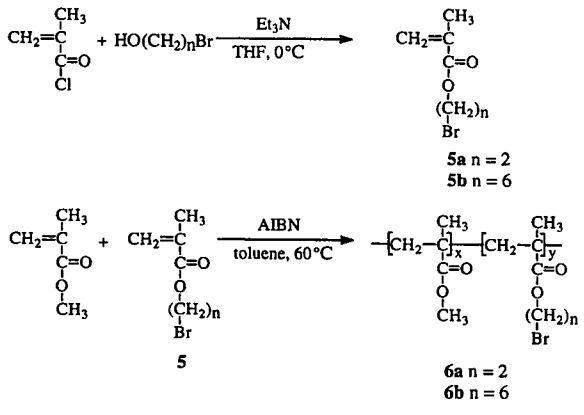
RESULTS AND DISCUSSION

Functionalized polymers with different spacers and degrees of loading with photoactive units were prepared according to the route shown in Schemes 3–6.

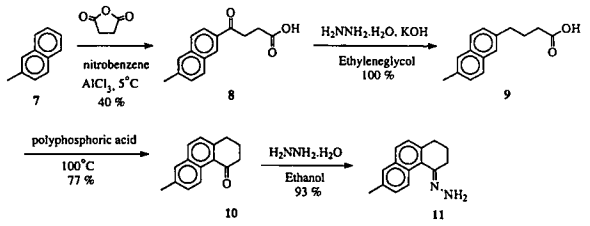
6-Bromohexyl methacrylate (BHMA) and 2-bromoethyl methacrylate (BEMA) were prepared from methacryloyl chloride and 6-bromohexanol or 2-bromoethanol in tetrahydrofuran (THF) at 0 °C, using triethylamine as HCl scavanger (Scheme 3). After the reaction, salts were filtered off and the monomer was isolated by distillation. Because of the low stability of the monomer it was immediately used for the polymerization reactions. Copolymerizations were performed in toluene with mixtures (9:1 ratios) of MMA and comonomers BEMA or BHMA using azobisisobutyronitrile (AIBN) as an initiatior at 60 °C (Scheme 3). Both polymers **6a** and **6b** contained around 8% of bromoalkyl side chains, after purification.

The photoactive chiral overcrowded alkene **1** was prepared in a multistep sequence which involved the preparation of the "upper" tetrahydrophenanthrene part and the "lower" thioxanthene part of the molecule, followed by coupling the two halves to form the sterically-demanding double bond. The synthesis of the upper part of 2-methoxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene **1** starts with a Friedel–Crafts acylation of 2-methylnaphthalene **7** with succinic anhydride in nitrobenzene at 5 °C, affording acid **8**, together with isomeric products due to acylation at other positions in the naphthalene ring.[24] (Scheme 4).

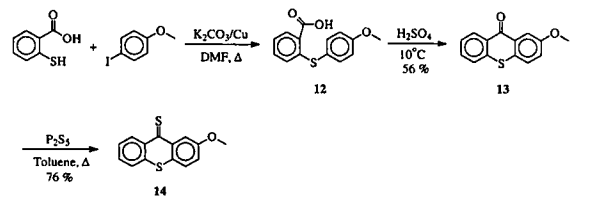
^{1}H NMR analysis showed that approximately 80% of the product consisted of **8**, which was separated from the other isomers via one crystallization from acetic acid according to the procedure of Haworth et al.[24] Wolff-



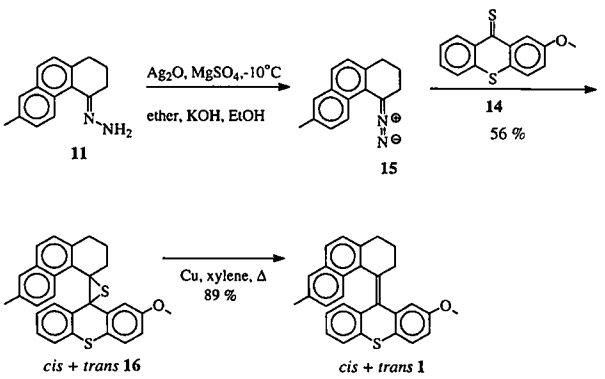
Scheme 3. Synthesis of 6-bromohexylmethacrylate and 2-bromoethyl methacrylate and copolymerization of MMA with BHMA (n = 6) or BEMA (n = 2)



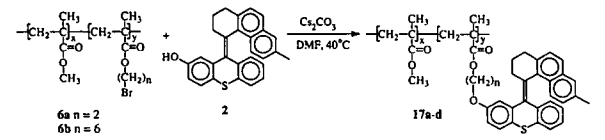
Scheme 4. Synthesis of the upper part



Scheme 5. Synthesis of the lower part



Scheme 6. Formation of the central double bond



Scheme 7. Coupling of the chiroptical switch to the functional polymer

Kishner reduction of the keto-acid followed by a ring closure in polyphosphoric acid furnished ketone **10** in 30% overall yield. This ketone was easily converted to hydrazone **11** by refluxing with an excess of hydrazine hydrate in ethanol.

The key step, which has been used frequently for the preparation of the basic skeleton of (substituted) 9H-thioxanthene-9-ones, involves a coupling reaction between an aromatic thiol group and an aryl halide (Scheme 5), although several approaches to achieve this transformation can be followed.[25]

The synthesis of 2-methoxy-9H-thioxanthene-9-one **13** is depicted in Scheme 5 and started from thiosalicylic acid and 4-iodoanisole, and was based on the method described by Vasiliu et al.[26] The dipotassium salt of thiosalicylic acid replaced the iodine atom from the 4-iodoanisole in the presence of copper powder in boiling dimethylformamide (DMF) to form an aryl-sulfur bond. The resulting benzoic acid **12** was converted to thioxanthone **13** by stirring in concentrated H_2SO_4. This was performed at 10 °C in order to suppress sulfonation, which can easily occur due to the presence of the electron-donating methoxy group. Transformation of the ketone into thioketone **14** was accomplished by refluxing with a twofold excess of P_2S_5 in toluene. The thioketone was isolated as a dark-green solid, which did not show any decomposition even after storage for several months at room temperature.

The strategy used successfully to prepare extremely hindered alkenes is based on the 1,3-dipolar cycloaddition between a diazo compound and a thioketone to form a thiadiazoline, followed by a twofold extrusion reaction as described by Barton[27] and Kellogg.[28] The hydrazone **11** was oxidized to the unstable dark-red diazo compound **15** with silver(I)oxide in ether at –10 °C in the presence of magnesium sulfate as desiccant. After filtration of the salts, the thioxanthone **14** was added to the cold solution of the diazo compound. Evolution of nitrogen was observed until the dark-red color of the solution had faded away. The intermediate thiadiazoline was not detected, indicating rapid decomposition to the more stable episulfide **16** (56%). The episulfides were obtained as cis-trans mixtures and used as such in the next step. Desulfurization of **16** with copper in boiling xylene afforded alkene **1** in 89% yield as a mixture of cis and trans isomers (50:50 ratio).

The cis and trans isomers of methoxy-substituted chiral alkene **1** are readily distinguished by their ^{1}H-NMR spectra. The methoxy singlet found in *trans*-**1** at 3.89 ppm, the normal position for this group, is shifted to 2.97 ppm in *cis*-**1** due to shielding by the upper naphthalene moiety. The mixture of alkenes *cis*-**1** and *trans*-**1** was separated into the four stereoisomers M-*cis*-**1**, P-*cis*-**1**, M-*trans*-**1**, and P-*trans*-**1** by HPLC using a (+)-poly(triphenylmethylmethacrylate)column with hexane/isopropanol 9:1 as eluent. The thermal racemization barrier for *cis*-**1** was determined by polarimetry. Upon heating of enantiomerically pure M-*cis*-**1** in *p*-xylene, racemization into P-*cis*-**1** was observed with $\Delta G^{\neq} = 26.4$ kcal mol^{-1} without the occurrence of thermal

cis–trans isomerization (e.g., M-*cis* ⇌ P-*trans*). To avoid any racemization in the final steps towards functionalized polymers **17a–d**, mild conditions had to be employed both in the deprotection step and the attachment to the copolymers **6a** and **6b** (Scheme 7). Following a number of procedures for cleaving the arene methoxy-ether it was found that treatment of **1** with BBr_3 in dichloromethane at 0 °C met this requirement to afford **2** in 93% yield. Coupling of both racemic and enantiomerically pure **2** to the functionalized PMMA copolymers was achieved using Cs_2CO_3 in DMF at 40 °C, followed by extensive purification to remove any uncoupled **2**. Initially these coupling reactions were performed at 40 °C. Repeated washing and reprecipitation of the polymers did not result in removal of the switching unit, and ^{1}H NMR spectra showed absorptions at 3.1 and 4.0 ppm originating from methylene groups of the aryl-alkyl ether moiety (cis–trans), indicating that the switches are covalently bound. The functionalized polymers prepared via this route are given in Table 1. The amount of chiroptical switch per polymer was determined by ^{1}H NMR comparing the integrations of the aryl-CH_3 absorptions at 2.35 ppm and the methoxy group of methylmethacrylate units at 3.60 ppm. The degree of functionalization in the copolymers could independently be determined by UV-Vis spectroscopy, using the known extinction coefficients of the switching unit at 309 and 332 nm. Infrared spectroscopy also clearly indicated the presence of arene units in the polymers. The new functionalized copolymers, bearing 1.5-4.7% chiroptical switches attached via two- and six-carbon spacers, showed excellent film-forming properties. High quality transparent films were obtained by solution casting from a 5% solution in chloroform or toluene of the polymer on quartz slides. As expected, none of the polymers coupled to a mixture of the four isomers of the switching units showed any CD signal. The CD spectrum of the uncoupled switching unit (P-trans) in dioxane, compared well to that of P-*trans*-**1** in hexane, whereas the CD spectrum of the polymer-bound switch in dioxane (polymer **17d**) still shows the typical absorption for P-trans in solution, but it shows a cutoff below 260 nm due to absorptions of the polymer backbone. Mixing polymers **6a** and **6b** with free M-*trans* isomer **1** resulted in the inverse CD-spectrum compared to the CD-spectrum of polymer **17d** with covalently bound P-*trans*-**1**, as expected. The intensity of the CD spectrum of the freshly prepared film of polymer **17d** was lower (approximately 10%) than estimated using the known amount of polymer and degree of functionalization.

This is probably due to the fact that some thermal racemization during the coupling of the switching unit to the polymer cannot be completely avoided. It is known that the used switches racemize rather fast at elevated temperatures, especially in solution.

Irradiation of P-*trans*-**1** with UV light at 300 nm results in a photostationary state composed of 64% M-*cis*-**1** and 36% P-*trans*-**1** in hexane, whereas irradiation with 350 nm light results in a photostationary state composed of 68% M-*cis*-**1** and 32% P-*trans*-**1**. Irradiation of thin films of polymer **17d** with covalently bound P-*trans*-**1** leads to a distinct change of CD signal. A typical example is seen in Fig. 1. The irradiation times needed to reach the photostationary states are, however, much longer for polymer films (90 min) than for solutions (30–60 s)[14] of the same chiroptical switch. It should be noted that the films remain optically active after irradiation; the decrease in CD absorptions is a result of formation of a photostationary state between M and P helices (approximately 65:35 ratio on the basis of the measured CD effect). The irradiation times may be shortened by switching above the glass transition temperature (T_g), while the photostationary states can be stabilized below T_g, but more stable switches are required to achieve this improvement. Subsequent switching by alternatively irradiating with 350 nm and 300 nm did not result in significant changes in the CD spectra. Due to the low loading in the chiral polymer **17d** and the

Table 1. Polymer chiroptical switches

Polymer	Basic polymer	Chiroptical switch **1**	Coupling T (°C)	Functionalization[a] (%)
17a	**6b**	mixture of isomers	60	1.5
17b	**6a**	mixture of isomers	40	4.0
17c	**6b**	mixture of isomers	40	4.3
17d	**6b**	P-trans	40	4.7

[a]Number of switches relative to the number of monomeric units, as determined by UV and ^{1}H NMR spectroscopy.

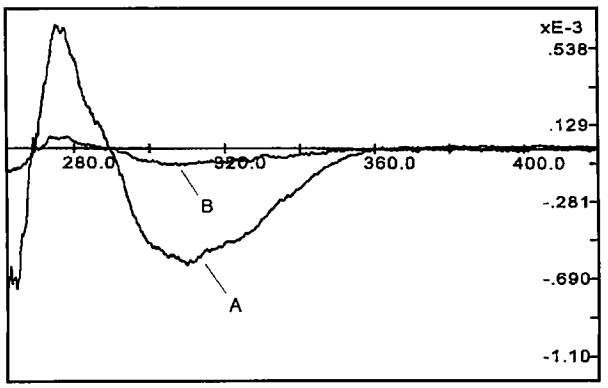


Fig. 1. CD spectra of a film of polymer **17d** before (A) and after (B) irradiation with 300 nm.

small changes in diastereomeric excess upon irradiation at different wavelengths with this particular helical alkene, accurate detection of the photomodulation of the film was not feasible. Furthermore, slight racemization of the switching unit due to the long periods that the film is exposed to the UV light can not be excluded at present.

By employing these new photoactive chiral polymers we have demonstrated that the chirality of the polymeric film can be modified by irradiation. Despite the shortcomings, such as long irradiation times, these materials have potential for optical data storage.

EXPERIMENTAL SECTION

Methods

All reactions and purifications were performed under a nitrogen or argon atmosphere unless otherwise stated. Toluene and tetrahydrofuran (THF) were distilled from sodium. Dimethylformamide (DMF) and dichloromethane were purified by a distillation from P_2O_5. Azobis-isobutyronitrile (AIBN) was recrystallised from ethanol and kept under a nitrogen atmosphere at –5 °C. Methyl methacrylate was purified by distillation from CaH_2 under a reduced nitrogen atmosphere. Irradiation experiments at 350 and 300 nm were performed using low-pressure 28 × 1-cm 8 W mercury lamps. ^{1}H NMR spectra were recorded on a Nicolet NT-200 or a Varian VRX300 spectrometer, UV spectra were recorded on a Philips PUL8700 single-beam spectrophotometer, differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC-7, circular dichroism (CD) spectra were recorded on a Jobin Yvon autodichrograph mark V, IR spectra were recorded on a Perkin Elmer 841 spectrophotometer. Resolution of the alkenes was achieved with HPLC using a water-cooled 4.6 × 250 mm (or 20 × 250 mm) (+)-poly(triphenylmethyl methacrylate) column (Daicel OT$^+$) with hexane/isopropanol (9/1) as an eluent.

*2-Bromoethyl Methacrylate (BEMA) (**5a**), 6-Bromohexyl Methacrylate (BHMA)(**5b**)*

5a and ***5b*** were prepared from methacryloyl chloride and 2-bromoethanol or 6-bromohexanol in THF at 0 °C, using triethylamine as a HCl scavenger.[29] After the reaction, salts were removed by filtration and the monomers were isolated by distillation. The product was characterized by ^{1}H NMR spectroscopy (–CH_2-Br:3.4 ppm). Because of the low stability of the monomer it was immediately used for the polymerization reactions.

*Copolymers **6a** and **6b***

The copolymers were prepared in toluene using AIBN as an initiator at 60 °C. MMA was mixed with the comonomer BEMA (**5a**) or BHMA (**5b**) in a 9:1 ratio.[30] The products were isolated by precipitation in pet-ether 40–60 and purified by reprecipitation from dichloromethane in pet-ether 40–60. The polymers were dried under vacuum at 40 °C for two days. P(MMA-co-BEMA) (polymer **6a**): ^{1}H NMR: –COO-CH_2-: 4.3 ppm, –CH_2-Br: 3.5 ppm. Anal. Calcd (from monomer feed): C, 55.9; H, 7.4; Br, 7.3. Found: C, 56.7; H, 7.5; Br, 6.0. DSC; T_g: 103 °C, GPC; M_n = 60000; M_w = 160000. P(MMA-co-BHMA) (polymer **6b**): ^{1}H NMR; –COO-CH_2-: 3.9 ppm, –CH_2-Br: 3.4 ppm, Anal. Calcd (from monomer feed): C, 57.4; H, 7.7; Br, 6.9. Found: C, 57.9; H, 7.8; Br, 5.8. DSC: T_g = 85 °C; GPC: M_n = 20000, M_w = 56000.

cis- *and* trans-2-*Hydroxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene (**2**)*

To a magnetically stirred solution of alkene **1** (400 mg, 0.97 mmol) in CH_2Cl_2 cooled at 0 °C was added BBr_3 (10 mL, 10 mmol, 1.0 M BBr_3 in CH_2Cl_2, 10 equiv), whereupon the color of the reaction mixture immediately turned red. After 30 min the temperature of the mixture was allowed to rise slowly. The conversion to **2** was complete in 2.5 h (TLC, SiO_2, CH_2Cl_2/hexane, 1/1, R_f **1** = 0.45, R_f **2** = 0.12). The dark brown mixture was poured into 100 mL of a well stirred mixture of H_2O and CH_2Cl_2, 1:1. The organic layer immediately turned purple; it was separated and the water layer was extracted with CH_2Cl_2 (100 mL). The combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and **2** was obtained as a foam (357 mg, 0.91 mmol, 93%). ^{1}H NMR (200 MHz) δ 1.86–2.27 (m, 2H), 2.34 (s, 3H), 2.94–3.17 (m, 2H), 3.28–3.43 (m, 1H), 5.90 (d, 1H), 6.29 (d, 1H), 6.37–6.51 (m, 1H), 6.66 (dd, 1H), 6.74–6.98 (m, 3H), 7.17–7.68 (m, 7H).

*Polymers **17a–d***

40 mg of alkene **2** was dissolved in DMF (10 mL) and the solution was heated to 40 °C. Then slowly 90 mg of Cs_2CO_3 was added, upon which the color of the solution turned from purple to brown. 0.11 g of the functionalized PMMA in 10 mL DMF was added and the mixture was allowed to react for 16 h. The reaction mixture was precipitated in water, resulting in a pink solid. The solid was reprecipitated from CH_2Cl_2 in pet-ether 40–60 and dried in vacuo. Yield: 50%; Anal. Calcd for P(MMA-BHMA) (assuming all alkyl bromide groups have reacted): C, 66.5; H, 7.5; O, 24.1; S, 1.8. Found: polymer **17a**: C, 59.9; H, 7.7; polymer **17c**: C, 62.8; H, 7.6; polymer **17d**: C, 63.2; H, 7.6. Anal. Calcd for P(MMA-BEMA) (assuming all alkyl bromide groups have reacted): C, 65.8; H, 7.3; O, 24.9; S, 1.9. Found: polymer **17b**; C, 61.7; H, 7.4. The amount of chiroptical switch per polymer was determined by ^{1}H NMR, comparing the intensity of the aryl-CH_3 group at 2.35 ppm to the methoxy group of MMA at 3.60 ppm. The number of switches could also be determined by UV spectroscopy, using the known extinction coefficients of the switch at 309 and 332 nm. These are different for the cis and trans isomers and can therefore also be used to determine the cis–trans ratio from the UV spectrum.[14] The infrared spectra of the polymer-coupled switches show new absorptions at 1600 cm^{-1} and 800–860 cm^{-1} due to the aromatic rings. In the ^{1}H NMR spectra absorptions at 3.1 ppm and 4.0 ppm (alkyl-aryl ether, CH_2 groups, cis and trans isomers) appear, indicating that the switches are covalently bound. DSC thermograms of the polymer-coupled switches did not show any additional transitions.

Preparation of the Thin Films

Polymer films were prepared by solution casting of a 5%

solution of the polymer in toluene on a quartz slide. The film of the polymer coupled to an optically-pure switch (polymer **17d**) was cast in the dark to avoid premature switching. The CD spectrum of the freshly prepared film was compared to that of polymer **17d** in solution (dioxane). The sample was irradiated with UV light (300 nm) and the CD spectrum was monitored as a function of irradiation time. After 90 min the CD spectrum did not change any more, indicating that a photostationary state had been reached. As a control, irradiations of solutions of **1** were performed (see also ref 14).

4-Oxo-4-[2-(6-methylnaphthyl)]butanoic acid (8)

This compound was prepared according to the method described by Haworth et al.[24] Starting from succinic anhydride (73.1 g, 0.73 mol) and 2-methylnaphthalene (**7**, 102.3 g, 0.72 mol), crystallization from acetic acid (700 mL) afforded pure **8** as a slightly brown solid (70.3 g, 0.29 mol, 40.3%): mp 158.3–161.0 °C (lit:[24] mp 162 °C); ^{1}H NMR (60 MHz) δ 2.50 (s, 3H), 2.80 (t, J = 7.0 Hz, 2H), 3.42 (t, J = 7.0 Hz, 2H), 7.17 (m, 5H), 8.40 (s, 1H); the acidic proton was not observed due to the presence of small amounts of acetic acid.

4-[2-(6-Methylnaphthyl)]butanoic acid (9)

Keto-acid **8** (60.0 g, 0.25 mol), KOH (42.0 g, 0.75 mol) and $NH_2NH_2.H_2O$ (33.0 g, 32 mL, 0.63 mol) were successively added to magnetically stirred diethylene glycol (300 mL). This dark brown mixture was heated at 120–140 °C for 4 h followed by slow distillation of the excess of $NH_2NH_2.H_2O$ and some formed H_2O until the inner temperature of the flask reached 200–210 °C and kept at this temperature for 4 h. After cooling to 20 °C, H_2O (150 mL) was added and this mixture was slowly poured into 20% aqueous HCl (800 mL) under stirring. The precipitated acid was isolated by filtration, washed with H_2O (500 mL), and dried in vacuo to afford acid **9** as a yellow solid (59.8 g, 0.26 mol, approximately 100%). This compound proved to be > 90% pure by ^{1}H NMR analysis and was used in the following step without further purification: mp 107.5–109.5 °C (lit:[24] 111–112 °C); ^{1}H NMR (60 MHz) δ 1.80–2.26 (m, 2H), 2.26–2.40 (m, 2H), 2.40 (s, 3H), 2.75 (t, J = 7.0 Hz, 2H), 7.05–7.90 (m), 8.45 (bs, 1H).

7-Methyl-1,2,3,4-tetrahydrophenanthrene-4-one (10)

To mechanically stirred polyphosphoric acid (700 mL) heated at 60 °C was added acid **5** (60.0 g, 0.26 mol) in 90 min. After the addition was complete, the temperature was raised to 100 °C and the mixture held at this temperature for 4 h. The mixture became homogeneous and the color changed to brown. After cooling to 50 °C the viscous liquid was poured into ice/water (1.5 L), to afford a dark brown solid, and stirred to decompose the polyphosphoric acid. The precipitated solid was isolated by extraction with Et_2O (4 × 250 mL). The combined Et_2O layers were washed with 5% aqueous HCl (1 × 200 mL), 10% aqueous NaOH (2 × 200 mL), saturated aqueous $NaHCO_3$ (1 × 200 mL), and brine (1 × 200 mL), dried (Na_2SO_4), and after evaporation of the solvent in vacuo, a brown oil, which slowly solidified, was obtained. This compound was purified by bulb to bulb distillation (150–170 °C, 0.1 mmHg) to yield **10** as a slightly yellow solid (42.5 g, 0.20 mol, 76.9%): mp 59.9–61.8 °C (lit:[24] 62–63 °C); ^{1}H NMR (300 MHz) δ 2.09–2.15 (m, 2H), 2.45 (s, 3H), 2.72 (dd, J = 7.3, 5.9 Hz, 2H), 3.01 (dd, J = 6.5, 5.9 Hz, 2H), 7.20 (dd, J = 8.8, 0.7 Hz, 1H), 7.42 (dd, J = 8.8, 1.5 Hz, 1H), 7.50 (s, 1H), 7.76 (d, J = 8.8 Hz, 1H), 9.31 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 21.09 (q), 22.86 (t), 31.25 (t), 40.86 (t), 126.20 (d), 126.69 (d), 126.81 (s), 127.09 (d), 129.22 (s), 130.69 (d), 132.79 (s), 133.37 (d), 135.08 (s), 145.58 (s), 200.19 (s, C=O); HRMS Calcd for $C_{15}H_{14}O$: 210.102, found 210.104.

7-Methyl-1,2,3,4-tetrahydrophenanthrene-4-one hydrazone (11)

After refluxing ketone **10** (20.0 g, 95.2 mmol) and $NH_2NH_2.H_2O$ (23.0 mL, 23.8 g, 475.0 mmol, 5 equiv) in absolute ethanol (100 mL) for 2 h, the yellow solution was filtered while hot, and upon cooling to room temperature **11** separated from the solution as yellow crystals (19.8 g, 88.3 mmol, 92.7%): mp 143.7–145.4 °C; ^{1}H NMR (300 MHz) δ 1.84–1.90 (m, 2H), 2.46 (s, 3H), 2.56 (dd, J = 6.6, 6.5 Hz, 2H), 2.74 (dd, J = 6.6, 5.9 Hz, 2H), 5.41 (bs, 2H, NH_2), 7.18 (d, J = 8.8 Hz, 1H), 7.32 (dd, J = 8.8, 1.5 Hz, 1H), 7.53 (s, 1H), 7.58 (dd, J = 8.8, 0.7 Hz, 1H), 8.96 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 21.12 (q), 21.33 (t), 25.54 (t), 31.01 (t), 126.38 (d), 126.85 (d), 126.87 (d), 127.42 (d), 128.52 (d), 128.61 (s), 133.59 (s), 134.08 (s), 134.10 (s), 137.86 (s), 148.24 (s); HRMS Calcd for $C_{15}H_{16}N_2$: 224.131, found 224.131; Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.36; H, 7.14; N, 12.50. Found: C, 80.66; H, 7.15; N, 12.50.

2-Methoxy-9H-thioxanthene-9-one (13)

Starting from thiosalicylic acid (53.9 g, 0.35 mol) and 4-iodoanisole (70.2 g, 0.35 mol), acid **12** was obtained prepared according to the procedure described by Vasiliu et al.[26] (≈ 70 g). Finely powdered **12** was added in 30 min to mechanically stirred H_2SO_4 (500 mL) at 10 °C for 45 min. The color of the mixture changed to blue, and after stirring for 45 min the now green-brown solution was poured onto ice (≈ 3 kg). The precipitated yellow solid was isolated by a difficult slow filtration, washed with water (500 mL) and saturated aqueous $NaHCO_3$ (250 mL), and the wet solid was dissolved in CH_2Cl_2 (2.5 L). The CH_2Cl_2 layer was washed with saturated aqueous $NaHCO_3$ (2 × 250 mL), brine (1 × 250 mL), dried (Na_2SO_4), and after evaporation of the solvent a light yellow solid was obtained which proved to be **13** (40.3 g, 0.17 mol, 56% based on 4-iodoanisole): mp 126.3–128.4 °C (lit:[31] 129 °C); ^{1}H NMR (300 MHz) δ 3.88 (s, 3H), 7.14–7.18 (m, 1H), 7.35–7.53 (m, 4H), 8.00 (d, J = 2.9 Hz, 1H), 8.55–8.58 (m, 1H); ^{13}C NMR δ 55.38 (q), 110.05 (d), 122.31 (d), 125.65 (d), 125.73 (d), 126.93 (d), 128.26 (s), 128.79 (s), 129.53 (d), 129.89 (s), 131.63 (d), 137.19 (s), 158.03 (s), 179.17 (s, C=O).

2-Methoxy-9H-thioxanthene-9-thione (14)

To a stirred solution of **13** (15.0 g, 62.0 mmol) in dry toluene (200 mL) was added P_2S_5 (27.5 g, 124.0 mmol). After 1 h TLC analysis (SiO_2, hexane/Et_2O 85:15, starting material R_f = 0.25, product R_f = 0.42) indicated the total conversion of **13** to thioketone **14**. The dark green residue obtained after evaporation of the solvents was dissolved in CH_2Cl_2 (200 mL) and filtered. Hexane (200 mL) was added, whereupon the thioketone began to separate from the solution. Upon cooling at –18 °C, **14** was obtained as dark green small needles in a

first fraction (6.2 g) and as a green-brown powder in a second fraction (5.9 g), which both proved to be pure thioketone (total amount: 12.1 g, 46.9 mmol, 76 %): mp 142.6–142.9 %C; ^{1}H NMR δ 3.96 (s, 3H), 7.27–7.31 (m, 1H), 7.44–7.51 (m, 2H), 7.57–7.63 (m, 2H), 8.59 (d, J = 2.2 Hz, 1H), 9.07–9.09 (m, 1H); ^{13}C NMR δ 55.50 (q), 113.86 (d), 122.38 (d), 124.21 (s), 125.86 (d), 126.65 (d), 127.08 (d), 131.14 (d), 132.05 (s), 133.61 (d), 136.66 (s), 138.22 (s), 158.73 (s), 208.81 (s, C=S); HRMS Calcd for $C_{14}H_{10}OS_2$: 258.017, found 258.017; Anal. Calcd for $C_{14}H_{10}OS_2$: C, 65.12; H, 3.87; S, 24.81. Found: C, 64.94; H, 3.95; S, 24.57.

cis- *and* trans-*Dispiro[7-methyl-1,2,3,4-tetrahydrophenanthrene-4, 2'-thiirane-3', 9"-(2"-methoxy)-9"H-thioxanthene] (16)*

A stirred solution of hydrazone **11** (672 mg, 3.00 mmol) in dry ether was cooled to –10 °C, whereupon $MgSO_4$ (approximately 1500 mg), Ag_2O (1.04 g, 4.50 mmol, 1.5 equiv) and a saturated solution of KOH in ethanol (1 mL) were successively added. The red solution of diazo compound **15** was filtered into another ice-cooled bulb. To this clear solution 2-methoxy-9H-thioxanthene-9-thione (**14**, 490 mg, 1.90 mmol) was added. Evolution of nitrogen was observed and the red color disappeared. The mixture of episulfides *cis*-**16** and *trans*-**16** precipitated from the Et_2O solution as a slightly yellow solid (ratio cis:trans, 50:50). Crystallization from ethanol yielded episulfides *cis*-**16** and *trans*-**16** (481 mg, 1.06 mmol, 55.8%, based on the amount of added thioketone), as a cis and trans mixture (ratio cis:trans, 17:83). No further attempts were made to separate these compounds. Only the NMR data of *trans*-**16** were fully resolved and are given: ^{1}H NMR (300 MHz) δ 1.25–1.50 (m, 2H), 1.90–1.95 (m, 1H), 2.30–2.38 (m, 1H), 2.35 (s, 3H), 2.41–2.57 (m, 1H), 3.47–3.58 (m, 1H), 3.77 (s, 3H, *trans*-OCH_3, the *cis*-OCH_3 was found at 2.98 ppm), 6.31 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 6.59 (ddd, J = 8.8, 7.3 Hz, 1.5 Hz, 1H), 6.77 (dd, J = 8.1, 2.9 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 7.14–7.53 (m, 6H), 9.31 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 20.94 (t), 21.11 (q), 29.76 (t), 34.99 (t), 55.44 (q), 59.93 (s, C-S), 61.48 (s, C-S), 124.64 (d), 125.30 (d), 126.21 (d), 126.26 (d), 126.63 (d), 126.82 (d), 126.87 (d), 127.16 (d), 127.57 (d), 128.99 (d), 129.20 (d), 129.39 (s), 130.33 (d), 131.07 (s), 132.50 (s), 132.58 (s), 133.02 (s), 133.92 (s), 134.42 (s), 135.06 (s), 140.01 (s), 158.20 (s); HRMS Calcd for $C_{29}H_{24}OS_2$: 452.127, found 452.126.

cis- *and* trans-*2-Methoxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene (1)*

To a stirred solution of a mixture of episulfides *cis*-**16** and *trans*-**16** (226 mg, 0.50 mmol, ratio cis:trans, 17:83) in xylene (10 mL) was added Cu-bronze powder (128 mg, 2.00 mmol). After refluxing for 2 h the mixture was cooled to room temperature. The brown colored copper residue was removed by filtration, the salts were washed with CH_2Cl_2 (20 mL) and the solvents were removed under reduced pressure. Alkenes *cis*-**1** and *trans*-**1** were obtained in a 50:50 ratio (187 mg, 0.45 mmol, 89.2%). Two crystallizations from ethanol yielded pure *cis* alkene **1** (74.3 mg, 0.18 mmol, 35.4%); *cis*-**1**: mp 179.0–179.4 °C; ^{1}H NMR (300 MHz) δ 2.01–2.23 (m, 2H), 2.34 (s, 3H), 2.34–2.41 (m, 1H), 2.97 (s, 3H), 3.06–3.13 (m, 2H), 3.32–3.40 (m, 1H), 5.95 (d, J = 2.6 Hz, 1H), 6.38 (m, 1H), 6.87 (dd, J = 8.8, 1.5 Hz, 1H), 7.21–7.60 (m, 9H); ^{13}C NMR δ 21.24 (q), 22.43 (t), 28.08 (t), 28.63 (t), 54.78 (q), 113.17 (d), 113.99 (d), 124.74 (d), 125.38 (s), 125.71 (d), 125.99 (d), 126.17 (s), 126.32 (d), 126.33 (d), 126.60 (d), 127.21 (d), 127.33 (d), 127.54 (d), 127.94 (d), 131.97 (s), 132.25 (s), 133.71 (s), 134.93 (s), 136.12 (s), 136.33 (s), 136.55 (s), 136.73 (s), 139.66 (s), 157.64 (s); HRMS Calcd for $C_{29}H_{24}OS$, 420.155, found 420.154; Anal. Calcd for $C_{29}H_{24}OS$: C, 82.86; H, 5.71; S, 7.62. Found: C, 82.88; H, 5.83; S, 7.63; *trans*-**1**: mp not obtained (the trans alkene was always contaminated by cis alkene); ^{1}H NMR (300 MHz) δ 2.10–2.19 (m, 1H), 2.32 (s, 3H), 2.32–2.36 (m, 1H), 3.05–3.16 (m, 2H), 3.30–3.37 (m, 1H), 3.89 (s, 3H), 6.30–6.37 (m, 2H), 6.81 (ddd, J = 8.8, 7.8, 1.5 Hz, 1H), 6.93 (dd, J = 8.8, 1.5 Hz, 1H), 7.19 (d, J = 2.6 Hz, 1H), 7.23–7.60 (m, 8H); ^{13}C NMR δ 21.25 (q), 22.25 (t), 28.29 (t), 28.50 (t), 55.38 q), 112.94 (d), 113.91 (d), 124.69 (d), 125.10 (d), 125.22 (s), 125.72 (d), 125.98 (d), 126.43 (d), 126.58 (d), 126.65 (s), 127.22 (d), 127.34 (d), 127.51 (d), 128.12 (d), 131.81 (s), 132.01 (s), 133.51 (s), 134.86 (s), 135.96 (s), 136.39 (s), 136.47 (s), 137.95 (s), 138.36 (s), 157.46 (s).

trans-**1**: UV (*n*-hexane, λ (∈)): 226.9 (58200) 309.1 (9630) 332.8 (8720)

CD (hexane/isopropanol 9:1, λ (Δ∈)): 232 (183) 256 (–60) 273 (–63)

cis-**1**: UV (*n*-hexane, λ (∈)): 229.3 (65000) 309.2 (10000) 332.4 (8500)

CD (hexane/isopropanol 9:1, λ (Δ∈)): 232 (176.0) 262 (–60.8) 310 (–15.3)

Determination of $\Delta^{\ddagger}G^{\theta}$ (polarimetry, *p*-xylene, 436 nm):

t °C	T(K)	k(s^{-1})	ln (k/T)	$\Delta^{\ddagger}G^{\theta}$	(kcal mol^{-1})
45.0	318.1	4.58 ± 0.1	10^{-6}	–18.06	26.43 ± 0.2
50.5	323.6	9.50 ± 0.1	10^{-6}	–17.34	26.43 ± 0.2
55.5	328.6	1.7 ± 0.03	10^{-5}	–16.78	26.47 ± 0.2
60.5	333.6	3.36 ± 0.08	10^{-5}	–16.11	26.43 ± 0.2
70.0	343.1	9.5 ± 0.1	10^{-5}	–15.10	26.49 ± 0.2
75.0	348.1	1.37 ± 0.02	10^{-4}	–14.75	26.63 ± 0.2
80.5	353.6	2.09 ± 0.02	10^{-4}	–14.34	26.77 ± 0.2
85.4	358.5	4.74 ± 0.05	10^{-4}	–13.54	26.57 ± 0.2

$\Delta^{\ddagger}H^{\theta}$ = 24.1 ± 1.0 kcal mol^{-1}, $\Delta^{\ddagger}S^{\theta}$ = –6.0 ± 2.9 cal mol^{-1} K^{-1}

REFERENCES AND NOTES

(1) Feringa, B.L.; Jager, W.F.; De Lange, B. *Tetrahedron* **1993**, *49*, 8267–8310.

(2) *Photochromism, Molecules and Systems in studies in Organic Chemistry 40*: Dürr, H.; Bouas Laurent, H., Eds.; Elsevier: Amsterdam, 1990.

(3) (a) Gilat, S.L.; Kawai, S.H.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 275–284. (b) Tachibana, H.; Azumi, R.; Nakamura, T.; Matsumoto, M.; Kawabata, Y. *Chem. Lett.* **1992**, 173–176. (c) Tachibana, H.; Nakamura, T.; Matsumoto, M.; Komizu, H.; Manda, E; Niino, H.; Yabe, A.; Kawabata, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3080–3081.

(4) Sponsler, M.B.; Zhang, J. *J. Am. Chem. Soc.* **1992**, *114*, 1506–1507.
(5) Feringa, B.L.; Huck, N.P.M.; van Doren, H.A. *J. Am. Chem. Soc.* **1995**, *117*, 9929-9930.
(6) Murata, K.; Aoki, M.; Nishi, T.; Ikeda, A.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1715–1718.
(7) (a) Ueno, A.; Anzai, J.; Osa, T.; Takahashi, K. *J. Am. Chem. Soc.* **1981**, *103*, 6410-6415. (b) Ueno, A.; Takahashi, K. Anzai, J.; Osa, T.; *Macromolecules* **1980**, *13*, 459–460.
(8) Shinkai, S.; Nakaji, T.; Nishida, Y.; Ogawa, T.; Manabe, O. *J. Am. Chem. Soc.* **1980**, *102*, 5860–5865.
(9) Willner, I.; Rubin, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 367.
(10) (a) Ringsdorf, H.; Cabrera, I.; Dittrich, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 76–78. (b) Cabrera, I.; Krongauz, V.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1178–1180.
(11) Ichimura, K.; Hosoki, A.; Ozawa, K.; Suzuki, Y. *Polym. Bull.* **1987**, *17*, 285–291.
(12) Ueda, M.; Kim, H.-B.; Ichimura, K. *Chem. Mater.* **1994**, *6*, 1771–1775.
(13) Jager, W.F.; de Jong, J.C.; de Lange, B.; Huck, N.P.M.; Meetsma, A.; Feringa, B.L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 348–350.
(14) Feringa, B.L.; Jager, W.F.; de Lange, B.; Meijer, E.W. *J. Am. Chem. Soc.* **1991**, *113*, 5468–5470.
(15) de Lange, B.; Jager, W.F.; Feringa, B.L. *Tetrahedron Lett.* **1992**, *33*, 2887–2890.
(16) de Lange, B.; Jager, W.F.; Feringa, B.L. *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 129–132.
(17) Jager, W.F.; de Lange, B.; Feringa, B.L. *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 133–138.
(18) Feringa, B.L.; Jager, W.F.; de Lange, B. *J. Chem. Soc., Chem. Commun.* **1993**, 288–290.
(19) Jager, W.F.; de Lange, B.; Schoevaars, A.M.; Feringa, B.L. *Tetrahedron Asymmetry* **1993**, *4*, 1481–1497.
(20) (a) Ciardelli, F.; Carlini, C.; Solaro, R.; Altomare, A.; Pieroni, O.; Houben, J.L.; Fissi, A. *Pure Appl. Chem.* **1984**, *56*, 329–342. (b) Altomare, A.; Ciardelli, F.; Lima, R.; Solaro, R. *Chirality* **1991**, *3*, 292–298. (c) Ciardelli, F.; Pieroni, O.; Fissi, A.; Houben, J.L. *Biopolymers* **1984**, *23*, 1423–1437. (d) Haitjema, H.J.; Von Morgen, G.L.; Tan, Y.Y.; Challa, G. *Macromolecules* **1994**, *27*, 6201.
(21) (a) Feringa, B. L.; de Lange, B.; Jager, W.F.; Schudde, E.P. *J. Chem. Soc., Chem. Commun.* **1990**, 804–805. (b) Hulshof, J. *Materials for Second Order Nonlinear Optics*, Ph.D. Thesis. University of Groningen, 1995.
(22) See, for instance, ref 20c.
(23) Haitjema, H.J.; Feringa, B.L., unpublished results.
(24) Haworth, R.D.; Letsky, B.M.; Mavin, C.M. *J. Chem. Soc.* **1932**, 1784–1792.
(25) See e.g: (a) Brindle, I.D.; Doyle, P.P. *Can. J. Chem.* **1983**, *61*, 1869–1871. (b) Protiva, M.; Jilek, J.O.; Pelz, K.; Vejdelek, Z.J. *Coll. Czech., Chem. Commun.* **1966**, *31*, 269. (c) Gilman, H.; Diehl. J.W. *J. Org. Chem.* **1959**, *24*, 1914–1916. (d) Mann, F.G.; Turnbull, J.H. *J. Chem. Soc.* **1951**, 747–755.
(26) Vasiliu, G.; Maior, O.; Rasanu, N. *Rev. Chim. (Bucharest)* **1968**, *68*, 561–565; *Chem. Abstr.* 38739 **1969**, *71*, 268.
(27) Barton, D.H.R.; Willis, B.J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305–310.
(28) Buter, J.; Wassenaar, S.; Kellogg, R.M. *J. Org. Chem.* **1972**, *37*, 4045–4060.
(29) Stanke, D.; Hallesleben, M.L.; Toppare, L. *Synth. Met.* **1993**, *55*, 1108–1113.
(30) Hallensleben, M.L., Stanke, D. *Macromol. Chem. Phys.* **1995**, *96*, 75.
(31) Roberts, K.C.; Smiles, S. *J. Chem. Soc.* **1929**, 863–872.