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Molecular Weight Optimum in the Mesoscopic Order of Chiral Fluorene (Co)polymer Films

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ABSTRACT: A chiral fluorene homopolymer (**PF**) and two new chiral alternating polyfluorenes, poly(fluorene-*alt*-benzothiadiazole) (**PFBT**) and poly(fluorene-*alt*-dithienylbenzothiadiazole) (**PFDTBT**), have been synthesized by palladium-catalyzed Suzuki polycondensations. In these polymers, chirality was introduced by attaching (*S*)-3,7-dimethyloctyl substituents to the 9-positions of the fluorene monomers. Upon thermal annealing, **PF** and **PFBT** undergo an irreversible phase transition to a liquid crystalline state that upon cooling to room temperature is vitrified and exhibits considerable circular dichroic (CD) effects. By contrast, **PFDTBT** forms an amorphous glass with hardly any CD activity. After fractionation by preparative size exclusion chromatography (SEC), the phase behavior of the low polydispersity polymers was studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and CD spectroscopy. Remarkably, after fractionation also for **PFDTBT** a CD effect was observed and for all three materials the maximum CD effects were recorded at intermediate polymer length, indicating the presence of an optimal molecular weight for the chiral organization. In addition to the influence of molecular weight on the supramolecular organization, also annealing temperature and time, as well as film thickness were investigated. The three polymers showed very different ordering kinetics while the temperature dependence was much more uniform. A nonlinear increase of CD values with film thickness was observed, giving rise to higher g-values in thicker films.

Introduction

Polyfluorene (**PF**)[1,2] and its copolymers[3,4] represent an intriguing class of π-conjugated polymers and are promising candidates for use in organic electronic devices such as polymer light emitting diodes (PLEDs),[2,3,5−9] and organic solar cells.[10−13] **PF** homopolymers are efficient blue emitters in photo- and electroluminescence (band gap 3.0 eV[9]), whereas alternating **PF**s offer the possibility to tune the band gap and emission color over a very wide range when combined with the appropriate aromatic comonomers.[3,4,9,14−20] Two of the most commonly used examples are poly(fluorene-*alt*-benzothiadiazole) (**PFBT,** band gap 2.3 eV[9]), and poly(fluorene-*alt*-dithienylbenzothiadiazole) (**PFDTBT,** band gap 1.8 eV[20]). **PFBT** is a yellow-green emissive polymer, exhibits excellent electron transporting properties and has been used extensively in devices such as polymer light emitting diodes[6,7,9] and organic photovoltaic cells.[11−13] **PFDTBT** is a so-called small band gap material commonly utilized in organic solar cells.[21,22]

As with all conjugated polymers, batch-to-batch variations in the molecular weights of **PF**s and its copolymers are common and can never be completely excluded because they are inherent to the synthetic procedures applied. Consequently, the influence of chain length on phase behavior, self-assembly, solid state morphology, optical properties and device performance has been studied in **PF**[23−27] and other conjugated polymers, such as poly(alkylthiophene),[28−32] poly(phenylene vinylene)[33,34] and poly(phenylene ethynylene).[35] For example, the field effect mobility of regioregular poly(3-hexylthiophene) has been shown to vary over several orders of magnitude for samples ranging from 3 to 40 kD,[32] accompanied by significant changes in thin film morphology. Also **PF**s exhibit a complex phase behavior[36,37] that delicately depends on average molecular weight,[24−26] side chain architecture[23,24] and film preparation conditions.[12,37,38] Optical and electronic characteristics of different **PF** phases can differ significantly from one another,[37,38] offering a possibility to fine-tune device properties. By contrast, the phase behavior of alternating **PF** copolymers has so far been less intensely studied.[39−41]

CD spectroscopy can be used as a sensitive tool to study phase behavior of **PF** homopolymers with enantiomerically pure chiral side chains because these materials exhibit extraordinarily high circular dichroic (CD) effects in annealed films.[42−45] The observation of a strong nonlinear increase of CD with film thickness has demonstrated that the optical activity of chiral **PF**s is not only an intrinsic property of the material,[44] but is also related to a mesoscopic phenomenon. Circular differential scattering[46] or selective reflection due to a cholesteric mesophase[47,48] or a helical arrangement of the polymer chains in the film[43,49] have been proposed as being the cause. Application of these materials in PLEDs led to circularly polarized electroluminescence with g_{CPEL} values exceeding those reported for other chiral polymers.[42,49,50] In addition to the possible applications in chiroptical electronic devices, the CD activity of chiral **PFs** can also be used to deepen the understanding of their supramolecular organization in organic semiconductor films. So far, research has been focused on chiral **PF** homopolymers[46,49] and oligofluorenes,[47,48] whereas very few examples of chiral alternating fluorene copolymers have been reported,[51,52] none of which shows CD effects in thin films. Consequently, the wavelengths at which strong CD effects are observed have until now been restricted to the high energy part of the visible spectrum (<500 nm). The research presented here deals with the synthesis, characterization and chiroptical properties of three chiral fluorene-based π-conjugated polymers (**PF**, **PFBT** and **PFDTBT**) with band gaps covering almost the entire visible range (Figure 1). The polymers have been separated into narrow molecular weight fractions by preparative size exclusion chromatography (SEC) and their phase behavior upon annealing in thin films was monitored by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and CD spectroscopy. In addition to molecular weight, supramolecular organization monitored by CD spectroscopy was found to

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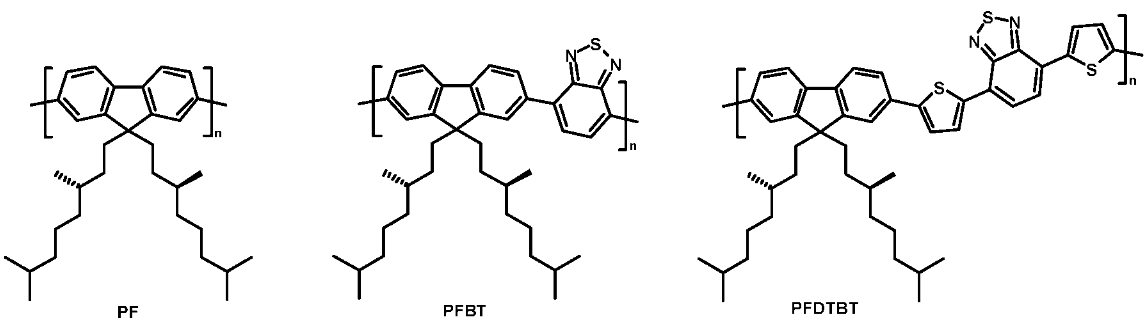

Figure 1. Chemical structures of the chiral fluorene polymers.

Table 1. SEC Characteristics of the Polymers

	M_n	M_w	PDI
PF	6930	15600	2.25
PFBT	4700	7510	1.60
PFDTBT	4140	6110	1.48

depend strongly on film thickness, annealing time and temperature. All these parameters have been varied in order to obtain maximum CD effects, which is assumed to coincide with the highest degree of internal order on the mesoscopic length scale.

Results and Discussion

Synthesis and Characterization of the Polymers. PF, PFBT, and **PFDTBT** were synthesized according to well-established literature procedures[9,21,53] utilizing a Suzuki polycondensation as the last step. The synthesis and characterization of the polymers are described in detail in the Supporting Information. By making use of an AA-BB type polycondensation, the chiral fluorene units in **PFBT** and **PFDTBT** were regularly alternating with benzothiadiazole or dithienylbenzothiadiazole, respectively. After Soxlet extraction of the lowest molecular weight components, analytical SEC revealed that all three materials still had rather low average degrees of polymerization and a broad molecular weight distribution (Table 1). Fractionation by preparative size exclusion chromatography, however, enabled us to obtain sufficiently high molecular weight samples of narrow polydispersity for a study on the chain length dependence of ordering processes in thin spin coated films (vide infra). A 50: 50 composition of chiral fluorene and benzothiadiazole or dithienylbenzothiadiazole in **PFBT** and **PFDTBT**, respectively, was confirmed by ^{1}H NMR spectroscopy, elemental analysis and MALDI−TOF−MS. ^{13}C NMR showed only one type of fluorene unit, supporting structural regularity.

Thermal Properties. In order to investigate the phase behavior of the polymers we used DSC and POM. It should be noted that the transition temperatures of polymers usually converge only for molecular weights above 10000 g/mol, which is clearly higher than that of our materials. Therefore the results presented in this section will most probably not be representative for the higher molecular weight materials usually used in electronic applications. Rather, they have to be seen in connection with the DSC and POM results presented further below, where fractions of various degrees of polymerization will be compared. The DSC curves (Figure 2) of all three polymers (isolated by precipitation) showed one endothermic peak during the first heating run that did not reappear upon cooling or during subsequent heating runs, indicating an irreversible first order phase transition. The corresponding heats of transition were significantly higher for **PF** and **PFBT** than for **PFDTBT** (Table 2). Upon cooling or repeated heating runs, the materials underwent a reversible glass transition, as was obvious from a step in the DSC curves. These observations suggest that annealing transforms an initially formed metastable state irreversibly into a thermodynamically stable glassy phase. The differences in transition enthalpies found between the three polymers point to a higher degree of reorganization involved in **PF** and **PFBT** than in **PFDTBT**.

POM studies revealed that at 150 °C, **PF** and **PFDTBT** were isotropic liquids, whereas **PFBT** was fluid, but exhibited a granular texture under crossed polarisers, indicating liquid crystallinity (Supporting Information). A similar texture was found in **PF** below 85 °C, whereas **PFDTBT** remained isotropic over the whole temperature range investigated. At room temperature, all polymers formed glassy solid films in agreement with results described in literature,[1] but only **PF** and **PFBT** were birefringent, exhibiting textures very similar to those found in their liquid crystalline states. Their appearance closely resembled textures observed in glassy cholesteric[46] or polydomain nematic[54] films of thermally annealed chiral oligofluorenes, suggesting that similar structures might be formed in our case.

Optical Properties in Solution and in Thin Films. UV−vis and photoluminescence spectra of the polymers were recorded in solvents of varying polarity (Supporting Information). In THF, toluene, and chloroform, the results were in agreement with those reported in the literature for achiral analogues[9] and indicated that the polymers were molecularly dissolved. This was also supported by the absence of CD effects in these solvents. In many cases inhomogeneous films were obtained when using solutions in pure chloroform or THF for spin coating. In order to get smooth homogeneous films, mixtures of THF (for **PF**) or chloroform (for **PFBT** and **PFDTBT**) containing a small percentage of chlorobenzene were used, similar to procedures reported earlier for the achiral analogues of **PFBT** and **PFDTBT**.[55] The UV−vis and photoluminescence spectra of the polymer films (Figure 3) showed red-shifted maxima compared to the THF solutions and were similar to those reported in the literature for achiral analogues.[6,9,21,53] Upon annealing to 150 °C a slight intensity decrease, but no significant spectral shifts of the absorption bands were observed. A very small increase at the low energy end of the bands indicated a contribution from scattering. Similarly, the fluorescence spectra did not change in shape, with the exception of a small increase of the green fluorenone emission of **PF**.[1] Overall, neither UV−vis absorption nor fluorescence spectroscopy clearly pointed to pronounced morphological changes upon annealing. By contrast, the CD spectra of **PF** and **PFBT** underwent clear changes (Figure 3). No CD effects were observed in any of the pristine films, but after annealing clear CD effects were found over the whole absorption range of the polymers. Consistent with results described in the literature,[42,43,49] the CD spectrum of **PF** consisted of a strong negative band at around 400 nm which was flanked by two weaker positive bands. For **PFBT** quite similar features were found that were shifted ca. 60 nm to the red, and additionally another negative band was present at ca. 340 nm. This demonstrates that chiral side chains not only induce CD effects in annealed **PF** films, but that similar

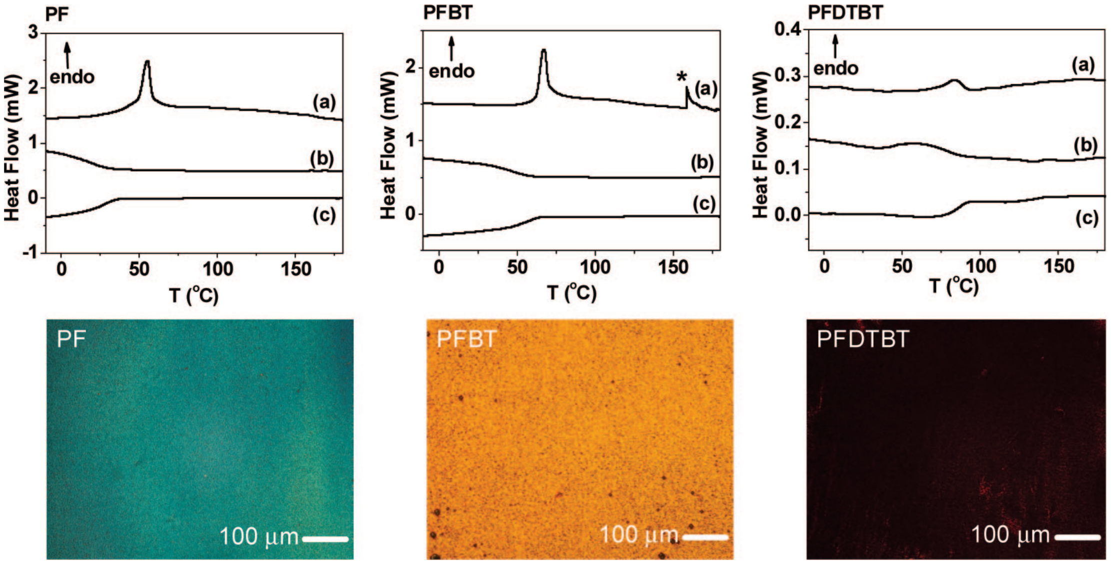

Figure 2. Top: DSC traces of **PF**, **PFBT** and **PFDTBT**. Key: (a) first heating run; (b) first cooling run; (c) second heating run. The asterisk marks an artifact that does not represent a thermal transition. Bottom: Optical micrographs of **PF**, **PFBT** and **PFDTBT** between crossed polarisers after annealing to 150 °C and subsequent cooling to room temperature.

Table 2. Thermal Characteristics of the Polymers

	$T_{\mathrm{trans}}{}^{a}$ (°C)	$\Delta H_{\mathrm{trans}}{}^{a}$ (J/g)	$T_{\mathrm{glass}}{}^{b}$ (°C)	$\Delta C_p{}^{b}$ (J/gK)
PF	55	5.8	28	0.20
PFBT	67	5.1	57	0.17
PFDTBT	83	1.3	86	0.17

[a] From first heating run. [b] From second heating run.

phenomena are also present in fluorene copolymers. Furthermore, CD spectroscopy is shown to be a more indicative and sensitive tool to investigate structural reorganization than UV−vis absorption and fluorescence spectroscopy. Contrarily, for **PFDTBT** hardly any CD activity was observed after annealing.

The observations made by CD spectroscopy coincide with the presence of birefringence in annealed **PF** and **PFBT**, as well as with its absence in **PFDTBT**. Furthermore, they suggest that the transitions found in the DSC curves of **PF** and **PFBT** mark the formation of a chiral liquid crystalline phase that upon cooling is vitrified with retention of its chiral organization, thus giving rise to the CD effects of the thin annealed films. In **PFDTBT** a different, nonchiral (and thus CD inactive) phase is formed that structurally does not differ so much from the initial state present after precipitation or spin coating.

Fractionation of the Polymers. In order to study the influence of the molecular weight on the thermal and chiroptical properties, all three polymers were fractionated by preparative SEC. Analytical SEC revealed that some fractions contained materials with chains much longer than the unfractionated original batches (M_n > 10000), whereas other fractions were mixtures of low molecular weight oligomers (Supporting Information). As expected, the polydispersities of all fractions were narrower than those of the original batches. In accordance with the increased conjugation length, for each polymer absorption and emission wavelengths increased with molecular weight (Supporting Information). As all fractions of **PF** turned out to be of relatively high molecular weight, for comparison also two monodisperse model oligomers (a trimer and a pentamer) which had been synthesized earlier[56] were used.

Thermal Properties of the Fractionated Polymers. Interestingly, not all fractions of **PF** and **PFBT** showed birefringence when heated under an optical microscope, but only those above a certain molecular weight threshold (ca. 6000 for **PF** and ca. 3000 for **PFBT**, see Supporting Information). Also, the textures of some of the higher molecular weight fractions of **PFDTBT** strongly resembled the granular texture observed for the other two polymers. Although already at 150 °C the material was fluid, its viscosity was still very high, so the polymers had to be heated to higher temperatures in order to observe clear textures.

Similar to the results described above for crude **PF**, DSC traces of all **PF** fractions showed an irreversible endothermic transition at ca. 50 °C during the first heating run (Supporting Information). No such peak was found in the short monodisperse oligomers. With increasing molecular weight, the peaks became sharper and their maxima slightly shifted toward higher temperatures. A distinct dependence of the transition enthalpy on the molecular weight was found, with a maximum at ca. 14000 g/mol. Unfortunately, only very few fractions of the other two polymers showed unambiguous peaks in their DSC traces (Supporting Information), which may be due to the small amounts of material we had available.

Chiroptical Properties of Thin Films of the Fractionated Polymers. In order to investigate the molecular weight dependence of the CD effects in the polyfluorenes, thin films of all fractions were prepared by spin coating and thermally annealed. Although identical conditions (solvent mixture, concentration, temperature, spin speed) were used, the samples of the lowest molecular weight gave somewhat thinner films. We attribute this to the influence of the chain length on the viscosity of the solutions. In general, however, film thicknesses varied only within a range of ca. 10%, allowing fair comparison. The absorption maxima of the lowest molecular weight samples were located at shorter wavelengths than those of fractions containing longer chains, showing that band gap convergence was only reached at higher degrees of polymerization. Furthermore, the emergence of long wavelength shoulders after annealing at 150 °C indicated solid state ordering especially in some high molecular weight fractions of **PFDTBT**. More pronounced than the changes in the absorption spectra, however, were those in the CD spectra. Whereas none of the films in its pristine state after spin coating showed any noticeable circular dichroism, several polymer fractions exhibited strong CD effects after annealing (Figure 4), surprisingly including several **PFDTBT** fractions, which had hardly been CD active prior to fractionation. For **PF** and **PFBT**, the observed spectra roughly resembled those found for the unfractionated polymers, although the ratio of the

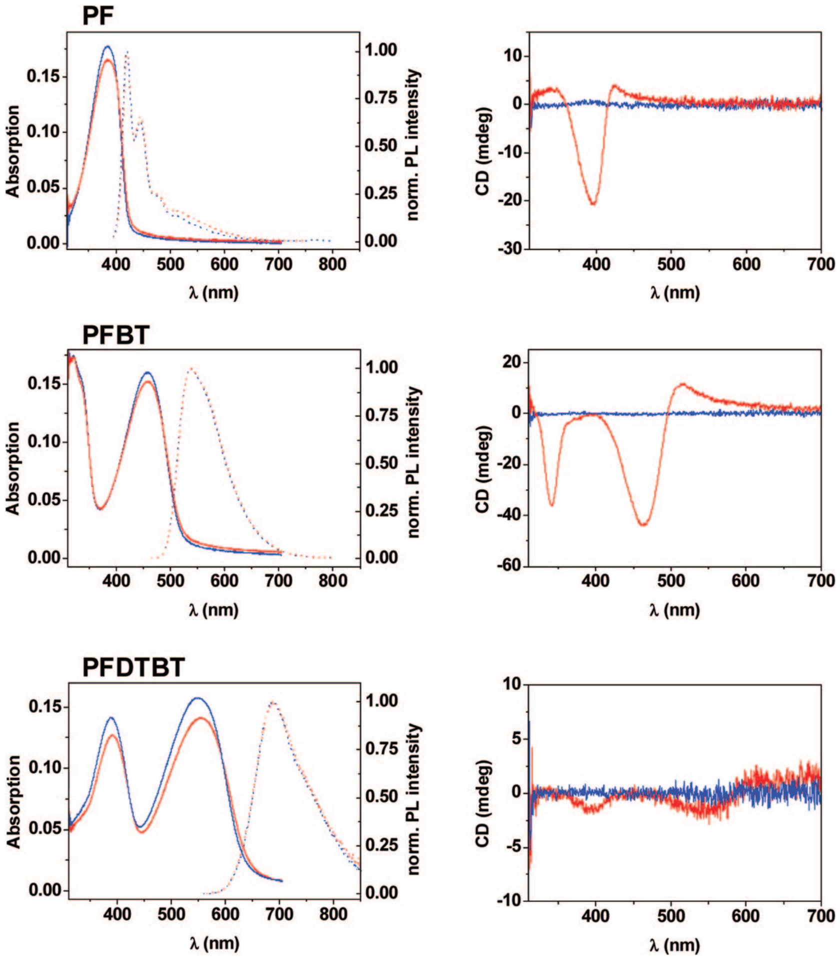

Figure 3. UV−vis absorption (solid), photoluminescence (dotted), and CD spectra of thin films of **PF**, **PFBT** and **PFDTBT** (blue: pristine, red: annealed for 2 h at 150 °C in nitrogen).

two lower positive side lobes (at ca. 350 and 420 nm for **PF** and at ca. 400 and 510 nm for **PFBT**) was subject to some variation. The CD spectra of the **PFDTBT** fractions had shapes similar to those of **PFBT**, but the respective features were further red-shifted. By contrast, none of the three polymers showed any significant linear dichroism effects in thin annealed films of various film thicknesses (Supporting Information).

All three polymers showed a comparable dependence of the maximal CD effects on their molecular weight (Figure 5). First, a certain lower threshold had to be overcome before any effect at all was visible.[57] This observation reveals that only above a certain molecular aspect ratio the molecules adopted a chiral supramolecular arrangement. When increasing the molecular weight further, first an increase, followed by a decrease in CD effect was observed, giving rise to a maximal CD effect at intermediate chain lengths. We attribute this to an improved stability of the liquid crystalline phase due to a lower concentration of chain ends and short chains. When the polymers became too long, however, the melt viscosities became too high resulting in lower CD effects due to a slowdown in the ordering kinetics. This assumption was further supported by the time dependence of the CD effects for samples of various molecular weight, which showed that longer annealing times increased the CD effects of high molecular weight fractions (vide infra).

Additionally, the molecular weight dependence of the maximum CD effects in the **PF** fractions was surprisingly similar to that of their transition enthalpies (determined by DSC during the first heating runs, vide supra): no CD effect was observed for the low molecular weight oligomers, and the maximum CD value was reached at the molecular weight that also had the highest heat of transition (approximate M_n ca. 14000). More generally speaking, a higher CD effect resulted in a higher transition enthalpy (Supporting Information). This observation is further support for our hypothesis that the magnitude of the CD effect can be used as a measure for the degree of order that emerges upon heating the polymers to their liquid crystalline state.

Time, Temperature and Film Thickness Dependence of Selected Fractions. The time dependence of the CD effects was determined using the following selected fractions: **PFf1** and **PFf4** (app. M_n 18800 and 9680, respectively), **PFBTf5** and **PFBTf8** (app. M_n 7080 and 3580, respectively) and **PFDTBTf1** and **PFDTBTf7** (approximate M_n 10940 and 5180, respectively), see Supporting Information for the nomenclature. The samples were chosen with respect to giving high CD effects and differing sufficiently in molecular weight in order to qualitatively determine the influence of melt viscosities on the ordering kinetics.

Concerning the rate with which the CD effect developed, clear differences were apparent not only between polymers of different chemical structures, but also within one type of polymer, when fractions with various molecular weight were compared (Figure 6). Both investigated fractions of **PF** as well as the lowest copolymer fractions (**PFBTf8** and **PFDTBTf7**) developed their maximal CD effect almost instantaneously (within less than 30 s of annealing). Then, a steady decline with further annealing was observed, which for **PF** was more pronounced in the lower molecular weight material (**PFf4**). By contrast, the emergence of CD was clearly slower for the longer

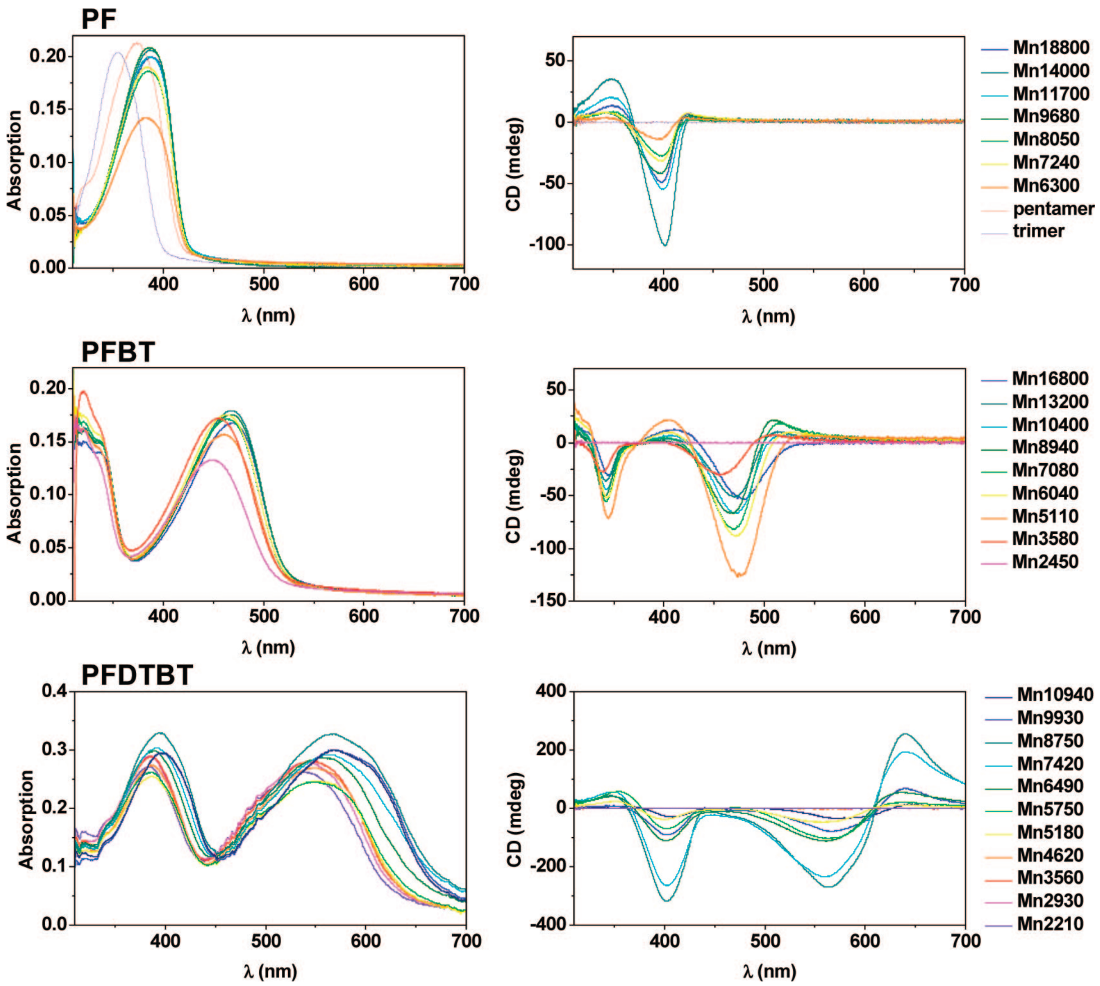

Figure 4. UV−vis absorption (left) and CD (right) spectra of polymers **PF**, **PFBT** and **PFDTBT** with various molecular weights after annealing at 150 °C in a nitrogen atmosphere. In the case of **PF**, also the spectra of two monodisperse oligomers (trimer and pentamer) are shown.

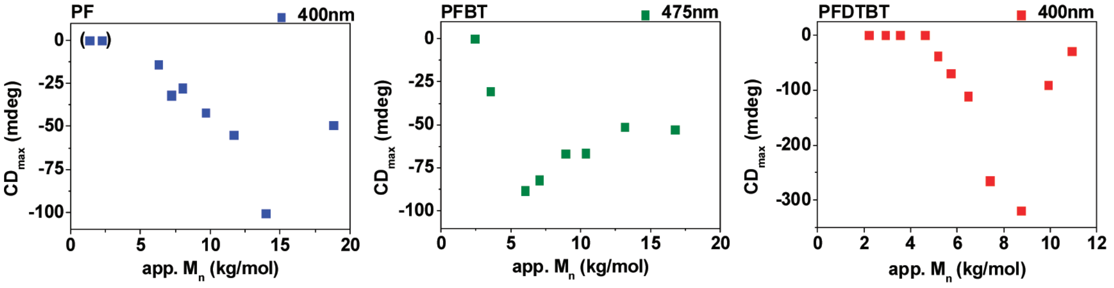

Figure 5. Molecular weight dependence of CD$_{max}$ in thin annealed films of **PF**, **PFBT** and **PFDTBT** ($T = 150$ °C). The two data points in brackets for **PF** are from monodisperse chiral fluorene trimers and pentamers, respectively.

fractions of the copolymers, i.e., **PFBTf4** and **PFDTBTf1**, which reached their maximal values only after 15 min and 9 h of annealing, respectively. Upon even further annealing, a steady decrease was observed for **PFBTf4**, and also **PFDTBTf1** showed a slightly lower CD after 24 h at 150 °C. In summary, it can be stated that all samples reached an optimum CD effect after having been annealed for a certain time and that the optimal time frame strongly varied with molecular structure and chain length. Even further annealing caused the CD signal to decline in all cases. Whether this reduction was due to a slow transition to another less ordered phase, or due to chemical decomposition, remains to be elucidated. For each type of polymer, the fractions of lower molecular weight reached their maximum CD effect earlier than the higher molecular weight fractions, and also the subsequent decrease in CD effect was faster. This is a clear indication for melt viscosity being the limiting factor in ordering kinetics. The fact that **PF** ordered more quickly than the copolymers might be explained by its higher density of flexible side chains, that upon melting provide a local environment of lower viscosity in which the conjugated backbones can move more easily.

The dependence of the CD effects on the annealing temperature and film thickness was determined using the following selected fractions, which all had given strong CD effects in the earlier measurements: **PFf3** (approximate M_n 11700) **PFBTf4** (approximate M_n 8940), **PFDTBTf3** (approximate M_n 8750) and **PFDTBTf4** (approximate M_n 7490), see Supporting Information for the nomenclature.

The influence of temperature was measured by annealing the films at various temperatures, followed by cooling, and measuring the CD effects at room temperature. All polymers showed a maximum in the CD effect after annealing at around

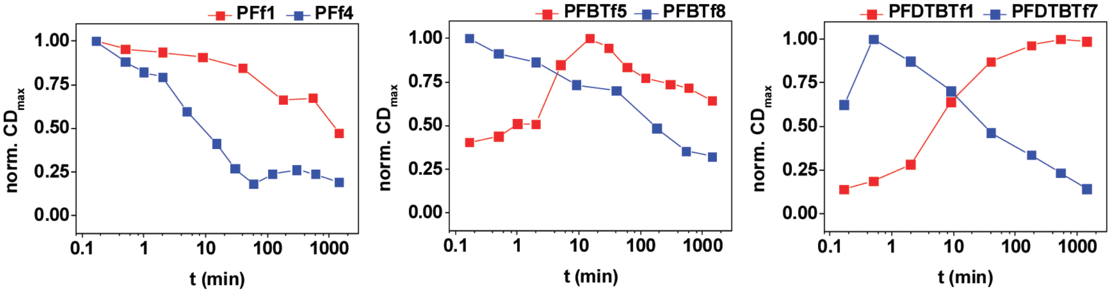

Figure 6. Annealing time dependence of CD_{max} in thin films of two fractions of **PF**, **PFBT** and **PFDTBT** (monitored at 400 nm (**PF**, **PFDTBT**) and 350 nm (**PFBT**), T_{ann} = 150 °C). For clarity, CD_{max} has been normalized and the time axis is drawn on a logarithmic scale. The lines are to guide the eye.

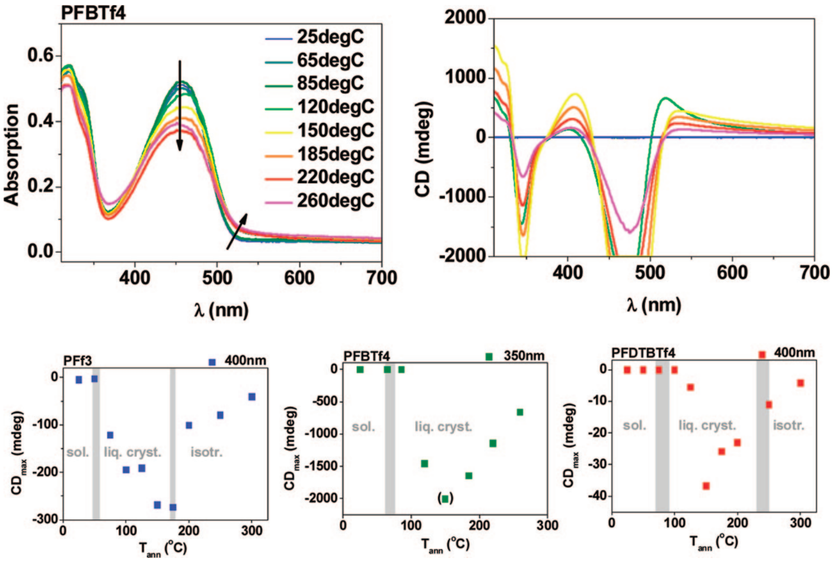

Figure 7. Annealing temperature dependence of the UV−vis (left) and CD (right) spectra in thin films of **PFBTf4** (same color code is used in both graphs) and annealing temperature dependence of CD_{max} in thin films of **PFf3**, **PFBTf4**, and **PFDTBTf4.** The gray bars mark the phase transition ranges as monitored by DSC (solid to liquid crystalline) and POM (liquid crystalline to isotropic). **PFDTf4** is still liquid crystalline at 320 °C. The data point in brackets is outside the measuring range of the CD spectrometer. As **PFBTf4** and **PFDTBTf4** did not show clear transition peaks in DSC, the values of fractions with similar molecular weight are shown here (**PFBTf3** and **PFDTBTf5**).

150 °C (Figure 7). Interestingly, for **PFf3** no CD effect was visible at 50 °C, whereas at 75 °C, a clear chiroptical activity was found, which was in good agreement with the phase transition temperature observed for this fraction by DSC (peak max. at 53 °C). This is further support for the assumption that the observed endothermic peak marks a reorganization process of the polymer chains that leads to a new supramolecular order which is responsible for the CD effects. Also, the maximum CD effect was reached at a temperature very close to the transition from liquid crystalline to isotropic as observed by POM. Thin films rapidly cooled from the isotropic state (and thus from higher temperatures) were presumably cooled too quickly in order to reorganize fully, which was reflected in a lower CD activity.[58] By contrast, the correlation between the transition temperatures and the magnitude of CD was much less pronounced for the alternating copolymers. Especially the decrease of CD was found to start at a temperature that was clearly lower than the liquid crystalline to isotropic transition. Whether this loss of order was due to chemical degradation of the benzothiadiazole units or a very slow transition to another thermodynamically stable phase remains to be elucidated.

In contrast to the clear differences in the CD spectra, annealing did not alter the UV−vis spectra very strongly and only a small decrease in intensity was observed (Figure 7 and Supporting Information), in accordance with earlier reported results.[41] Importantly, no shifts of the absorption maxima were observed, nor did any additional peaks appear, as would be expected if a β-phase (similar to **PF**s with linear side chains[37,38]) had been formed. Again, CD spectroscopy offers an additional and sensitive tool that clearly reveals structural changes in cases where UV absorption measurements do not.

As the film thickness dependence of chiral homopolymeric **PF** had already been reported earlier,[45] we focused on thin films of **PFBTf4** and **PFDTBTf3** (Figure 8). Similar to the chiral **PF**, a nonlinear increase in CD and g-values was observed when thicker films were measured. This observation suggests that similar structural features of the films are responsible for the observed CD effects in chiral **PF** homopolymer and alternating fluorene copolymers. Furthermore, a chiral arrangement of the chromophores leading to exciton-coupled CD spectra does not suffice as an explanation because it predicts g-values to be independent of film thickness. From these observations we conclude that, similar to what has been reported for **PF**,[44] the CD activity of **PFBT** and **PFDTBT** cannot be an intrinsic property of the materials, but must related to supramolecular order on larger length scales. The fact that the spectra of very thick films strongly tail at the low energy end (see Supporting Information), leading to significant CD activity at wavelengths where no absorption is present is another sign that the CD effect is not intrinsic in nature. As with **PF** films, a possible explanation is selective scattering[46] or preferred reflection of light of one handedness[47,48] due to chiral mesoscopic order in a cholesteric glass.

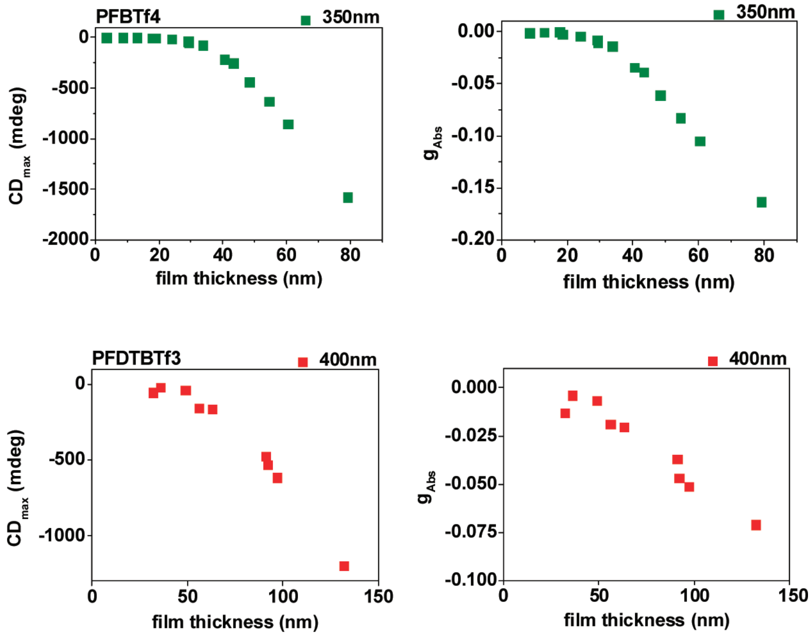

Figure 8. Film thickness dependence of CD$_{max}$ and g_{Abs} in thin annealed films of **PFBTf4** and **PFDTBTf3**.

Conclusion

Three chiral polyfluorenes—one homopolymer (**PF**) and two alternating copolymers (**PFBT** and **PFDTBT**)—have been prepared by Suzuki polycondensations. Precipitation from a good solvent or spin coating, which are fast processes compared to the chain ordering kinetics of polymers, trap these materials in a metastable state of low internal order, but thermal treatment induces the irreversible formation of a stable chirally ordered (probably cholesteric) mesophase. This transition has been followed by various techniques (DSC, POM, and CD spectroscopy) and occurs both in bulk and thin films. Cooling form the liquid crystalline state to room temperature leads to the formation of a glass in which the chiral order is retained, causing selective transmission of circularly polarized light.

After fractionation on molecular weight, we were able to investigate the influence of four factors on the degree of supramolecular order by CD spectroscopy. Our results reveal the existence of a minimum chain length threshold that has to be overcome before any chiroptical activity is observed. With further increase of molecular weight, CD effects first increase until an optimal value is reached, beyond which a decrease is observed. DSC and POM studies of various **PF** and **PFBT** fractions are consistent with these observations. In addition to molecular weight, also annealing time, annealing temperature and film thickness have critical effects on the intensity of the optical activity.

We have demonstrated that both chain length and postdeposition treatment are important factors governing the organization of conjugated polymers in thin films. For monitoring these structural changes in chiral polymer films CD spectroscopy is a sensitive tool, particularly in combination with other characterization techniques such as DSC and POM. In particular, the existence of a molecular weight optimum for the CD effect strongly suggests that more attention should be paid to the molecular weight averages and distributions of organic polymeric semiconductors. By providing an improved understanding of the solid state organization processes in chiral fluorene based polymers, this approach might also yield further insights useful for organic electronics where typically achiral materials are used. Since a detailed knowledge of and control over the spatial arrangement and distribution of polymer chains in the active layer is indispensible for a rational optimization of the device performance, we anticipate that our method is a beneficial contribution to the field.

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Supporting Information Available: Text giving synthetic procedures, characterization of the polymers and supplementary experiments, a scheme showing the synthetic route, figures showing the NMR spectra, micrographs of the crude products, UV−vis and photoluminescence spectra, analytical SEC traces, DSC traces, linear dichroism specta, correlation of the CD effect with transition enthalpy, annealing temperature dependence of the UV−vis spectra, and CD spectra, and tables summarizing the optical properties and fractionation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(57) Although for **PF** all fractions gave CD effects, shorter monodisperse oligomers do not.
(58) It should be noted that for amuch longer chiral **PF** sample (M_n ca. 170000) a different temperature dependence has been reported (refs 41 and 48), which is most probably due to much slower ordering kinetics in this high molecular weight polymer.

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