Macromolecules **1999,** *32,* 227−230

Notes

Principles of "Majority Rules" and "Sergeants and Soldiers" Applied to the Aggregation of Optically Active Polythiophenes: Evidence for a Multichain Phenomenon

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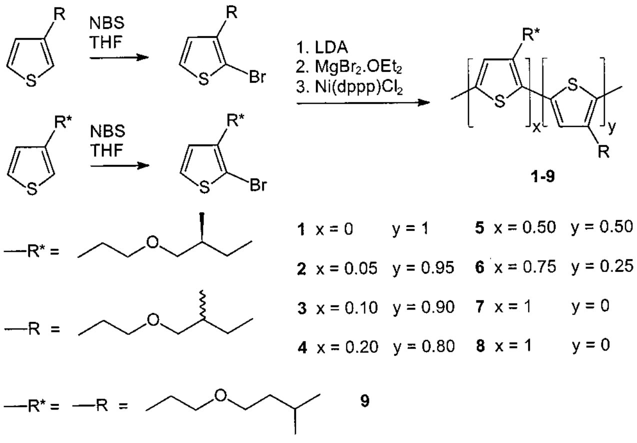
Received August 27, 1998
Revised Manuscript Received November 9, 1998

In many polymers, e.g., polypeptides, polymethacrylates, polysilanes, polyisocyanides, and polyisocyanates, the backbone adopts a helical conformation. A preference for one helical sense, *P* or *M*, can be obtained by introducing optically active monomers, which give rise to an additional element of asymmetry in the main chain or in the side chains of the polymer.[1] Such a preference can also be induced by an optically active solvent.[2] Cooperative effects of the monomer units along the polymer backbone may result in a nonlinear relation between the specific optical rotation and the enantiomeric excess (*ee*) of chiral units present in the polymer.[3] For the stiff helical polyisocyanates, these cooperative effects have led to observations referred to as "majority-rules" and "sergeant-and-soldiers" principles.[4,5] It has been shown that poly(*n*-alkyl isocyanate)s adopt an extended helical conformation in which long stretches of one handedness—referred to as the cooperative length L_c—are separated with high-energy reversals. When small portions of external chirality are added, cooperative effects strongly favor one helical sense. The external chirality can arise from the use of a small excess of one enantiomer over the other in the side chain—majority rules—or from the presence of only a small ratio of chiral side chains versus achiral side chains—sergeants and soldiers—and even chiral solvents can be used. More recently, it has been shown that these effects are operative in several polymers with a preferred helical backbone,[6] as well as in associates of discotic molecules in solution. In the latter the overall chirality is due to a chiral packing of the disks in a stack, while the expression of one handedness is obtained by chiral solvents or chiral side chains.[7]

π-Conjugated polymers carrying chiral side chains as solubilizing substituents form a special class of optically active polymers.[8] In general, these chiral *π*-conjugated polymers only exhibit strong chiroptical properties when the polymer chains aggregate into chiral superstructures. Recent reports on optically active polythiophenes show that the chiral aggregation in these systems can be influenced by subtle differences in the structure (e.g., regioregularity and substituents) and the ordering conditions (e.g., solvent and temperature).[9] To obtain insight into the ordering of *π*-conjugated polymers carrying optically active side chain substituents and the nature of their chiroptical properties, we set out to investigate the extent to which majority-rules and sergeants-and-soldiers principles are operative in chiral polythiophenes. Here we describe the organization of the polymer chains as a function of the optical purity of the side chain substituents and mixing−annealing experiments of chiral and achiral polythiophenes.

Scheme 1. Synthesis of Regioregular 3-Substituted Polythiophenes 1−9



The synthesis of polythiophenes **1**−**9** is outlined in Scheme 1. The 3-substituted thiophenes were prepared from 2-(3-thienyl)ethanol by reaction with the tosylates of either enantiomerically pure (*S*)-(−)-2-methyl-1-butanol, racemic 2-methyl-1-butanol, or 3-methyl-1-butanol. Selective bromination of these 3-substituted thiophenes at the 2-position was accomplished using NBS in THF. Polymers **1**−**9** were prepared by the McCullough procedure in a regioregular fashion.[10] For polymers **2**−**6**, the optically active (*S*) and racemic 2-bromo-3-[2-(2-methylbutoxy)ethyl]thiophene monomers were mixed in different ratios and polymerized. Salts and short oligomers were removed from the reaction mixtures by Soxhlet extractions with methanol and hexane, respectively. The polymers were isolated in moderate yields (10−30%) in a final Soxhlet extraction with chloroform. The ^{1}H NMR spectra of polymers **1**−**9** show a single well-defined symmetric peak in the aromatic region, related to the protons at the 4-position. The ^{13}C NMR spectra reveal four sharp resonances for the aromatic carbon atoms of the thiophene rings. These results are consistent with a well-defined regioregular head-to-tail structure. Obviously, neither NMR nor any other technique can give information on the actual stoichiometry of both enantiomers incorporated in polymers **2**−**6**. However, it is plausible to assume that the reactivity of both enantiomers is the same, since the synthesis is performed under conditions in which the chains are molecularly dissolved. Therefore, we will

10.1021/ma981349y CCC: $18.00

Table 1. Molecular Weight (M_w) and Polydispersity (D) of 1−9

polythiophene	(S)-*ee* (%)	M_w (kg/mol)	D
1	0	10.4	1.4
2	5	17.6	2.0
3	10	18.6	2.8
4	20	13.8	1.2
5	50	12.8	1.6
6	75	12.5	1.4
7[a]	100	27.0	2.0
8[a]	100	15.7	2.0
9		17.3	2.1

[a] Polymers **7** and **8** were prepared independently and differ by M_w.

assume in the following that the composition of the polymer chains is consistent with the monomer feed ratio and that the optically active monomers are randomly distributed along the polymer chains.[11] The molecular weight M_w and the polydispersity D ($= M_w/M_n$) of polythiophenes **1**−**9** as determined by SEC in tetrahydrofuran against polystyrene standards are presented in Table 1.

The UV/vis spectra of polythiophenes **1**−**7** dissolved in chloroform exhibit an inhomogeneously broadened π−π^* absorption band with $\lambda_{max} = 445$ nm. This absorption band shows no resolved vibrational fine structure and is associated with a conformationally disordered polymer chain. Under these conditions no optical activity is observed for the π−π^* transition as investigated with circular dichroism (CD) spectroscopy, irrespective of the *ee* of the chiral side chains. When the polymers are dissolved in a poor solvent, e.g., in 1-decanol, a highly ordered aggregated form is obtained when the solution is allowed to cool slowly from 393 K to ambient temperature. The UV/vis spectra of the solutions containing aggregates of **1**−**7** in 1-decanol are significantly red-shifted and exhibit a number of vibronic peaks and shoulders (Figure 1). Both the red shift and the appearance of vibrational fine structure indicate an increase of effective conjugation length and of conformational order in this aggregated form. The spectra shown in Figure 1 are normalized with respect to the absorption at 603 nm and demonstrate that the relative intensity of the vibronic peaks has no direct relation to the *ee*. The UV/vis spectra of **1**−**7** in 1-decanol closely resemble those of solution-cast films.

Except for the racemic derivative, the CD spectra of all polymers **1**−**7** in 1-decanol reveal a bisignate Cotton effect at the π−π^* transition which exhibits vibrational fine structure (Figure 1). The CD effect increases with increasing *ee*. The Cotton effect demonstrates that aggregation in a poor solvent is associated with the organization of the polymer chains into an optically active structure. The bisignate nature of the CD spectra, which is characteristic of exciton coupling between transition dipole moments on adjacent polymer chains,[12] supports our proposition that the optical activity results from a chiral orientation of polymer chains. For individual polymer chains with a helical conformation, the CD effect is not expected to be bisignate. We, therefore, propose that in polymers **2**−**7** the CD effect originates from essentially planar polymer chains that have a helical interchain order, rather than from an intramolecular helical conformation, in close similarity with the packing of cholesteric liquid crystals.[13,14] The preference for one handedness in the chiral orientation of the polythiophene chains results from the interaction between optically active side chains on adjacent main chains.

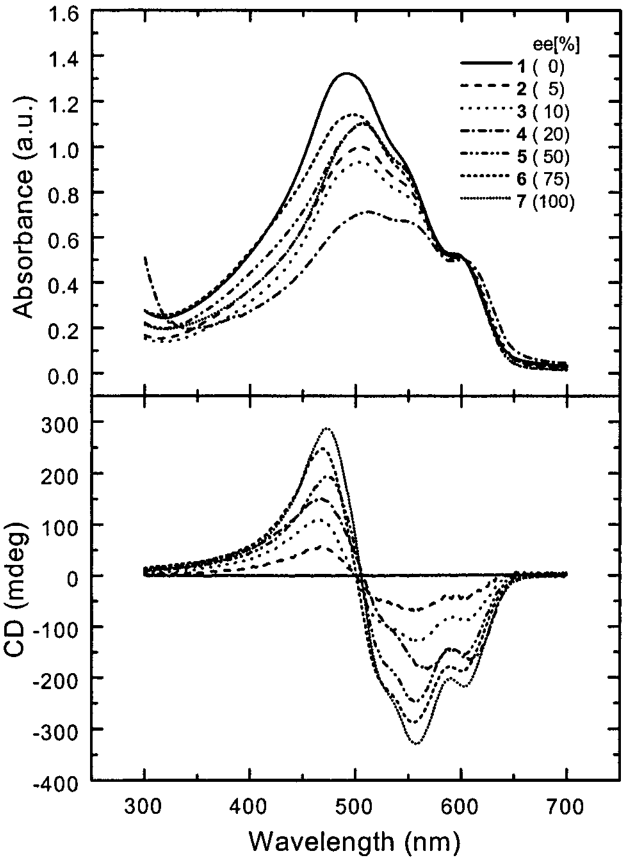


Figure 1. UV/vis and CD spectra of **1**−**7** (0−100% *ee*) in 1-decanol. The spectra are normalized with respect to the absorption at 603 nm. The experiments were carried out with polymer concentrations of ca. 30 μg/mL.

To measure the extent of optical activity associated with the main chains as a function of the *ee* of the side chains, we have plotted the anisotropy factor g ($g = \Delta\epsilon/\epsilon$, where ϵ is the extinction coefficient and $\Delta\epsilon$ the difference of the extinction coefficients of left and right circularly polarized light) at 603 nm of polymers **1**−**7** vs the *ee* in Figure 2.[15] The g value serves as a concentration-independent measure for the circular polarization in absorption of the aggregated phase, since the molecularly dissolved chain has a negligible absorption at 603 nm. Figure 2 shows a strongly nonlinear relation between the g value and *ee*. This effect indicates the presence of a cooperative behavior of the chiral side chains in the aggregation process and gives evidence that the concept of majority rules, originally developed for helical main chain polymers, also applies to the aggregation of polythiophenes in chiral superstructures. In this respect it is interesting to note that the R and S enantiomers of the 2-methylbutyl group are known for their ability to assume different conformations with very similar external shapes, and they can interchangeably enter the same space. This principle is exemplified by isoleucine in which disorder occurs through interchange of ethyl and methyl groups.[16]

When aggregated solutions of stereoregular **8** ($M_w = 15.7$ kg/mol) and achiral polythiophene **9** ($M_w = 17.3$ kg/mol) are prepared separately in 1-decanol and subsequently mixed at ambient temperature, the UV/vis spectra are simple linear superpositions of the two individual spectra, and the intensity of the CD spectrum

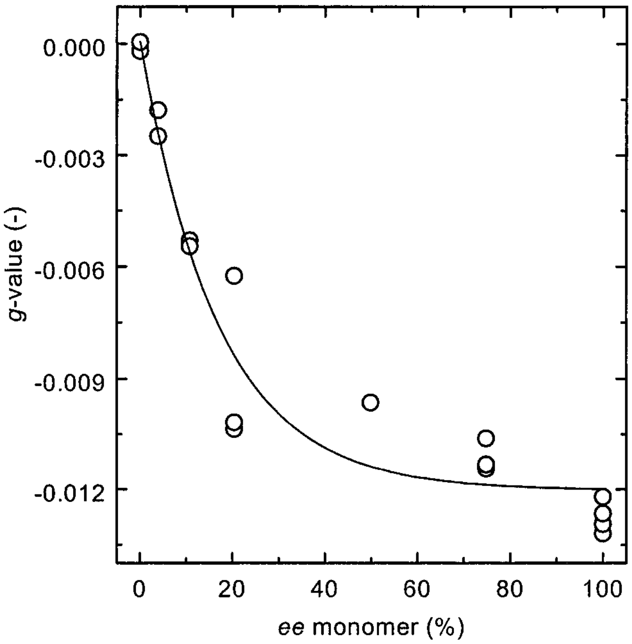


Figure 2. Anisotropy factor *g* at 603 nm for **1**−**7** (0−100% *ee*) in 1-decanol. The multiple entries at given *ee* are multiple determinations with the same polymer.

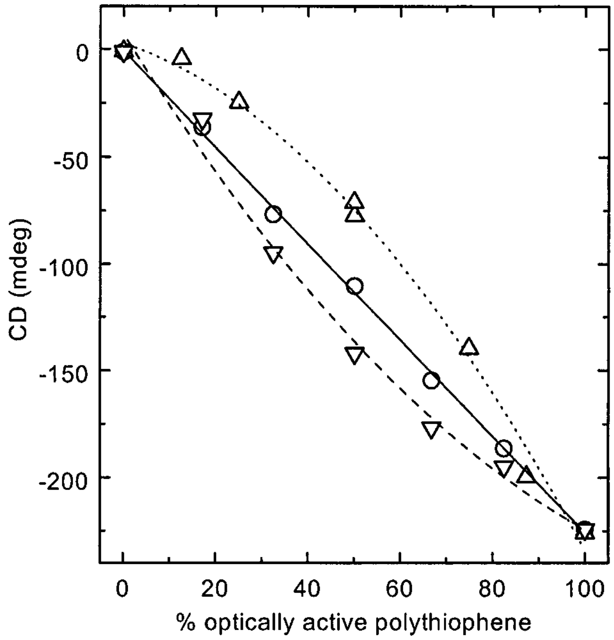


Figure 3. CD effects of mixed aggregates of stereoregular **7** or **8** with **9** in 1-decanol: (○) mixing at room temperature; (▽) mixing of **7** and **9** followed by annealing to 393 K and slow cooling to 293 K; (△) mixing of **8** and **9** followed by annealing to 393 K and slow cooling to 293 K. The experiments were carried out with polymer concentrations of ca. 30 μg/mL.

increases linearly with the weight ratio **8**:**9** (Figure 3, ○). However, when the mixtures are subsequently brought to a molecularly dissolved form by heating to 393 K and then allowed to cool slowly to ambient temperature, the outcome of the experiment changes. While the UV/vis spectra remain unaffected by this procedure, the intensity of the CD spectra is reduced. Figure 3 shows the reduced CD intensity at 603 nm of annealed samples (△) as compared to the CD spectra of the simple mixing experiments (○). When the same procedure is applied to a sample of stereoregular **7** with a higher molecular weight (M_w = 27.0 kg/mol) in combination with **9** (M_w = 17.3 kg/mol), an increase in the CD effects is observed (Figure 3, ▽). The opposite outcome of the mixing/annealing experiment of **8** with **9** compared to **7** and **9** might be an indication that the molecular weight is an important parameter in the aggregation and, hence, in the optical activity of chiral polythiophenes.

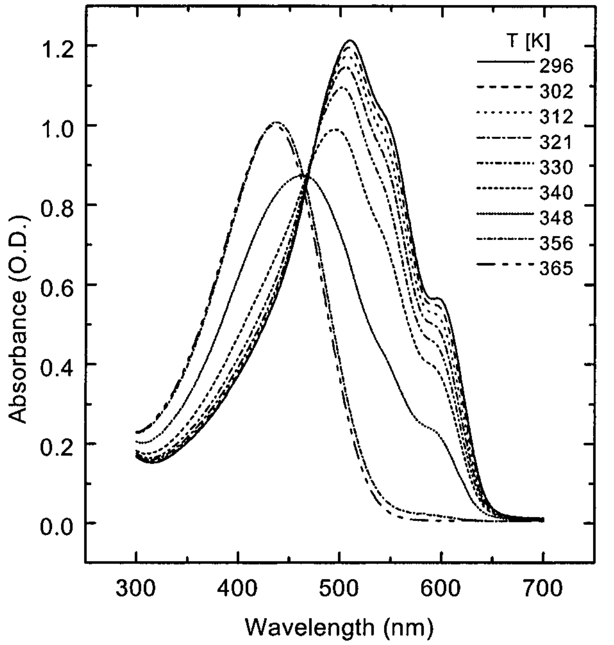


Figure 4. Variable temperature UV/vis spectra of polymer **8** in 1-decanol. Concentration = ca. 30 μg/mL.

To address the effect of M_w on the aggregation in more detail, the individual aggregation behavior of **7**, **8**, and **9** in 1-decanol has been studied with UV/vis spectroscopy as a function of temperature. Figure 4 shows the thermochromic behavior of **8** as an example. As shown in Figure 5, the temperature regions in which the transition between a disordered and ordered phase is observed differ for the three polymers. For high molecular weight polythiophenes **7** and **9** the transition between molecularly dissolved chains and aggregated chains occurs at a higher temperature than for **8**.

With this result, the different outcome of the mixing/annealing experiments of **7**/**9** and **8**/**9** can tentatively be explained by the assumption that "seed" aggregates are initially formed from the polymer chains that aggregate at higher temperatures. These seeds are either optically active due to the presence of chiral side chains or optically inactive due to the presence of achiral side chains. The seed aggregates then grow, by incorporating shorter chains, enforcing a handedness on achiral chains when they are incorporated in chiral aggregates, and vice versa. Hence, in the first experiment the achiral seeds formed from achiral **9** prevail, since the transition to an aggregated phase in **9** occurs at a higher temperature than for **8**. This results in a decrease of the overall CD effect when chains of **8** are incorporated into these aggregates. On the other hand, seeds of **7** will have a chiral superstructure, and hence the CD effect increases when chains of **9** are incorporated. Further support for this tentative explanation comes from a mixing/annealing experiment of **1** and **8** (not shown) where an increase of the CD effect is also observed.

These mixing/annealing experiments show unambiguously not only that the circular dichroism associated

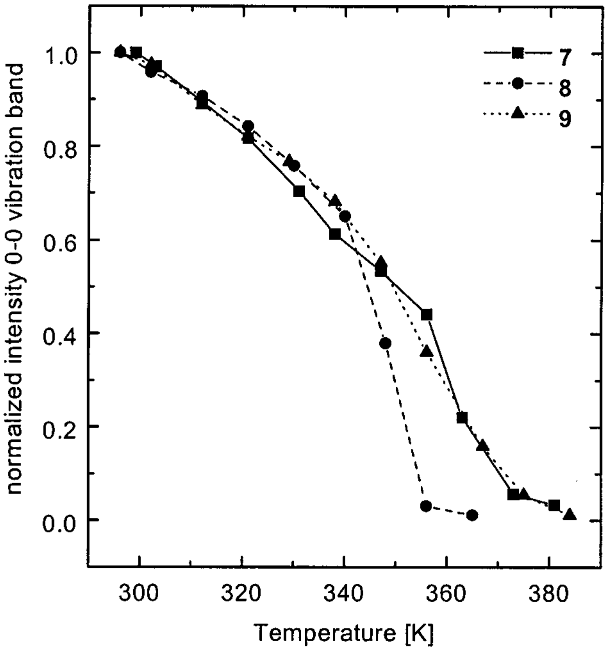


Figure 5. Relative intensity of the 0−0 vibronic transition at ca. 600 nm for polymers **7**, **8**, and **9** as a function of temperature determined from UV/vis absorption spectra recorded in 1-decanol.

with the $\pi-\pi^*$ transition of these polythiophenes has a multichain origin but also that a kind of sergeants-and-soldiers principle is operative. The chirality of the longest polymer chains controls the overall optical activity of the polythiophene aggregate.

We have shown that cooperative interactions between chiral and achiral side chains affect the optical activity of the polythiophene aggregates in a nonlinear fashion. The experiments show that the majority-rules principle is applicable to polythiophenes carrying both *R* and *S* optically active side chains. The magnitude of the effect, however, is less pronounced than for the helical main chain polyisocyanates. The mixing−annealing experiments give direct evidence of interactions between different polymer chains during the ordering process and give credence to a kind of sergeants-and-soldiers principle in which the longest chains determine the chirality of the aggregated form.[17] This process strongly supports the proposal that the aggregation of π-conjugated polymers is a multichain event even in the case of very dilute solutions.

Acknowledgment. This research has been supported by an unrestricted research grant of Philips Research.

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MA981349Y