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The First Optically Active Polycarbazoles

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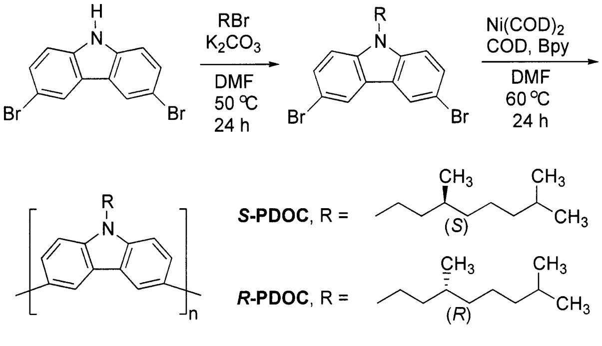
The highly ordered chiral structures in naturally occurring polymers play a significant role in determining their precise and sophisticated biochemical functionalities. The design of synthetic helical polymers capable of emulating the chiral recognition properties of biopolymers is currently a focus of much interest. Enantioseparation, catalysis, and sensing are among the more promising applications of molecular recognition based on responsive three-dimensional intramolecular or intermolecular superchiral structures.[1−8] Optically active conjugated polymers[9−11] represent an attractive class of chiral macromolecules adaptable to this purpose because their chiral behavior can be augmented by nonlinear electrically conductive or optical properties[12−15] arising from conjugation along the backbone. In this Communication, we report the first example of optically active polycarbazoles. These novel chiral π-conjugated polymers are proposed to adopt a highly ordered chiral backbone conformation within a single polymer chain, but a chiral interchain π-stacking structure in their aggregates. The maintenance of the second-order chiral backbone conformation along each polymer chain during aggregation leads to a novel type of higher order chiral superstructure in the aggregates, suggesting that optically active polycarbazoles will be useful tools for developing and understanding chiral polymeric materials.

Poly[*N*-(*R*)- or (*S*)-3,7-dimethyloctyl-3,6-carbazole]s (*R*- or *S*-PDOC) were synthesized in 60−70% yield using our modified nickel(0) coupling method (Scheme 1).[16]

Scheme 1. Synthesis of Optically Active Polycarbazoles



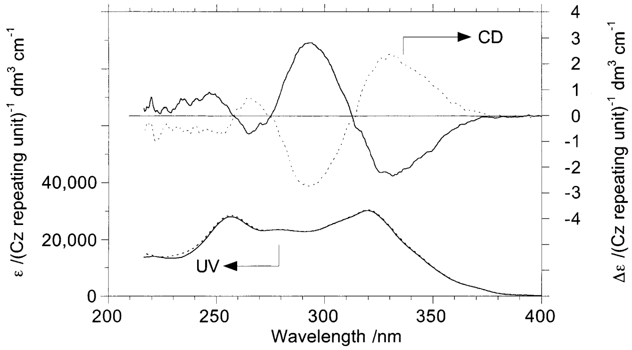


Figure 1. UV−vis and CD spectra of *S*-PDOC (M_w = 70 600, M_w/M_n = 2.38, DP$_n$ (number-average degree of polymerization) = 97) (solid lines) and *R*-PDOC (sample molecular weight: M_w = 79 800, M_w/M_n = 1.54, DP$_n$ = 169) (dashed lines) in THF at 20 °C (sample concentration: 4 × 10^{-5} M, based on carbazole repeating unit).

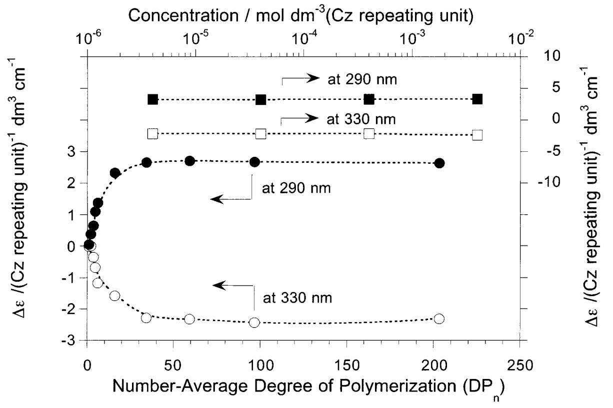


Figure 2. Concentration (squares) (M_w = 70 600, M_w/M_n = 2.38, DP$_n$ = 97) and molecular weight (circles) (sample concentration: 4 × 10^{-5} M, based on carbazole repeating unit) dependence of the CD of *S*-PDOC in THF at 20 °C.

The weight-average molecular weights (M_w) of *R*- and *S*-PDOC were 79 800 (M_w/M_n = 1.54) and 70 600 (M_w/M_n = 2.38), respectively. The structures of both the monomers and polymers were confirmed by ^{1}H and ^{13}C NMR and by elemental analyses. Differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) were carried out to determine the thermal transition and degradation behavior of the polymers. The DSC measurements on *R*-PDOC showed a glass transition temperature of 156 °C and 155 °C for *S*-PDOC. On the basis of the TGA measurements, both *R*- and *S*-PDOC display a high thermal stability. The 5% weight loss temperatures of the polymers during heating runs were 410 °C for *R*-PDOC and 400 °C for *S*-PDOC.

In the circular dichroism (CD) spectra of *R*- and *S*-PDOC in tetrahydrofuran (THF) (Figure 1), mirror-image bisignated Cotton effects were clearly observed in the π−π^* transition region. To elucidate the origin of the observed Cotton effects, the polymer concentration dependence of the CD and ultraviolet−visible absorption (UV−vis) signals was measured in THF (Figure 2). These results demonstrate the independence of both the CD and UV−vis signals on *S*-PDOC concentration over a broad range (10^{-6}−10^{-3} mol L^{-1}), indicating that the interchain interaction is minimal. Thus, the observed

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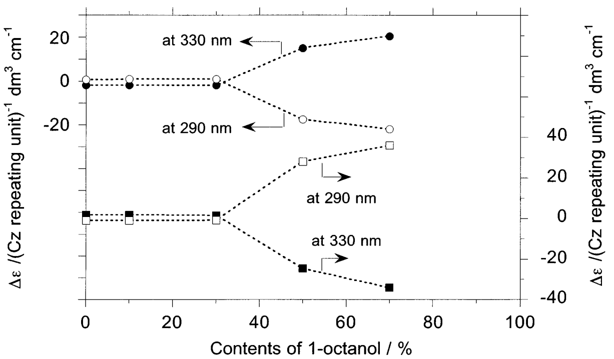

Figure 3. Solvent effect on the CD of *S*-PDOC ($M_w = 70\ 600$, $M_w/M_n = 2.38$, $DP_n = 97$) (circles) and *R*-PDOC ($M_w = 79\ 800$, $M_w/M_n = 1.54$, $DP_n = 169$) (squares) dependent on 1-octanol contents in THF/1-octanol cosolvent system at 20 °C (sample concentration: 4×10^{-5} M, based on carbazole repeating unit).

chiroptical properties can be accounted for by the chirality of the individual polymer chains.

To further confirm this, solvent effects on the optical properties of *S*-PDOC were investigated. In a series of cosolvent systems consisting of THF and 1-octanol (a poor solvent for the polymers) in different ratios, a significant solvent dependence in the CD spectra was observed (Figure 3). At lower 1-octanol content (10−30%), the CD is identical to that in THF (see Supporting Information). A dramatic change occurred when the 1-octanol content reached 50%: not only the absolute magnitude of the original CD near 290 and 330 nm increased remarkably, but also the sign of the CD reversed at both wavelengths. Minimal change was found in the CD and UV−vis spectra before and after filtration through a 0.45 μm membrane at lower content of 1-octanol (0−30%), while complete disappearance of both CD and UV−vis signals was observed when the 1-octanol content reached 50%, clearly indicating the formation of aggregates in the latter case. These results, together with the concentration independence of CD and UV−vis spectra, indicate the different origins of the observed optical activity at different 1-octanol concentrations. At lower 1-octanol contents, the chiroptical properties of the polymer originate from an intramolecularly chiral structure corresponding to a molecularly dispersed state, whereas in the aggregates they arise mainly from the interchain chiral stacking superstructure.[17]

The possible chiral motifs in an optically active conjugated polymer in a molecularly dispersed state are (1) a higher order structure with preferential screw sense helicity in the monomolecular polymer[9] and (2) a predominantly unidirectionally coupled conformation of neighboring repeating units or one involving limited backbone segments.[22] The CDs of *S*-PDOC having different molecular weights (see Supporting Information) were measured in THF (Figure 2). The molar CD intensity increased continuously when the number-average degree of polymerization (DP_n) was less than 34, while it reached a constant value when DP_n exceeded 34, indicating the existence of second-order chiral structure in the individual polymer chains. Molecular mechanics calculations (see Supporting Information) were performed on a (*S*)-3,7-dimethyloctyloligocarbazole with 30 repeating units terminated with hydrogen. Two local energy minima corresponding to opposite helices with dihedral angles at around 140° and 230° were found, which would be consistent with the existence of a helical conformation in each polymer chain, accounting for the observed optical activity in the solution state.[23]

Effective conjugation along the backbones of conjugated polymers, strongly associated with the absorption maxima and extinction coefficients of their absorption spectra, can be significantly affected by conformational changes in the main chains arising from the response to certain external stimuli such as solvent, temperature, and ionic effects, a phenomenon which has found extensive applications in sensing technology.[12] Conjugated polymers can also change their backbone conformation remarkably upon formation of aggregates, resulting in a large red shift in their UV−vis absorption and quenching of their luminescence, which has been attributed to a nonplanar−planar conformation transition driven by interchain $\pi-\pi$ stacking.[24] It is noteworthy that minimal change was observed in the UV−vis spectra (see Supporting Information) of *S*-PDOC before and after the formation of aggregates. As the relative amount of 1-octanol in the solvent is increased, the λ_{max} are almost unchanged, while a sideband at around 348 nm due to the 0−0 transition[25] slightly increases in intensity, indicating minimal change in the backbone conformation. On the basis of these observations, we propose that the chiral structure incorporated in each individual polymer chain is maintained after aggregation, forming a chiral superstructure via a stacking process. This apparent rigidity of the intramolecular chiral backbone conformation in the aggregates may provide a novel basis for the possible application of polycarbazoles in material science, especially when the intramolecular chiral structure in the solid state is crucial to the chemical performance of the material.

It should be noted that the difference in polydispersity values of *R*-PDOC (1.54) and *S*-PDOC (2.38)[26] has no effect on their chiroptical properties in the molecularly dispersed state (mirror images with similar intensities, Figure 1), consistent with the CD and UV−vis molecular weight independence of *S*-PDOC over a high molecular weight range (Figure 2). However, a remarkable difference in their optical activities was observed for the aggregated state: the magnitudes of both peaks in the bisignated CD spectrum of *R*-PDOC (~40) were much larger than those of *S*-PDOC (~20) (Figure 3), most probably because of a narrower molecular weight distribution in the former case, producing a smaller structural difference between polymer chains and thus favoring more efficient $\pi-\pi$ stacking.

In summary, we have described a novel chiral conjugated polymer, the first polycarbazole optically active in both molecularly dispersed and aggregation states. A second-order chiral backbone conformation incorporated in each single polymer chain and a superchiral structure based on interchain $\pi-\pi$ stacking are proposed to account for the observed chiroptical spectra in solvents favoring dispersion or aggregation, respectively. Theoretical calculations show that chiral polycarbazoles most probably adopt a helical conformation along each polymer backbone. The negligible effect in the absorption spectra of aggregated polycarbazoles indicates the maintenance of the single-chain chiral backbone conformation. This unusual phenomenon in aggregation effect on optical properties of a conjugated polymer provides a novel concept in macromolecular superchiral arrangements. The rigidity of the monomolecular chiral conformation, good thermal stability, and also the presence of nitrogen atoms in the backbone providing potential sites for molecular detection or derivatization suggest that the polycarbazole system is a promising candidate for creation of novel chiral polymeric materials.

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Supporting Information Available: Details of syntheses and purifications, ^{1}H and ^{13}C NMR data, elemental analyses data, and concentration, molecular weight, and solvent-dependent CD and UV−vis spectra for the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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