Molecular Motors

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A Thermal and Solvocontrollable Cylindrical Nanoshutter Based on a Single Screw-Sense Helical Polyguanidine**

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Controlling and switching the chiroptical properties, for example, electronic circular dichroism (ECD) and optical rotation, of helical polymers continues to attract great interest because of potential applications in sensor data storage, optical devices, and liquid crystalline displays.[1] Thermo-driven and/or solvent-driven switching helical polymers in particular have been studied extensively; examples include poly(L-aspartate β-esters),[2] polyisocyanates,[3] polysilanes,[1d,4] and polyacetylenes.[5] These helical polymers possess chiral moieties, which are introduced from chiral monomers, into the polymer backbones or side chains. These switching phenomena are generally interpreted to date as helical inversions that occur in the polymer backbones and which are driven by thermal or solvent-polarity changes.

We recently reported a novel thermal and solvocontrollable switching polyguanidine (poly-**1**, Figure 1), which was synthesized by helix-sense-selective polymerization of an achiral monomer.[6] Three possible mechanisms were proposed to explain this interesting switching phenomenon: helix inversions φ,[2–5] imine inversions ω,[7] and/or rotations around the $N{-}C_{\text{anthracene}}$ bonds θ[8] (Scheme 1). The switching phenomenon was further studied by using vibrational circular dichroism (VCD)[9] and computational modeling techniques to determine the specific mechanism. We herein report that the switching phenomenon arises from large-amplitude ordered synchronous wagging of the anthracene units without helical and imine inversions. This system is a new model for a nano molecular motor:[10] a cylindrical nanoshutter that transforms the low-input energy of thermal and/or solvent-polarity changes to mechanical output (work) through the synchronous wag of the aligned anthracene units. We also assigned the helicity of poly-**1** as *P* by means of density functional theory (DFT) calculations[11] and showed that it remains fixed during the reversible shuttering phenomenon.

Regioregular, stereoregular poly-**1** ($M_w = 16\,000$, $M_w/M_n = 2.7$) was obtained by helix-sense-selective polymerization of an achiral carbodiimide of **1** using chiral catalyst R–Ti.[6a] The chirality of this macromolecule is because of 1) its single-handed screw sense and 2) the stereoregular registry of both the anthracene units and the projection angle of the imine groups.

Full racemization requires transition through a symmetric intermediate which involves inversion of the helix sense φ and at least one or both of the molecular motions: free rotations around $N{-}C_{\text{anthracene}}$ θ and imine inversion ω. The complete racemization of poly-**1** in toluene requires high temperatures of nearly 80 °C for reaction times longer than 100 hours.

However, the ECD and UV/Vis spectra of poly-**1** are reversibly switched when a solution of poly-**1** in toluene is heated and cooled cyclically between 25 and 60 °C (Figure 2A). Poly-**1** shows a positive Cotton effect of $\Delta\varepsilon = +2.0\,\text{M}^{-1}\,\text{cm}^{-1}$ at 382.0 nm and 25 °C, but a negative one of $\Delta\varepsilon = -2.6\,\text{M}^{-1}\,\text{cm}^{-1}$ at 382.0 nm and 60 °C. Poly-**1** shows an intense absorption of $\varepsilon = 5400\,\text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda_{\max} = 384.4$ nm and 25 °C, but a less intense absorption of $\varepsilon = 4700\,\text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda_{\max} = 382.4$ nm and 60 °C, thus corresponding to the ECD switching. It is of note that the wavelengths of the absorption maxima undergo a slight blue/red shift along with the heating–cooling cycles. Very large changes in the optical-rotation values are also observed between 31 and 40 °C (e.g., +297–−77°). The optical-rotation data indicate that the switching temperature is 38.5 °C. This switching phenomenon also can be observed when the polarity of the solvent is changed (Figure 2B). For example, the ECD spectra of poly-**1** exhibit a negative Cotton effect in the polar solvents THF (dipole moment $\mu = 1.75$ D, dielectric constant $\varepsilon' = 7.5$) and $CHCl_3$ ($\mu = 1.15$ D, $\varepsilon' = 4.8$) at 25 °C, thus resembling that observed in toluene ($\mu = 0.31$ D, $\varepsilon' = 2.4$) at the higher temperature of 60 °C. The switching point occurs at 10 vol % of toluene in a mixed solvent system of THF/toluene.

Of the three possible mechanisms to explain this interesting switching phenomenon, that is, helix inversion, imine inversion, and/or rotation around the $N{-}C_{\text{anthracene}}$ bonds, partial rotation (reorientation) around the $N{-}C_{\text{anthracene}}$ bonds is the lowest-energy process. Notably, the free rotation around $N{-}C_{\text{anthracene}}$ is prohibited because the distance between two anthracene units is less than the length of one anthracene unit. Reversible switching occurs quickly (within seconds) in both the thermo-driven process at the lower temperature of 38.5 °C in toluene and in the solvent-driven process relative to the time-consuming (100 hours) and energy-demanding (80 °C) full-racemization process. This increase implies that the imine configuration inversion and the helix inversion in poly-**1** are not involved in the reversible switching process.

The barrier of imine inversion in small molecules is in the range 20–26 $\text{kcal}\,\text{mol}^{-1}$ (coalescence temperatures are in the range 50–180 °C).[7] The required temperature is much higher than the switching temperature of 38.5 °C, which is hence further indication that the imine inversion is unlikely in the observed switching process.

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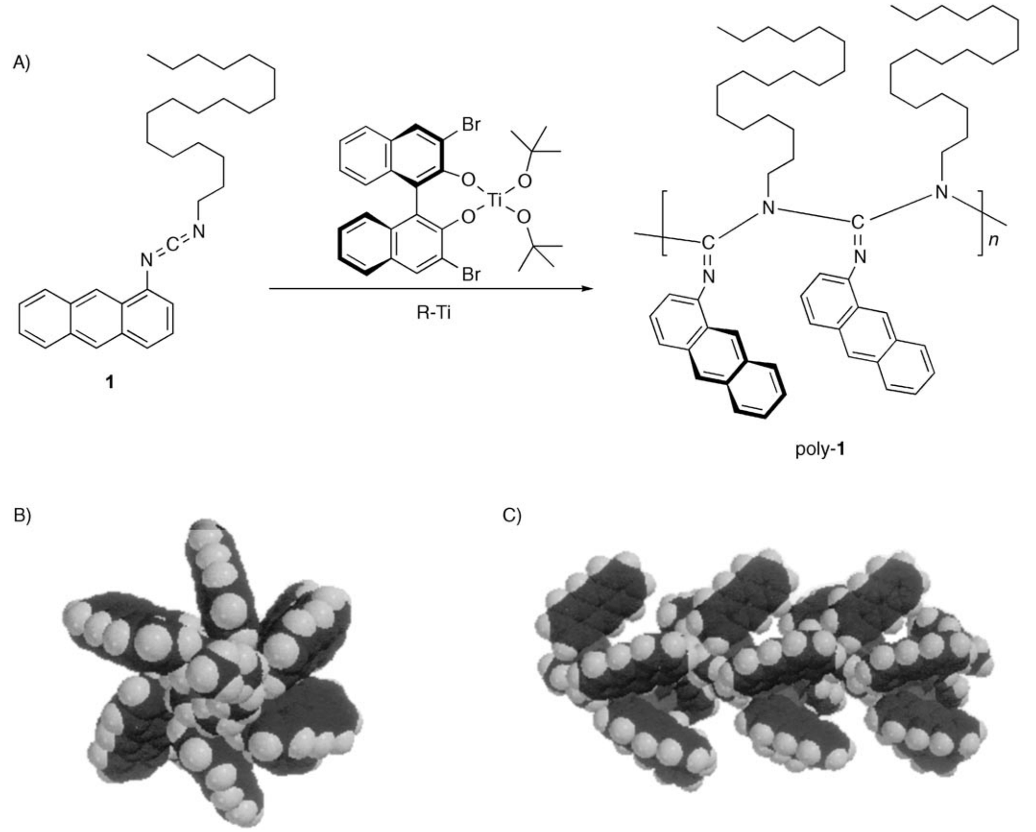
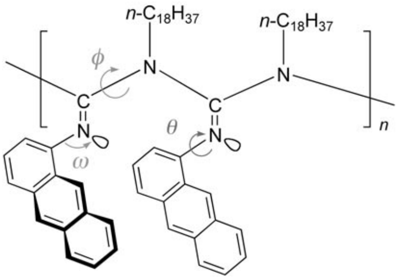


Figure 1. A) Synthesis of regioregular, stereoregular poly-**1**. B) Top view and C) side view of the 6_1-helical structure of poly-**1** (18-mer). Methyl groups replace *n*-octadecyl groups in poly-**1** to clarify the orientation of the anthracene units.



Scheme 1. Three possible molecular motions in the helical poly-**1**.

Standard variable-temperature (VT) ^{1}H and ^{13}C NMR spectroscopic experiments to elucidate the origin of the switching process were attempted (see the Supporting Information). However, these studies proved inconclusive because of signal broadening. VCD studies were then carried out in the polar solvent $CHCl_3$ and the less-polar solvent toluene at various temperatures to clarify the nature of the switching phenomenon in poly-**1** (as observed from the ECD and optical-rotation studies). To our surprise, the VCD spectra of poly-**1** remained unchanged except for a slight variation in intensity, unlike the ECD spectra. Typical VCD spectra of poly-**1** in $CHCl_3$ and toluene at 25 °C are shown in Figure 3B,C in which a large bisignate couplet at 1641 cm^{-1} is exhibited that matches the vibrational absorbance of imine groups in the polyguanidine backbone (Figure 3A). The concentrations used for the measurement of VCD are significantly greater than those for ECD. The ECD was measured at the concentrations used for the VCD studies to determine whether concentration may have had an influence. We found, however, that ECD spectra at higher concentrations have the similar ECD values as those at lower concentrations. These VCD data strongly support that the chirality of the helical polyguanidine backbone does not change during the reversible switching of the observed ECD and optical-rotation properties. The extremely slight change in the VCD intensity also implies that there is no change in the helical pitch during this switching process.

These two contradictory observations, namely, switching of the ECD and optical-rotation properties with temperature and solvent polarity and the lack of such switching of VCD, can only be reconciled if the anthracene units are considered to wag synchronously around the $N{-}C_{anthracene}$ bonds (thereby acting like a shutter). In that event, the orientation of the anthracene units relative to the position of the lone-pair electrons on the nitrogen atoms changes, which in turn changes the lone-pair/π-electron interactions, and hence the ECD and optical-rotation properties, but the chirality sensed by the vibrations of C=N bonds is not effected.

The blue/red shifts in the UV/Vis absorption and ECD bands above and below the switching temperature (Figure 2), also suggest that the orientation of the anthracene units cooperatively switch relative to the helix director (namely, wagging around $N{-}C_{anthracene}$ θ). Further computational mod-

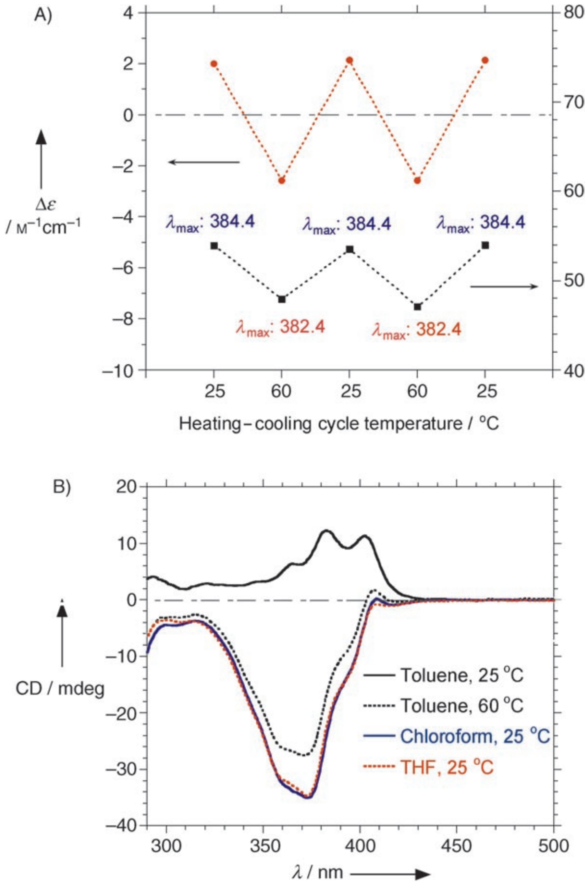


Figure 2. A) Heating–cooling thermal cycles of poly-**1** in toluene ($c = 2.1\times10^{-4}$ M, path length = 10 mm); wavelength for $\Delta\varepsilon$ is 382.0 nm. B) ECD spectra of poly-**1** in toluene at 25 and 60 °C, in $CHCl_3$ at 25 °C, and in THF at 25 °C; the intensities of the corresponding UV/Vis absorption maxima are normalized to 1.0. Very slight changes were observed in the ECD spectra of poly-**1** in THF and $CHCl_3$ when the solutions were heated to 50 °C. The ECD spectra of poly-**1** are independent of concentration in the range 2.1×10^{-4}–5.3×10^{-2} M. Dihedral angles [°] of **2**: C1-N2-C3-N4 −150, C1′-N2′-C3′-N4′ −153, N2-C3-N4-C5 −166, N2′-C3′-N4′-C5′ −168, C3-N4-C5-C6 63, C3′-N4′-C5′-C6′ 66, N2-C3-N2′-C3′ −103.

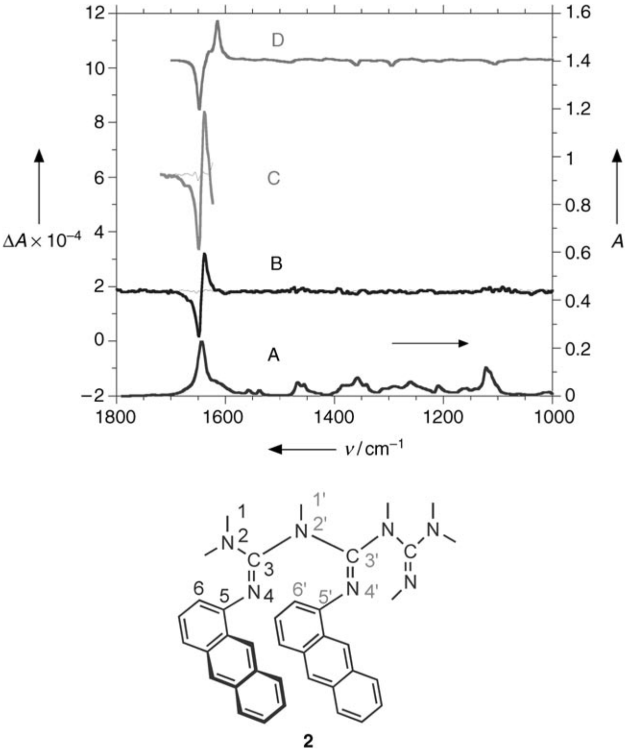


Figure 3. A) The experimental vibrational absorbance and B) VCD spectra of poly-**1** in $CDCl_3$ at 25 °C ($c = 10.0$ mg mL^{-1}, path length = 300 μm). c) VCD spectrum of poly-**1** in toluene at 25 °C ($c = 20.1$ mg mL^{-1}, path length = 200 μm) is also shown. The solvent absorption and VCD values were subtracted from the corresponding experimental spectra. The flat thin lines represent the noise level in the VCD spectra. D) The optimized *P* model **2** and its VCD spectrum calculated by density functional theory using B3LYP functional and 6-31G(d) basis sets. The calculated frequencies were scaled with 0.9613.

eling on this system was carried out to confirm these suggestions. Our working model (Figure 4) consists of a lower-energy state (**I**, $\mu_{\mathbf{I}} = 6.9$ D), which has the dipole moments of the flipping ends of the anthracene aligned opposing the helix director, and a higher-energy state (**II**, $\mu_{\mathbf{II}} = 7.7$ D), which has the dipole moments of the anthracenes aligned with the helix director; the polar solvents stabilize the more polar second state. In this reversible cooperative switching process, the chirality, the imine configuration, and the helical pitches remain unchanged.

It is a challenge to assign the chirality of poly-**1**. We built and initially optimized model compound **2** (Figure 3) with molecular mechanics MMFF94,[13] and optimized its *P* structure by DFT at the B3LYP/6-31G(d) level[14] with the Gaussian98 program. The VCD spectrum, calculated at this optimized geometry, is in excellent agreement with the experimentally observed VCD spectra of poly-**1** (Figure 3 D), thus indicating that poly-**1** is a *P* structure.

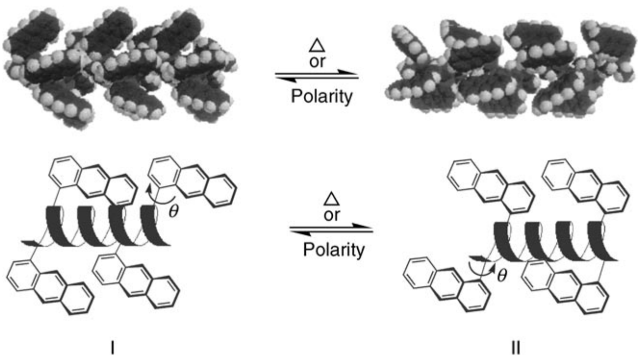


Figure 4. Theoretical models of the two states which result from the shutter-like motions of the anthracene unit. The geometries of these two states were determined by optimization of the repeat unit at the semiempirical level (AM1)[12] and then optimization of the 18-mer at the molecular-mechanics level (MMFF94).[13]

We have clarified the mechanism of the unusually large reversible thermo- and solvent-driven shuttering phenomenon of poly-**1**. We have also successfully assigned the helicity of poly-**1** as *P* and showed that it remains fixed during the reversible shuttering phenomenon. This anthracene-containing polyguanidine nanoshutter underwent large-amplitude ordered synchronous wagging of anthracene units relative to the helix director when actuated by a change in energy caused by temperature or solvent polarity, and exhibited two important criteria for the bottom-up construction of a nanomachine. Further modification and applications (e.g., display technology) are currently under investigation.

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