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Stable Helical Polyguanidines: Poly{*N*-(1-anthryl)-*N'*-[(*R*)- and/or (*S*)-3,7-dimethyloctyl]guanidines}

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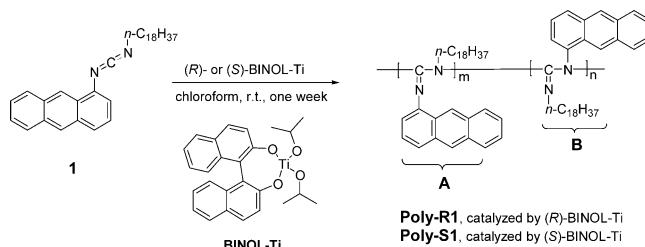
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Helical polymers are of interest due to broad potential applications, which include molecular recognition, molecular scaffolding for controlled alignment of functional groups or chromophores, and ordered molecular alignment in solids such as that in liquid crystalline materials.¹ Synthetic helical polymers can be classified into two categories: fluxional and nonfluxional chains. Fluxional chains have low helix inversion barriers that allow frequent occurrences of helix reversals. Examples include polysilanes,² polyisocyanates,³ and poly(*cis*-acetylenes).⁴ The removal and introduction of helix reversals can be a dynamic process, and reversible equilibrium between the two helical states (*P*- and *M*-handed) can be sometimes observed. Nonfluxional helices, the rarer of the two categories, have higher inversion barriers typically introduced by incorporating bulky side chains that hinder main chain bond rotations. Examples include isotactic poly(trityl methacrylate),¹ polychloral,⁵ and polyisocyanides.⁶ Because of their high inversion barriers, there are examples where these materials can be isolated in kinetically controlled conformations, KCCs, that do not correspond to the thermodynamically controlled conformation (TCC) minimum. Annealing at elevated temperatures will often allow these materials to adopt their low-energy helical conformations. Herein, we wish to report a new polyguanidine derivative wherein the KCC and TCC are equivalent. This coincidence results in unusually robust helical materials.

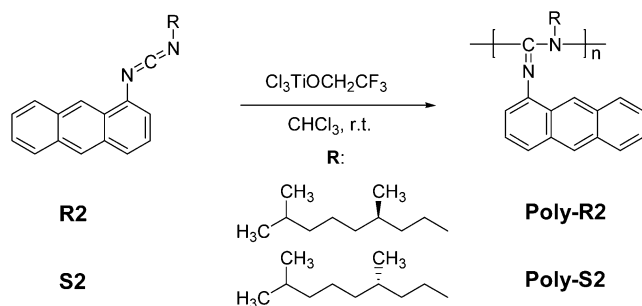
Among the helical polymers, we are particularly interested in polyguanidines featuring stiff polymer backbones.⁷ We recently reported the living polymerization of carbodiimides catalyzed by titanium complexes and/or copper amidinate complexes.⁸ Polyguanidines having homochiral side chains show an interesting phenomenon that if dilute solutions are annealed at higher temperatures, their optical rotations change sign, or dramatically increase in magnitude, which can be ascribed to an evolution of polymer chains from KCCs to TCCs.⁹ We have reported an optically active polyguanidine, poly{*N*-[(*R*)-2,6-dimethylheptyl]-*N'*-hexylguanidine}, whose highly disordered KCC ($[\alpha]_{365}^{20} = +7.5^\circ$, hexane) evolved into an ordered helical TCC structure ($[\alpha]_{365}^{20} = -157.5^\circ$) when annealed.^{9a}

For many applications (e.g., chromatography, optical materials, etc.), highly stable helices are required.¹ One interesting challenge is the design of a stable polyguanidine helix with the same KCC and TCC. In some helical polymers, intramolecular hydrogen bonds and bulky side chains can stabilize their helices. Of the two approaches, incorporating a bulky side group on the polymer backbone is preferred because hydrogen bonds are readily broken by thermal stimuli.⁴ It is the latter approach we chose to pursue. To provide steric bulk and a UV-vis chromophore suitable for studying the polymer conformations in organic solvents, we selected to use anthracene as the side chains for the polymer. We herein report the first example of the stable polyguanidine helices of **Poly-R2** and **Poly-S2** (Scheme 2) in solutions.

Scheme 1



Scheme 2



To test whether anthracene side chains provide sufficient steric bulk to stabilize the helix, we studied the polymers with these side chains from achiral monomers. Using (*R*)- and (*S*)-**BINOL-Ti** (Scheme 1), the best chiral catalysts for asymmetrical polymerization of achiral carbodiimides,^{9b} we obtained soluble **Poly-R1** ($[\alpha]_{\text{D}}^{20} = +130^\circ$, toluene) and **Poly-S1** ($[\alpha]_{\text{D}}^{20} = -51^\circ$, toluene). The large optical rotations suggest that **Poly-R1** and **Poly-S1** adopt helical conformations in toluene with opposite preferred handed screw sense. Three guanidine absorptions in IR at 1641, 1620, and 1608 cm^{-1} suggest that **Poly-R1** and **Poly-S1** are not regioregular polymers, but have mixed **A**- and **B**-segments (Scheme 1). These regioisomers may result from the polymerization process in which different catalytically active species exist in solution. They can be monomeric, open, dinuclear, trinuclear, and trimeric forms of **BINOL-Ti**.¹⁰ It is also possible that the two segments comprise different polymer chains. When annealed in toluene at elevated temperatures (70–80 $^\circ\text{C}$), the optical rotation of **Poly-R1** goes to zero, indicating that the helix undergoes a racemization process. Kinetic studies reveal this to be a slow process with an activation energy of ca. 36 kcal/mol. This is the highest polyguanidine inversion barrier reported to date.

Stable one-handed helical polymer requires regioregular main chains and bulky side groups to prevent conformational racemization by external stimuli. We then turned to the polymerization of chiral monomers. Using titanium(IV) trifluoroethoxide catalyst (Scheme 2), we obtained **Poly-R2** and **Poly-S2** in high yields. Contrary to **Poly-R1** and **Poly-S1**, **Poly-R2** and **Poly-S2** show a sharply single guanidine absorption peak at 1622 cm^{-1} in IR,

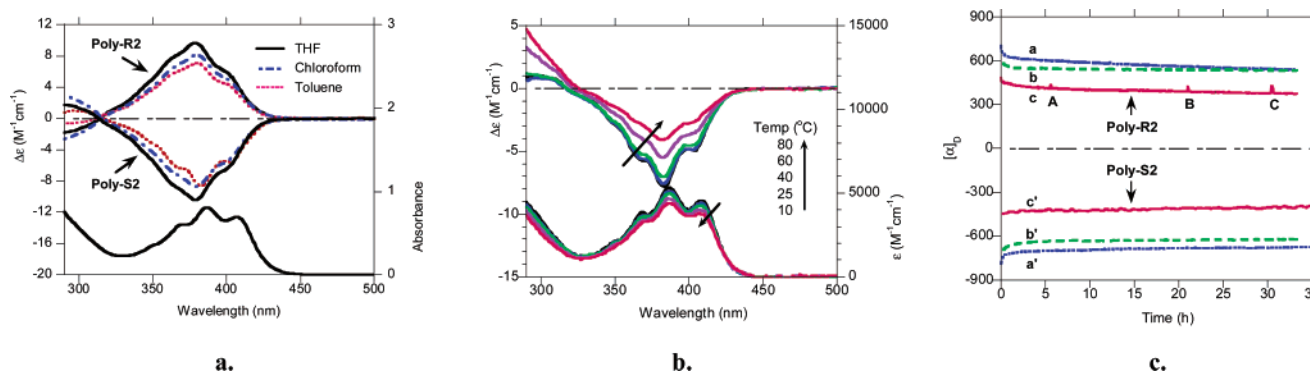


Figure 1. (a) CD (top) and UV-vis (bottom) spectra of **Poly-R2** and **Poly-S2** in solutions at 25 °C. (b) CD (top) and UV-vis (bottom) spectra of **Poly-S2** in toluene at different temperatures. These changes are fully reversible. (c) Specific rotations as a function of annealing time. **a** and **a'**, in THF at 50 °C; **b** and **b'**, in chloroform at 50 °C; **c** and **c'**, in toluene at 80 °C.

indicating that the polymer main chains are almost uniformly regioregular. This is also supported by powered X-ray diffraction data. A sharp reflection peak at $2\theta = 5.48^\circ$ indicates that **Poly-S2** is a crystalline polymer possessing a uniform structure. ^1H NMR measurements indicate the aromatic group is located on the imine. It is worth noting that Lu et al. also reached the same conclusion for poly{*N*-[(*R*)-2,6-dimethylheptyl]-*N'*-phenylguanidine}.^{9b}

The specific rotations of **Poly-R2** ($[\alpha]_D^{25} = +791^\circ$, toluene) and **Poly-S2** ($[\alpha]_D^{25} = -778^\circ$, toluene) are opposite in sign and much greater in magnitude as compared to their corresponding monomers of **R2** ($[\alpha]_{577}^{25} = -2.7^\circ$, toluene) and **S2** ($[\alpha]_{577}^{25} = +2.6^\circ$, toluene), implying that **Poly-R2** and **Poly-S2** adopt regular one-handed helical conformations with opposite screw sense in solution. This is further confirmed by CD spectroscopy. **Poly-R2** and **Poly-S2** show mirror-image intense CD signals in THF, chloroform, and toluene, which correspond to their UV-vis absorptions (Figure 1a).

External stimuli such as solvent polarity or temperature can dramatically affect the chain conformations. This phenomenon is always observed for polyguanidines. However, the UV-vis/CD spectra of **Poly-R2** and **Poly-S2** in different solvents used here including toluene, chloroform, and THF exhibited the same shape, indicating that the solvation did not cause any significant conformational change of the helix (Figure 1a). The solvents may only slightly affect the orientation of side chains. Contrary to all other polyguanidines, **Poly-R2** and **Poly-S2** also show remarkable helical stabilities when heated. As an example in toluene, the optical rotations and UV-vis/CD spectra (Figure 1b) almost exhibit no changes below 55 °C. The slight decrease in intensity of UV-vis/CD spectra above 60 °C is fully reversible and believed to be due to the orientational perturbation in the side chains other than the helical reversion in the main chain. This is because that, even at 80 °C, the Kuhn's dissymmetry ratio, $g_{\text{abs}} (= \Delta\epsilon/\epsilon)$, of **Poly-S2** is as large as -1.1×10^{-3} , 1 order higher than that of rodlike one-handed helical [(*S*)-2-methylbutyl](*n*-hexyl)polysilylene in solution at a low temperature of -80°C .¹¹ Additional strong evidence is shown in Figure 1c. Contrary to all other polyguanidines synthesized to date, the optical rotations of **Poly-R2** and **Poly-S2** remain constant even after the samples were annealed in different solvents at high temperatures for more than 34 h.¹² This is consistent with no helical inversion occurring even after annealing at higher temperatures.

In summary, we here reported the first stable polyguanidine helices in solutions, even after they were annealed at higher

temperatures, whose TCC and KCC are essentially the same. Such extremely stable helical polyguanidines will offer utility potential, for example, in applications such as chiral HPLC stationary phase and novel liquid crystalline materials.¹

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Supporting Information Available: Experimental details for the monomer synthesis, polymerization, and other related characterization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The slight decrease in the optical rotations at the beginning of annealing is due to the lower temperature in the sample cell. This is because that 25 °C sample solution was injected into the sample cell when the annealing process starts. Further evidence is that the perturbation points (A, B, and C) in line c in Figure 1c result from the addition of coolant into the thermo-control circulating system.

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