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Reassessing the Regioregularity of *N*-(1-Naphthyl)-*N*′-(*n*-octadecyl)polycarbodiimide Using Solution Infrared Spectroscopy

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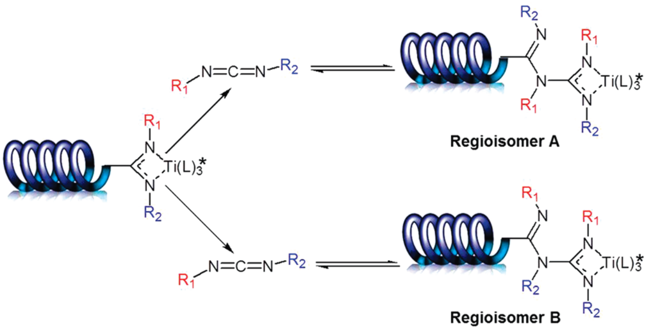
S *Supporting Information*

INTRODUCTION

Polycarbodiimides present an interesting class of synthetic helical macromolecules with potential frontier applications in chiral-sensory, optical-sensory, liquid crystalline, and data storage devices, to name a few.[1] One unique utility for these polymers is the ability to incorporate two synthetically selective pendant groups per repeat unit on the polymer backbone. Such utility allows the freedom to tailor the properties of these systems through careful selection of the two pendant groups. Symmetric polycarbodiimides (those with two identical pendant groups per repeat unit) have comprised a bulk of the initial studies performed on polycarbodiimide systems.[2−6] However, as synthetic advancements have progressed, many recently discovered polycarbodiimides are shown to have a breadth of new properties through the use of nonsymmetric carbodiimide monomers (those with two different pendant groups).[7−14] Although the different pendant groups allow new avenues of discovery, nonsymmetric monomers have the ability to undergo two different insertion pathways during chain propagation (Scheme 1). This results in a polymer with the possibility of two different regioisomers along the chain which are identified by the connectivity of the pendant groups to the imine versus the amine nitrogen on the repeating amidinate−polycarbodiimide backbone.

Identification of the regioregularity (or irregularity) of nonsymmetric polycarbodiimides is an ongoing effort, largely utilizing pendant groups that are sufficiently different in character (i.e., aryl−alkyl polycarbodiimides). A majority of our current research using aryl−alkyl polycarbodiimides has been focused on a unique reversible conformational switching phenomenon that occurs at relatively low temperatures in a variety of solvents.[9,10,13,14] An understanding of the regioregularity of these dynamic systems is undoubtedly important to fully decipher the mechanistic details of the conformational transition. The C═N stretch(es) observed in the infrared spectra of thin films seemed likely to provide a fingerprint of the regiochemistry of these polycarbodiimides comprised from nonsymmetric monomers with an aryl and an alkyl pendant group. The basis for this claim is the affect that an aryl versus an alkyl substituent will have on the C═N stretch force constant on the representative imine. Prior to this work, all infrared spectra of these polycarbodiimides has been done in the solid state: either by compressing them into a potassium bromide pellet or casting thin films of the polymers onto potassium bromide windows. In a specific example, we reported that a film of *N*-(1-naphthyl)-*N*′-(*n*-octadecyl)polycarbodiimide (**Poly-1**) cast from chloroform at room temperature (Figure 1a) exhibits two distinct absorption maxima at 1620 and 1640 cm^{-1}.[13] We assigned these absorptions to the stretch of C═N-alkyl and C═N-aryl bonds along the backbone and suggested that the two peaks correlated with the regioirregularity of the polymer. Therefore, at that time, **Poly-1** was deemed regioirregular when two pronounced imine stretches were observed.

Scheme 1. Schematic Representation of the Polymerization of Nonsymmetric Carbodiimide Monomers That Can Result in Two Regioisomers Depending upon the Insertion Pathway of Monomer into the Enantiomerically Pure Titanium−Amidinate Active Chain End



However, further characterization of the previously synthesized symmetric *N*,*N*′-dibenzylpolycarbodiimide[15] (**Poly-2**, Figure 1b) surprisingly revealed multiple imine absorptions (1649 and 1624 cm^{-1}) in the solid cast film even though, for this polymer, only one regioisomer is possible. With this observation, it was deemed necessary to reassess our assignment of multiple imine absorptions in an infrared spectrum as a signature of the inherent regioirregularity of **Poly-1**, and herein we discuss further investigations using variable temperature attenuated total reflectance IR spectroscopy (VT-ATR-IR) spectroscopy in solution.

EXPERIMENTAL SECTION

Materials. 1-Aminonaphthalene, 1-aminohexane, benzylamine, *n*-octadecyl isocyanate, *n*-hexyl isocyanate, 1,1′-carbonyldiimidazole, and triethylamine were purchased from Aldrich (Sigma-Aldrich, Milwaukee, WI). Common laboratory solvents were purchased from the NCSU Department of Chemistry stockroom via Fisher Scientific, Fair Lawn, NJ, and used without further purification unless otherwise noted.

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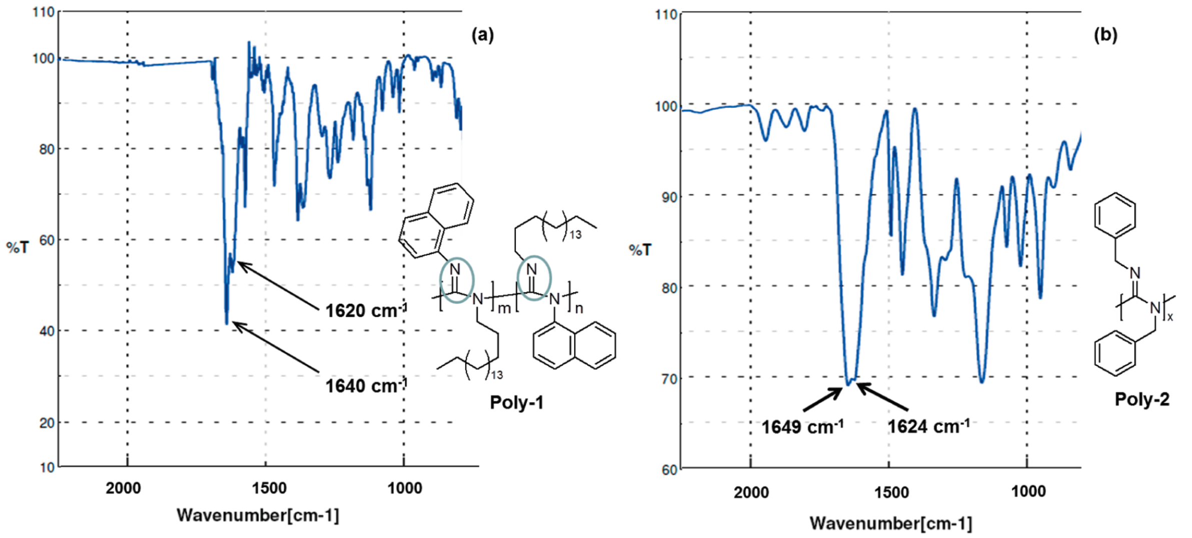

Figure 1. (a) IR spectrum of a **Poly-1** thin film cast from $CHCl_3$ showing the two imine stretches at 1640 and 1620 cm^{-1}. (b) IR spectrum of a **Poly-2** thin film cast from $CHCl_3$, which can only adopt one regioisomer but also exhibits two imine stretches.

Solvents used for polymerization or catalyst synthesis were dried, distilled, degassed, and stored over molecular sieves under a nitrogen atmosphere prior to use.

Synthesis of Monomers and Polymers. *N*-(1-Naphthyl)-*N*′-(*n*-octadecyl)polycarbodiimide (**Poly-1**),[13] *N,N*′-dibenzylpolycarbodiimide (**Poly-2**),[15] and *N,N*′-di-*n*-hexylpolycarbodiimide (**Poly-3**)[2,6,16,17] have been previously synthesized and characterized. Any specific information and changes to the general synthesis procedure can be found in the Supporting Information.

Synthesis of Catalysts. **Poly-1** was synthesized using an (*R*)-(+)-1,1′-bi-2,2′-naphthoxy (BINOL)titanium(IV) diisopropoxide catalyst synthesized according to previous literature.[13] **Poly-2** and **Poly-3** were synthesized using the previously reported trichlorotitanium(IV) 2,2,2-trifluoroethoxide catalyst.[7]

IR Spectroscopy. Solid state (thin film) infrared spectra were obtained with a Jasco FT-IR 140 Fourier transform infrared spectrometer using crystalline potassium bromide windows purchased from Aldrich. Solution infrared spectra were obtained using a Mettler Toledo ReactIR 15 with a silver halide FiberConduit probe assembly and a diamond ATR sensor. All solution spectra were corrected with respect to a room temperature solvent blank. In a typical experiment, 100 mg of polymer was dissolved in 10 mL of solvent in a 20 mL scintillation vial with a small stir bar. The tip of the ReactIR probe was submerged into the polymer solution carefully to ensure that no air bubbles were trapped underneath the sensor. The temperature was controlled using an acetone/dry ice bath (for temperatures less than 0 °C), an ice water bath (for 0 °C), an ambient water bath, and a heated water bath for above ambient temperatures.

Other Instrumentation. ^1H and ^{13}C NMR analyses were performed on a Mercury 300 or 400 spectrometer using deuterated solvents (Cambridge Isotope Laboratories) with tetramethylsilane internal standard. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer.

■ RESULTS AND DISCUSSION

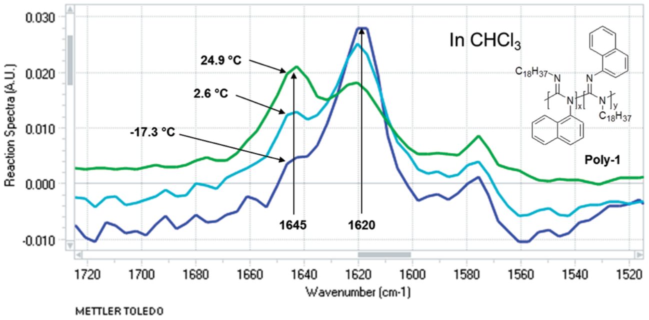

Figure 2. VT-ATR-IR spectra of the imine stretching region of a chloroform solution of **Poly-1** (10 mg/mL) at 24.9, 2.6, and −17.3 °C.

VT-ATR-IR spectra, in the imine stretching region of a chloroform solution of **Poly-1** (10 mg/mL), were measured at three temperatures upon cooling 24.9 °C, to 2.6 °C, and −17.3 °C (Figure 2). Cooling the polymer solution below −25 °C resulted in visible precipitation.

As observed in the thin film (Figure 1a), the room temperature spectrum exhibits two imine stretches at 1620 and 1645 cm^{-1}. However, upon cooling there is a noted loss of intensity of the 1645 cm^{-1} peak and an increase in the 1620 cm^{-1}. This variation in the relative intensity of the two peaks is reversible upon warming the solution back to room temperature. Furthermore, the two peaks show an isosbestic point, which demonstrates that both absorptions emanate from the same chromophore (i.e., the imine stretch). The low temperature and relatively small temperature window over which this transition occurs are inconsistent with the assignment of the two imine stretches as being due to the connectivity of pendant groups along the polymer backbone as initially hypothesized. However, the observed appearance−disappearance of these IR absorptions directly parallels the temperature range (−10 to 20 °C) over which the previously reported chiro-optical conformational changes are observed for this polymer in $CHCl_3$.[13]

To confirm the correlation between the chiro-optical changes and the variation in the imine stretches, VT-ATR-IR spectra of a THF solution of **Poly-1** (10 mg/mL) were measured (Figure 3). The chiro-optical changes of a THF solution of **Poly-1** are observed between 10 and 35 °C, which is significantly elevated

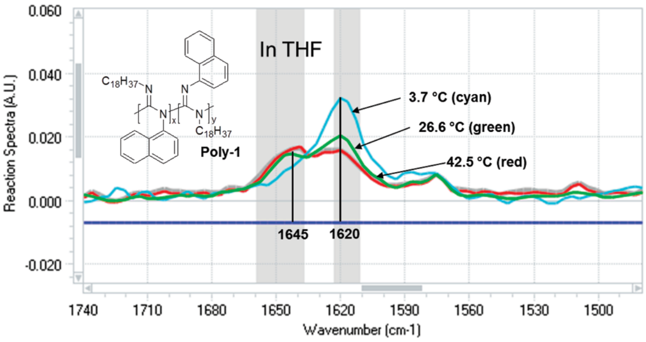

Figure 3. VT-ATR-IR of **Poly-1** (10 mg/mL) in THF at 3.7, 26.6, and 42.5 °C.

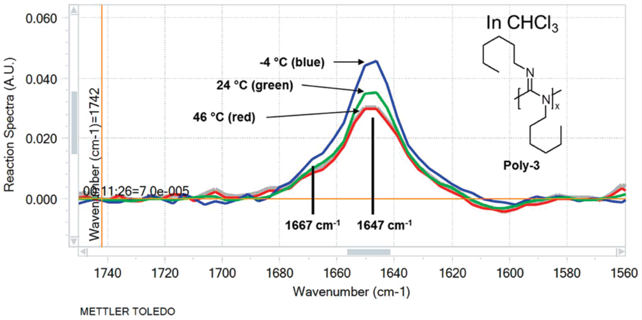

Figure 4. VT-ATR-IR spectra of **Poly-3** (10 mg/mL) in $CHCl_3$.

from the same transition in $CHCl_3$.[13] As shown in Figure 3, above room temperature (42.5 °C) the two imine stretches are observed with roughly equal intensity. However, consistent with the temperature range for the chiro-optical transition, upon cooling to 3.7 °C the peak at 1645 cm^{-1} diminishes whereas the peak at 1620 cm^{-1} becomes more intense. These variable temperature polymer/THF solution spectra were obtained by immersing the solution into three different water baths (an ice bath, a room temperature bath, and a 50 °C bath) to quickly change the solution temperature. Observing the kinetics of the transformation was limited by the heat transfer between the sample solution and the water baths; i.e., the change occurs as fast as the solution temperature can be changed. However, we know that these conformational transitions can occur within seconds when we dramatically quench the polymer solution at different temperatures.

Di-*n*-hexylpolycarbodiimide (**Poly-3**) exhibits no reversible chiro-optical changes in solution. Therefore, as a negative control, VT-ATR-IR spectra of **Poly-3** dissolved in chloroform (10 mg/mL) were obtained. As shown in Figure 4, a strong imine absorption at 1647 cm^{-1} is observed with a shoulder at 1667 cm^{-1}. This spectrum is analogous to that of the low-temperature conformation of **Poly-1**, but with the overall imine absorptions shifted to a higher energy. There is only a limited temperature response observed in the spectra of **Poly-3**. No significant change in the relative intensity of the two peaks is observed, consistent with the absence of any chiro-optical transition. There is a slight increase in the overall intensity of the absorption when moving from higher to lower temperatures, and this is consistent with all solution VT-ATR-IR measurements.

On the basis of all of the above data—(a) the observation of two imine stretches in **Poly-2** for which only one regioisomer is possible, (b) the ΔT of the observed transition which is much smaller than would be expected (required) for isomerization between regioisomers, and (c) the transition observed in the VT-ATR-IR spectra mirrors the previously observed chiro-optical transitions—we conclude that the relative intensity of the two imine stretches is not a signature of the extent of regioregularity of the polymer.

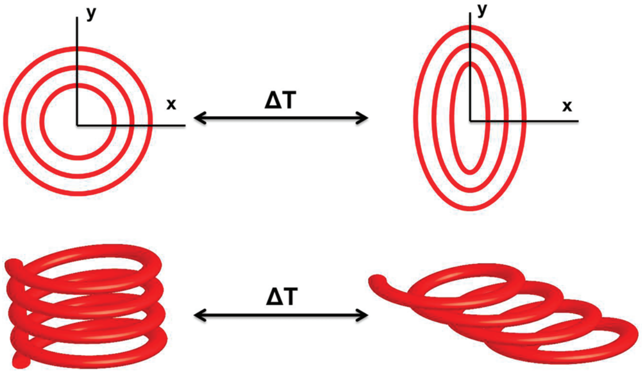

Figure 5. One possible change in the symmetry elements of a helical polymer from a circular helix, where the *x*- and *y*-axes are degenerate, to an elliptical helix (squashed slinky), where the *x*- and *y*-axes are no longer degenerate.

Current research is being conducted toward determining what may be occurring to result in the observed spectral changes between these two imine IR stretches, and their correspondence with the polymer chiro-optical transition. Our current hypothesis is that this reversible phenomena reflects a change in the symmetry of the helical polymer (Figure 5). For example, in a circular helix, the *z*-axis is unique but the *x*- and *y*-axes are degenerate and transform together as an e-irreducible representation. Thus, imine stretches orthogonal to the helix direction will similarly transform with e symmetry. By contrast, if the helix undergoes some type of deformation (e.g., a squashed slinky distortion), then the degeneracy of the *x*- and *y*-axes would be broken. Correspondingly, one would expect a splitting of the IR stretches of functional groups oriented radially to the helix. If this model is correct, the lower temperature conformer, with predominately a single imine stretch, adopts a nearly circular helix, whereas the higher temperature conformer, with two distinct imine stretches, adopts a helical distortion. Changes in the extent to which the aryl pendant groups π-stack along the polymer backbone may be the driving force for the conformational switching in addition to the proposed helical distortion. Supporting this idea is the fact that only polycarbodiimides with aryl groups with a particular size and spatial arrangement have been observed to undergo this kind of chiro-optical switching.[9,10,13,14]

■ CONCLUSIONS

VT-ATR-IR spectroscopy in solution reveals the two imine stretches observed for **Poly-1** is not a signature of the regioregularity of this polymer. Rather, this reversible modulation of the intensities of these imine stretches accompanied by their isosbestic point vary in a manner that mirrors previously observed chiro-optical transitions and likely reflect a break in symmetry. This data further indicates that **Poly-1** and other nonsymmetric polymers with multiple imine absorptions may be more regioregular than originally anticipated.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Further characterization of reported polymers and monomers and additional thin film infrared spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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