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Notes

Lyotropic Liquid Crystalline Properties of Poly(*N*,*N*′-di-*n*-hexylguanidine)

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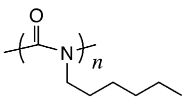
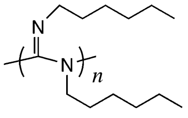
Introduction

Stiff-chain polymers are of interest because of their unusual properties. An important subset of this class is the helical macromolecules, which encompass both natural[1] (e.g., α-helical polypeptides, cellulosics, and the polynucleic acids) and synthetic polymers (e.g., polyisocyanates,[2] polyisocyanides,[3] and poly(*cis*-acetylenes)[4]). Not only is the intrachain conformation of the stiff helical polymers important, but also is their interchain ordering and packing. The importance of the latter manifests itself in their liquid crystalline behaviors[1b] and has ramifications in the design of supramolecular hierarchical structures. Within the synthetic helical systems, the lyotropic liquid crystalline properties of poly(*n*-hexyl isocyanate) have been studied in detail.[5] Generally, and like many other stiff-chain polymers, poly(*n*-hexyl isocyanate) is known to display lyotropic nematic mesophases. Recently, in our group, the synthesis of a new class of related helical polymers, the polycarbodiimides (or polyguanidines), has been developed through a living route using a number of organometallic complexes as catalysts.[6] Like the polyisocyanates, the rigidity of the polyguanidine backbone results from the combination of the coplanarity of the guanidinyl repeat units and the steric hindrance of adjacent side chains.[2,7,8] By way of comparison, the polyguanidines possess two side chains per repeat while the polyisocyanates possess just one. One of our goals in synthesizing the polyguanidines was to increase their chain stiffness and helix inversion barriers, vis-à-vis the polyisocyanates, by increasing the intramolecular steric interactions through these added side chains. This also gives us an opportunity to explore how the side chain density influences the intermolecular solution and solid-state structures of these polymers. To this end, the lyotropic liquid crystalline properties of poly(*N*,*N*′-di-*n*-hexylguanidine), poly-**I**, were investigated using small-angle X-ray diffraction and optical polarizing microscopy.



Poly(n-hexylisocyanate)



Poly-**I**

Experiment

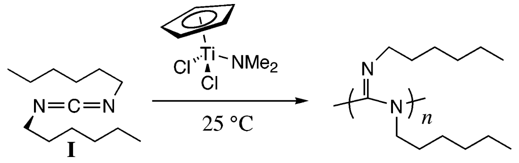
General. All glassware was either flame-dried or oven-dried overnight. Unless otherwise noted, all solvents were reagent grade and used without further purification except for drying over 3 Å molecular sieves. Chloroform used for polymerizations was purified by chromatography through alumina and Q5 copper catalyst to remove water and oxygen, respectively. *N*,*N*′-Di-*n*-hexylcarbodiimide, **I**, was prepared following literature methods.[6c]

Polymerization. Bulk polymerization of **I** was carried out at room temperature at a monomer/catalyst ratio of 100:1 in an inert atmosphere glovebox under dry nitrogen. Dichloro-(η^5-cyclopentadienyl)(dimethylamido)titanium was used as a catalyst for the polymerization. After gelation, the reaction mixture was diluted with wet toluene and the polymer precipitated from methanol. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 0.60−1.00 (br, s), 1.00−1.47 (br, m), 2.80−3.20 (br, s), 4.00−4.20 (br, s). ^{13}C NMR ($CDCl_3$) (ppm): 14.14, 22.92, 27.73, 29.17, 31.92, 32.34, 48.76. IR (thin film): 2957 (s), 2929 (s), 2858 (s), 1467 (m), 1353 (m), 1285 (m), 1248 (m), 1209 (m), 1181 (m), 1106 (s), 1058 cm^{-1} (w). Anal. Calcd for $(C_{13}H_{26}N_2)_n$: C, 74.23; H, 12.46; N, 13.32. Found: C, 74.38; H, 12.10; N, 13.12.

Preparation of Liquid Crystalline Solution. The solutions used were prepared at 20% (weight of polymer/[weight of polymer + weight of toluene]) for the optical polarizing microscope and 16.1% for small-angle X-ray diffraction.

Results and Discussion

Poly-**I** was prepared by the living polymerization of carbodiimide **I** in bulk using the half-metallocene catalyst, dichloro(η^5-cyclopentadienyl)(dimethylamido)titanium (eq 1).



(1)

The polymerization proceeds smoothly at room temperature, and a white, fibrous polymer is obtained after work-up and purification by repeated precipitations from methanol. The first isolated polymer is found to be semicrystalline as shown by its X-ray diffractogram (Figure 1). The X-ray pattern shows one strong peak at $2\theta = 6.8°$, which corresponds to a long-range spacing of 13 Å, and is assigned to the interchain packing distance. The spacing value is slightly smaller than 14.9 Å, which is the approximate interchain distance calculated by molecular modeling assuming that all the methylene pairs have trans conformations. The shorter experimental distance can be accounted for by both deviations from the all-trans configurations and interdigitation of the side chains. The X-ray diffractogram also shows a broad

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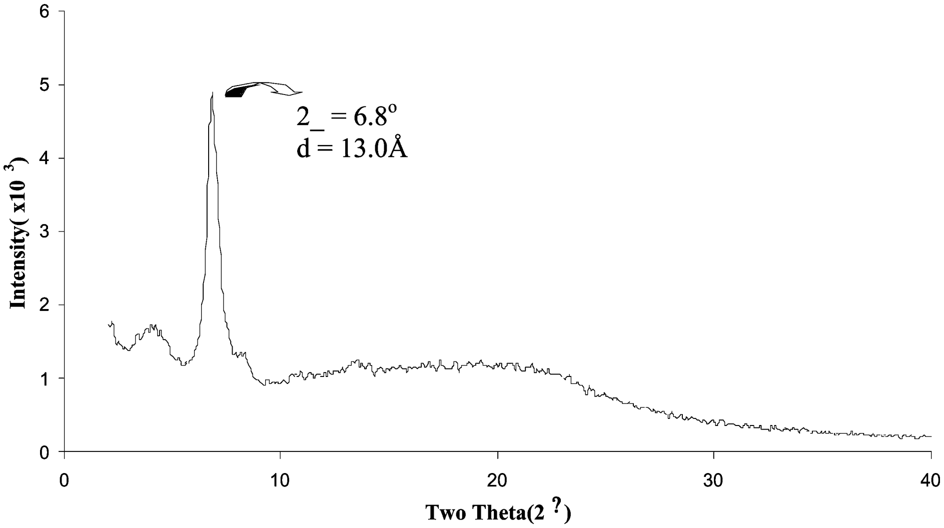

Figure 1. Powder X-ray diffraction pattern of poly(*N*,*N*′-di-*n*-hexylguanidine) (poly-**I**) at room temperature.

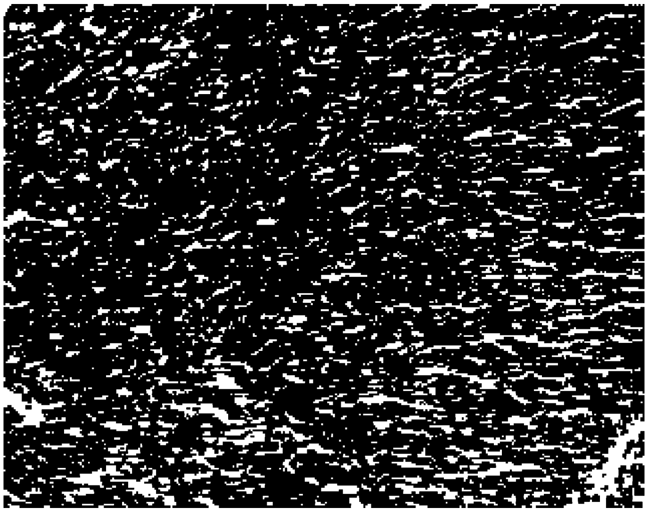

Figure 2. Polarized optical microscopic image obtained from 20% (w/w) solution of poly(*N*,*N*′-di-*n*-hexylguanidine) (poly-**I**) in toluene at 45 °C (magnification 200×).

peak around $2\theta = 20°$. This corresponds to both second-order diffraction of the low-angle peak and to the lateral spacings between side groups within the layers formed by polymer main chains.

In general, the polyguanidines show very high solubilities that depend on the identity of the side chains and the solvents can range from hexane to water.[9] Hence, we have been able to explore the concentrated solution behaviors of these materials. The characteristics of the mesophase obtained from a 20% solution (w/w) of the polymer in toluene at 45 °C were investigated using an optical polarizing microscope (Figure 2) and 16.1% (w/w) solution using small-angle X-ray diffraction (Figure 3). The solution at 45 °C shows a clear schlieren texture in the optical polarizing microscopic image, and the polymer solution displays the same texture over a broad concentration range greater than 16% (w/w) at 45 °C. The X-ray diffraction study provides more detailed information about the mesophase structure. The diffractogram solution again shows a strong diffraction ring that corresponds to the strong peak observed in the X-ray diffraction pattern of the solid polymer, lending evidence that the polymer solution has positional as well as orientational order of the polymer backbones. The same spacing and alignment of polymer molecules observed in the solid state are maintained in the concentrated solutions. Thus, the mesophase structure is assigned as a layered smectic phase with the helical backbones held apart by a corona of paraffin side chains. The proposed layered mesophase structure of the polymer is shown in Figure 4.

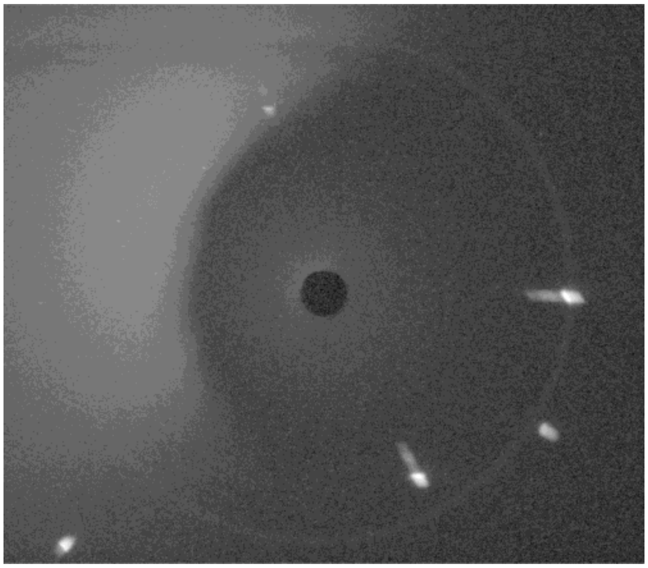

Figure 3. Small-angle X-ray diffraction pattern of the 16.1% (w/w) solution of poly(*N*,*N*′-di-*n*-hexylguanidine) (poly-**I**) in toluene at ~45 °C.

The liquid crystalline behavior of poly-**I** in solution is of higher order and different from the related poly(*n*-hexyl isocyanate) that is known to form a lyotropic nematic mesophase (i.e., possesses orientational order but no positional order). We ascribe this difference to the increased density of identical side chains in poly-**I** that provides a more uniform and impenetrable barrier between the helical backbones. Poly(*n*-hexyl isocyanate), with its lower density of side chains, may allow for a higher freedom of the motion of the main chain and less uniform spacing. The identical nature of the side chains in the polyguanidines is also important. If the two side chains in the guanidinyl repeat differ in size, e.g.,

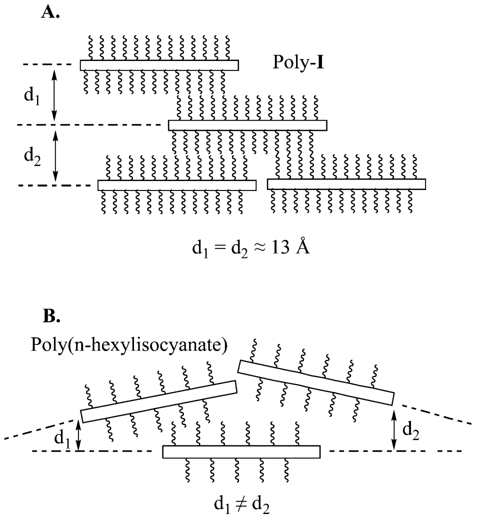

Figure 4. Schematic representation of (A) the smectic phase of poly-**I** and (B) the nematic phase of poly(*n*-hexyl isocyanate).

methyl and 1-phenylethyl, then the order of the mesophase is reduced and nematic phases are observed.[10]

Conclusion

From polarizing microscope and small-angle X-ray diffraction studies, it was found that solutions of poly(*N*,*N*′-di-*n*-hexylguanidine) over a critical concentration form a layered, smectic structure. This differs substantially from the nematic phase displayed by poly(*n*-hexyl isocyanate). We believe the differences arise from both the increased density and uniform nature of the hexyl side chains of poly-**I**. These side chains form a corona barrier that acts to effectively separate the polymer backbones in this uniform manner. Studies of the liquid crystalline properties of polyguanidines having different side chains, such as nonsymmetrical, chiral side chains and side chain mesogens, are currently in progress.

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(9) In the solid state, polyguanidines are converted back to their corresponding monomers at relatively low temperature, the value of which depends on the identity of the side chains. For most polyguanidines, the decomposition occurs at a temperature below any phase transitions, which precludes thermotropic liquid crystalline studies.

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