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SYNTHESIS OF MATERIALS WITH SELF-ORDERING CHIRAL MACROMOLECULES

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ABSTRACT

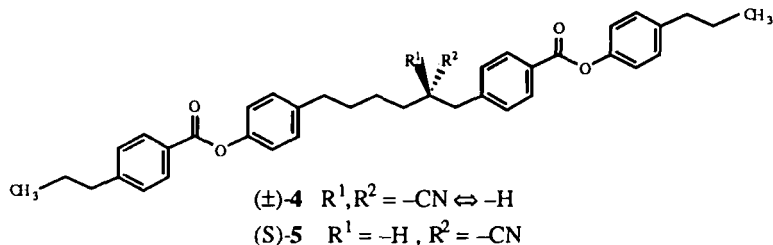
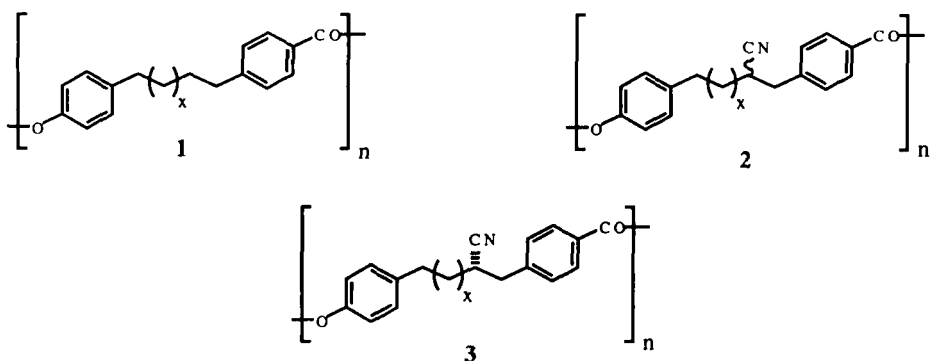
The present work focuses on chirality, functionalization, and molecular shape to establish links between molecular architecture and the spatial organization of polymer chains in organic materials. The approach used was to synthesize chiral and racemic homologous polymers exhibiting a preference for extended chain conformations and having the strongly dipolar cyano group as a substituent of the stereogenic center. The strong dipole moment at the chiral center offered potential to combine strong long-range forces with chiral recognition. Electron and optical microscopies were our selected tools to probe three-dimensional structures, and nonlinear optics was used to measure the properties of the materials obtained. We found that the relative stereochemistry of the repeat unit dipole impacts significantly on global chain symmetry and its packing mode. Enantiomeric enrichment of chains changed hexagonally packed cylindrical molecules to board-like molecules which pack edge-to-edge in an orthorhombic lattice. Interestingly, enantiomeric enrichment of chains enhanced the second-order nonlinear optical susceptibility of films prepared from these macromolecules.

INTRODUCTION

In spite of many remaining challenges, our ability to control molecular structure in polymers is ahead of our understanding of how their

covalent structure controls three-dimensional organization. It is this organization that controls the properties of materials, and therefore using molecular synthesis to arrive at three-dimensional microstructures should be our goal in polymer chemistry as we approach the 21st century. In the present work we focus on chirality, functionalization, and molecular shape to establish links between molecular architecture and the spatial organization of polymer chains in organic materials. Molecular shape is a variable of interest in order to promote the incidence of mesophases; that is, phases with order parameters that are intermediate between those of amorphous solids and three-dimensional crystals.

The specific approach used in this work was to synthesize chiral and racemic homologous polymers and their racemic model compounds. It was also our objective to introduce a very strong dipole moment in a stereogenic center of the repeat in order to combine the potential for strong long-range forces with chiral recognition among chains. The presence of 50 or more of these stereogenic centers in a chain was likely to impact on the organization of molecules in condensed phases. Electron and optical microscopies were our selected tools to probe three-dimensional structures, and nonlinear optics was used to measure the properties of the materials obtained. The linear polymeric structures synthesized and their respective dimeric model compounds are shown below.



These structures must satisfy the stringent chirality model which considers chains to be infinite one-dimensional objects. The model requires the absence of reflection planes, inversion centers, or glide planes in these infinite objects. Common stereoregular polymers with isotactic and syndiotactic structures do not satisfy these requirements, and thus one option is to consider regiochemical order in condensation polymers to construct chiral chains. One specific construction would be isoregic backbones built from enantiomerically enriched monomers which yield chains such as that represented by Structure 3. In this cyano-substituted polymer the only symmetry element left is translational polar symmetry, and therefore all requirements for chirality are satisfied. Structure 2 represents the analogous racemic polymer in which chains are in principle Bernoullian sequences of repeats having either absolute configuration. Finally, Structure 1 is the achiral parent backbone unfunctionalized with the strong dipole moment. For this study we synthesized backbones with seven carbons in the aliphatic spacer as well as those with six for Structures 1-3.

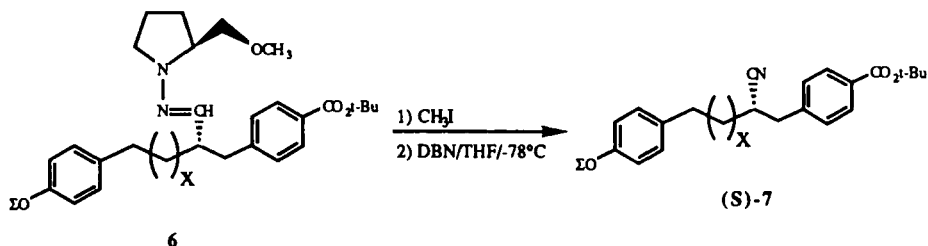
EXPERIMENTAL

Detailed descriptions of the syntheses of linear polymers as well as those of their dimeric and oligomeric model compounds have been published elsewhere [1-3]. Another publication from our laboratory describes analogous comb polymers and their precursor monomers [4]. The preparative chemistry of the enantiomerically enriched macromolecules studied here required two critical methodologies reported by our group. One was the direct polyesterification of hydroxyacids under mild conditions [1] and the other was the construction of nitriles with absolute stereocontrol [2]. Characterization of materials by DSC was carried out in a Perkin-Elmer 4 differential scanning calorimeter, the optical microscope used was a Leitz Laborlux 12 pol polarizing microscope coupled to a Leitz hot stage, and the electron microscope was a Philips EM 420 operating at 100 kV. The experimental details of the nonlinear optical set up are described in another manuscript from our laboratory [5].

RESULTS AND DISCUSSION

As detailed in our previous papers, the monomer synthesis is a 15-step construction with overall yields in the range of 4-8%. After a series of steps, we obtain the chiral hydrazone 6 (from *S*-aminomethoxymethyl-

pyrrolidine) which is in turn alkylated with α -bromo-*t*-butyltoluate at the α -position by using Ender's asymmetric alkylation chemistry [6]. This reaction transfers chiral information from the pyrrolidine ring to the newly formed stereocenter.



The chiral hydrazones are converted to the chiral nitriles through a methodology developed in our laboratory [2].

Minimized conformations of monomers with six and seven carbons in the aliphatic spacer (not shown here) reveal an extended shape for the even one and a kinked nonlinear shape for the odd spacer molecule. When electron diffraction patterns were obtained from shear-oriented thin films of the various polymers, we discovered remarkable differences in three-dimensional organization of the molecules as subtle molecular changes were made in the repeating units. The actual patterns can be found in another manuscript [7], but we review here the main differences observed among the homologues. The unfunctionalized parent backbone with seven carbons in the spacer organizes into a highly crystalline solid. It is very interesting that complete ordering frustration occurs when the CN dipole is introduced in the repeat with configurational disorder. The remarkable aspect of this observation is that the highly crystalline solid is transformed into a glassy substance by subtle substitutional differences occurring "every 16 atoms" along the chain. Enantiomeric enrichment of the single stereogenic center of the large repeat leads once again to the formation of a crystalline solid. That is, when common handedness among the dipoles restores translational symmetry, a high degree of order occurs again. Interestingly, in spite of the total ordering frustration in the odd racemate, the removal of "one carbon" from the spacer results in an intermediate level of order short of three-dimensional crystallization. However, analogous enantiomerically enriched chains reveal a level of crystallinity which is unusual in synthetic polymers, with more than 50 reflections in the electron diffraction pattern.

Electron diffraction has also revealed interesting differences in the global symmetry of chains as controlled by stereochemistry of the nitrile dipoles. Configurational disorder in even spacer backbones results in chains of cylindrical symmetry. This is indicated by the observed hexagonal packing of these molecules. However, board-like shapes are induced in similar chains by enantiomeric enrichment since orthorhombic packing is observed in the chiral system. Furthermore, these board-like chains pack edge-to-edge, suggesting molecular recognition among homochiral dipole moments. This mode of chain packing is not observed when the nitrile groups are removed from the molecular backbone or when the concentration of heterochiral pairs of dipoles increases. Again, one must appreciate how dilute are the stereogenic centers in the structure versus how significant are the differences in three-dimensional organization caused by their relative configuration. Table 1 summarizes our observations on structure in this family of six homologous polymers.

Other interesting differences in physical structure were revealed by electron microscopy of the various samples. The most important effect was finding that extended chain crystals tend to form in systems containing even spacer chains. In odd spacer chains, on the other hand, chain-folded crystals appear to form as revealed by the thickness of crystals observed by transmission electron microscopy. The fundamental reason for this difference in the organization of molecules within the crystals is not known. One could speculate that the differences expected in global shape among the even and odd chains play some role in the nature of the crystals formed.

The DSC scans of chiral and racemic systems having even spacer are

TABLE 1. Three-Dimensional Structures in Homologous Polymers

Polymer	Physical structure	Molecular packing
1 , $x = 4$	Crystal	Orthorhombic
2 , $x = 4$	Glass	Random
3 , $x = 4$	Crystal	Orthorhombic
1 , $x = 3$	Crystal	Pseudo-hexagonal
2 , $x = 3$	Smectic mesophase	Hexagonal
3 , $x = 3$	Crystal	Orthorhombic

consistent with our findings by diffraction techniques. Figure 1 shows a DSC scan of the racemate and that of the chiral system. A single phase transition is observed in the racemate which we attribute to the isotropization transition of the smectic mesophase that appears to be stable even at room temperature. The chiral system, on the other hand, shows two transitions, the first possibly being a crystal to mesophase transition.

The interesting contrast in three-dimensional organization linked to the stereochemistry was revealed very clearly by the dimeric model compounds. In these small molecules there is even further dilution of nitrile dipoles since there is only a single stereogenic center in a model compound containing 40 backbone atoms or so. Yet we found remarkable contrast between the racemic and the enantiomerically enriched model compounds. The enantiomeric model compound reveals a strong tendency to crystallize, forming extremely large spherulites. The racemate of the dimer, on the other hand, can be frozen into a liquid crystalline glass as revealed by birefringent frozen droplets. These droplets apparently crystallize from the glassy state, but polymerization of 50 or more stereogenic centers leads to a vitrified mesophase at room temperature.

In order to complete the materials science paradigm, we must understand how the three-dimensional organization of molecules affects physical properties. In the present study we have studied the second harmonic generation of thin films containing the molecules of interest for this purpose. These studies are of interest not only because frequency doubling of laser beams is an interesting phenomenon but also because second harmonic generation is an interesting probe for molecular motions. The results, as shown in Table 2, are interesting and reveal that the chiral system generates a higher second harmonic signal relative to the racemate. In both cases the signals generated by films have reasonable temporal stability. This observation suggests that polar crystals form in the chiral system and that these crystals align in an external electric field. Details of these measurements and their implications in terms of molecular structure versus properties are discussed elsewhere [7].

It is possible to construct a different architecture, namely that of a comb polymer containing the linear polymer's repeat unit as part of the side-chain structure. We have prepared a number of these structures in which the chiral hydroxyacid repeat unit with seven carbons in the spacer is buried as a graft in the teeth of comb polymers [4]. Some of the molecules synthesized have deuterated side chains which have been useful in the determination of enantiomeric excess values by NMR. The

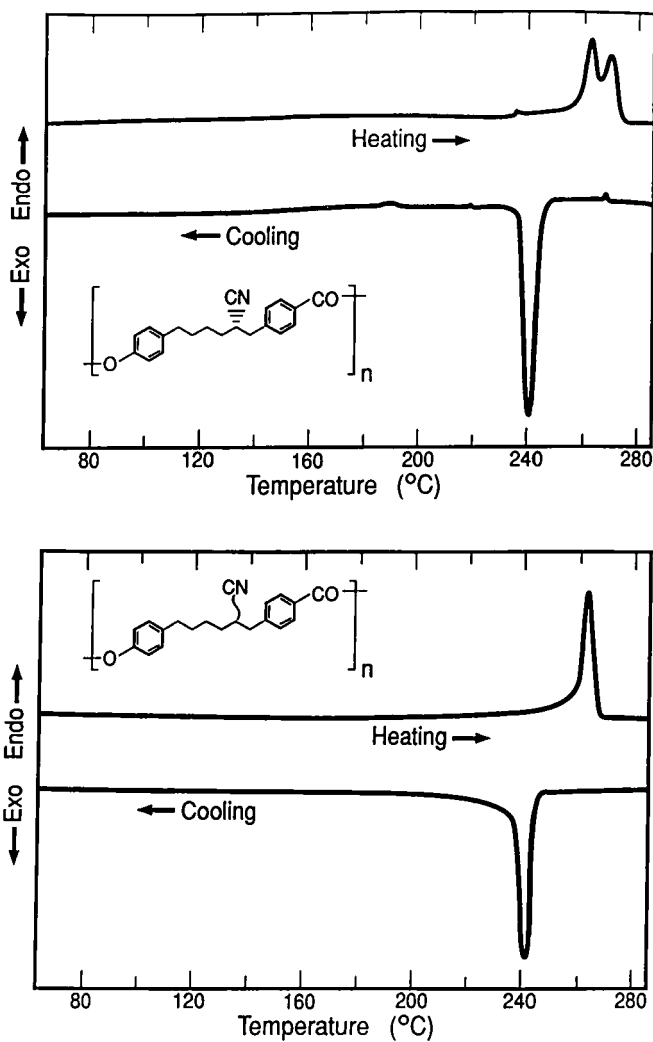


FIG 1. Differential scanning calorimetry scans of the enantiomerically enriched Polymer 3 and its configurationally disordered Analogue 2.

TABLE 2. Second-Order Nonlinear Optical Susceptibility Values

Polymer	$\chi^{(2)}$, esu
Enantiomerically enriched (2), $x = 3$	3.73×10^{-10}
Racemic (3), $x = 3$	1.44×10^{-10}

objective was to synthesize structures that would exhibit liquid crystalline phases, and their design included side chains that were longer and more flexible than those of conventional side-chain liquid-crystal polymers. The additional flexibility originates in the aliphatic spacer present in the middle of the side chain. An interesting fact was to find that the minimized conformation for the monomeric precursor to the side-chain liquid-crystal polymer was definitely atypical of molecules known to form mesophases. We certainly found that such molecules organized into smectic phases, and the minimization reminds us how important intermolecular forces are in determining three-dimensional structures. Figure 2 shows a typical optical microscopy texture of the smectic comb polymer.

In the work discussed so far there is evidence that the strong dipoles with handedness experience homochiral recognition. This is suggested by the edge-to-edge packing of chains when a given absolute configuration of the dipole moment is preferred. It is also suggested by the limited tendency of racemic dimers to order.

Recently Andelmann and DeGennes published work on chirality forces based on a simple model of tripod molecules at the air-water interface [8]. In this work the partition functions Z_{++} and Z_{+-} for homochiral and heterochiral recognition are compared and some general rules derived from the simple model. Even though it is certain that this model does not capture the complexity of our systems, it is interesting that it predicts homochiral recognition when discrete charges occupy the corners of the tripod and coulombic forces are involved in intermolecular interactions among chiral molecules. Our very strong nitrile dipole might be virtually decomposed into discrete charges, in which case homochiral recognition would be predicted by the simple model. This issue will be explored further in future publications from our laboratory.

One may conceive that the ultimate phenomenon in chiral recognition is chemical reaction between pairs of functions that have a given relation-

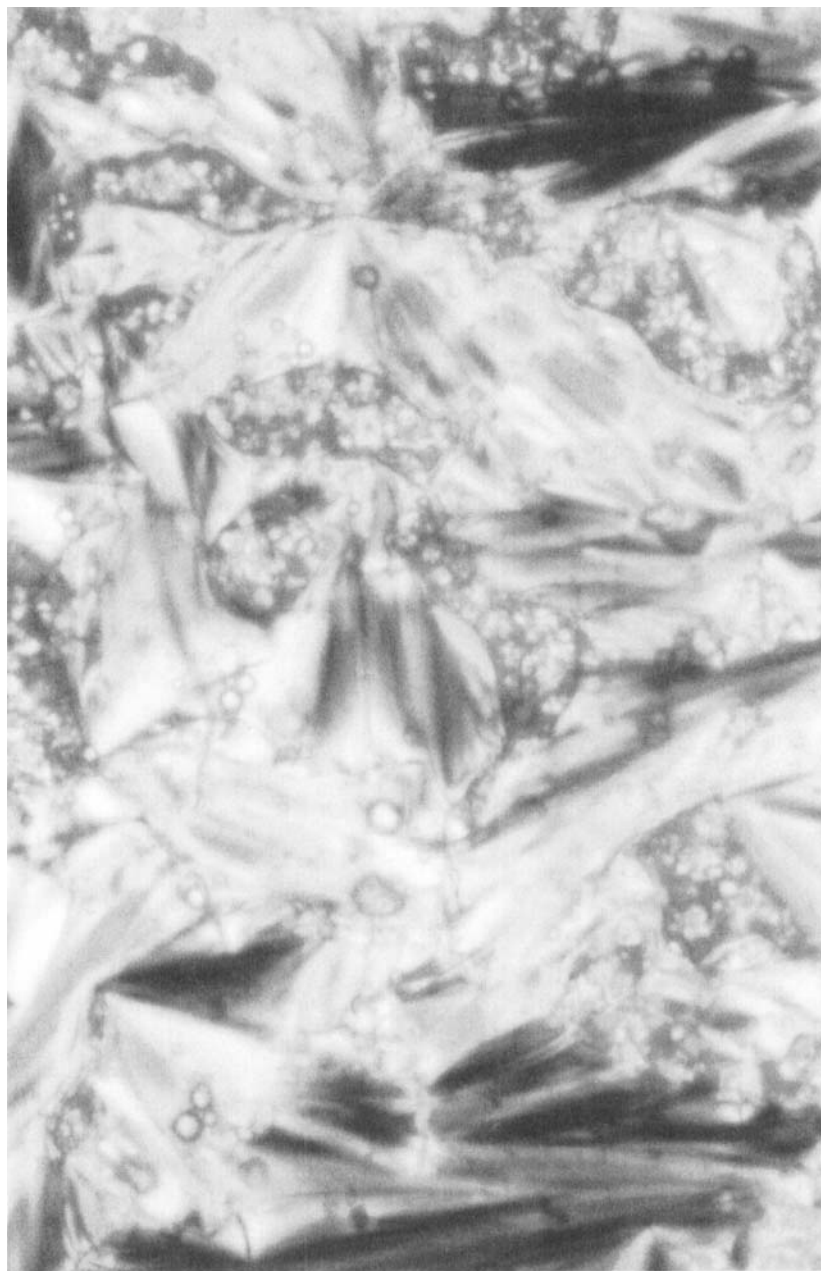


FIG. 2. Texture characteristic of smectic phases observed in the comb polymer containing the chiral hydroxyacid in the side-chain structure.

ship in relative configuration. As future papers from our group will show, we have found evidence for a selective chemical reaction among molecules of common configuration. These reactions have the potential to yield two-dimensional polymers which are monodisperse in molecular thickness and exhibit very interesting physical properties.

CONCLUSIONS

We have succeeded in synthesizing a homologous series of linear and comb polymers, some of which contain strong dipole moments with handedness. These macromolecules have been extremely useful in systematic studies of materials chemistry, revealing clearly that dipole stereochemistry impacts significantly on global chain symmetry, three-dimensional organization, and physical properties. Establishing these links is critical for the further development of the field of materials chemistry.

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