Long-Range Chiral Induction in Chemical Systems with Helical Organization. Promesogenic Monomers in the Formation of Poly(isocyanide)s and in the Organization of Liquid Crystals

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Abstract: The preparation of optically active poly(isocyanide)s derived from chiral promesogenic monomers is reported. Remarkably, the stereogenic carbon atom in the monomer is able to pass its chiral "information" to the growing polymer backbone which is at least 14 atoms (approximately 16 Å) remote from it. The sense of helical induction in these conformationally rigid polymers is compared to the helical sense of the cholesteric phases, as well as to the helical senses of chiral smectic C phases, induced by the monomers in nematic and smectic C phases, respectively. Both relate to the odd−even rules for chiral sense changes in liquid crystalline phases. The role of noncovalent interactions in the polymerization has been proven by performing the reactions at various concentrations and in different solvents—the chiral induction from monomer to polymer is greatest in most concentrated reactions and in solvents with a balance between high dipolarity−polarizability and low hydrogen bond accepting and cavitational terms, as determined by an LSER analysis.

Introduction

Helical chirality[1] is a central feature of chemical systems which are involved in a wide variety of biologically[2] and technologically[3] important processes. This source of optical activity may be a result of *conformational preferences around covalent bonds* or of *intermolecular relationships governed by noncovalent interactions* (Figure 1). These phenomena are exemplified by atropoisomeric molecules, including polymers[4] and chiral liquid crystals,[5] respectively, and both these media are of well-established interest in the study of organic stereochemistry.

Helical or similar atropoisomeric conformations[4] are present in several synthetic polymers,[6−10] including poly(isocyanide)s.[11] We were drawn to the latter family of macromolecules since the stereoselectivity of the reactions leading to their formation as well as their chiroptical properties have been studied in some detail.[12] Diastereoselective polymerization reactions of isocyanides have generally been performed on monomers in which the stereogenic center is the carbon atom connected to—or in close proximity to—the nitrogen atom of the isocyanide group.

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(11) Poly(isocyanide)s is the nomenclature recommended by IUPAC, although these polymers have also been described as poly(iminomethylene)s and more systematically as poly(carbonimidoyl)s. For reviews, along with references therein, on these polymers, see: (a) Millich. F. *J. Polym. Sci., Macromol. Rev.* **1980**, *15*, 207−253. (b) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11−19. See also: (c) King, R. B.; Borodinsky, L. *Macromolecules* **1985**, *18*, 2117−2120. (d) Abdelkader, M.; Drenth, W.; Meijer, E. W. *Chem. Mater.* **1991**, *3*, 598−602. (e) Hong, B.; Fox, M. A. *Macromolecules* **1994**, *27*, 5311−5317.

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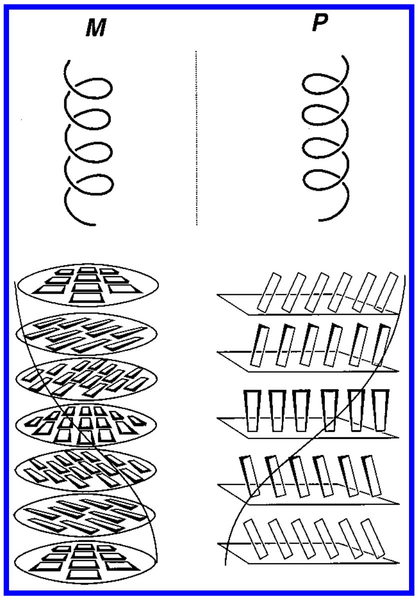
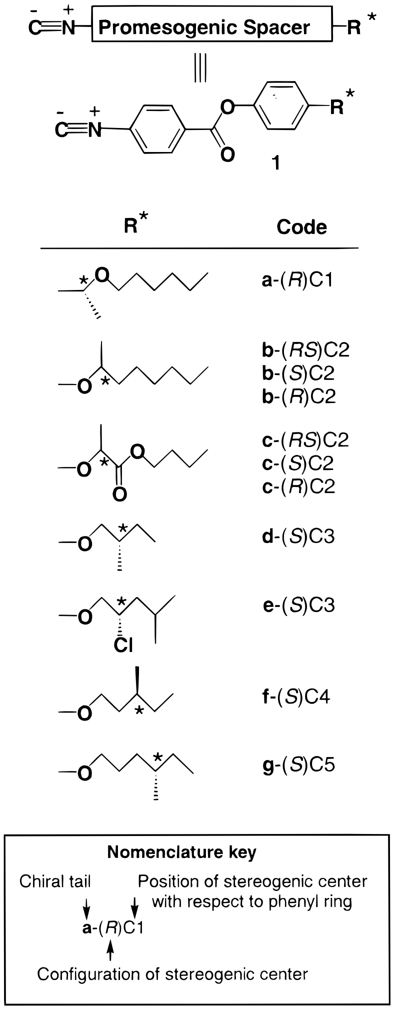


Figure 1. Schematic representations of helices in the *M* and *P* forms of atropoisomeric macromolecules (top), in the *M* organization of a cholesteric mesophase (bottom left) and in the *P* organization of a chiral smectic C mesophase (bottom right).

Which of the two diastereomeric conformations[13,14] is adopted preferentially is determined largely by steric interactions, in polymerizations operating under predominantly kinetic control.[15] In contrast, the helicity present in cholesteric and smectic liquid crystals (Figure 1) is a result of the relative orientations between separate molecules,[5] governed by weak noncovalent intermolecular interactions, and dependent on the position of the stereogenic center with regard to the rigid mesogenic core. The odd−even rules are applicable to cholesteric[16] (N*) as well as to chiral smectic C[17] (S_c*) liquid crystals, when the dipole associated with the stereogenic center is considered.

A combination of these two types of helicity within a single family of chemical structures is an academically intriguing goal, which might spawn macromolecules of technological interest.[18] We therefore designed the monomer drawn in cartoon form at the top of Scheme 1, in which the polymerizable isocyanide group is separated from a stereogenic center by a promesogenic core. Initially, we chose the phenyl benzoate group as the spacer in monomer **1** (Scheme 1)—as this structural feature is frequently encountered in thermotropic liquid crystals.[19] Somewhat remarkably, in certain instances the stereogenic center in the monomer induces the preferential creation of one of the diastereomeric forms of the polymer, at a distance of at least 16 Å.[20] In this paper, we report the effects of changing the position and environment of the stereogenic center attached to the promesogenic core. The senses of the helices present in the polymers at the macromolecular level are compared with those induced by the promesogenic monomers at the mesoscopic level in liquid crystalline mixtures forming the N* and S_c* helical mesophases. This comparison leads to interesting conclusions regarding the applicability of the odd−even rules in the three types of media, which present distinct helical organization.

Scheme 1



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[13] Some cautionary reports concerning the interpretation of chiroptical properties of these polymers (not derived from aryl isocyanides) have been published, which cast doubt on the 4_1 helical conformation. See: (a) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C., III *Macromolecules* **1988**, *21*, 1839−1846. (b) Pini, D.; Iuliano, A.; Salvadori, P. *Macromolecules* **1992**, *25*, 6059−6062. For a view against the helical structure based on the solution conformation of a trimer, see: (c) Spencer, L.; Kim, M.; Euler, W. B.; Rosen, W. *J. Am. Chem. Soc.* **1997**, *119*, 8129−8130.

[14] For calculations concerning the backbone conformations of aliphatic oligo(isocyanide)s, see: Clericuzio, M.; Alagona, G.; Ghio, C.; Salvadori, P. *J. Am. Chem. Soc.* **1997**, *119*, 1059−1071.

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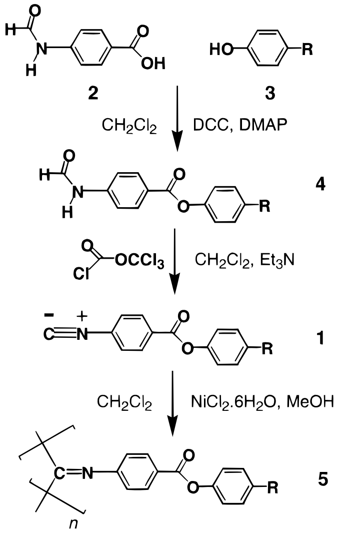
[18] The functionalization of polymers with promesogenic groups is widely used for the creation of side-chain liquid crystalline systems, although in these cases the promesogenic group is generally separated from the polymer backbone by a long and flexible spacer. See, for example: Walther, M.; Finkelmann, H. *Prog. Polym. Sci.* **1996**, *21*, 951−979.

[19] For discussions concerning the role of the phenyl benzoate group in liquid crystals, see: (a) Castellano, J. A.; McCaffrey, M. T.; Goldmacher, J. E. In *Liquid Crystals 3*; Brown, G. H., Labes, M. M., Eds.; Gordon and Breach: New York, 1972; Vol. II, pp 597−618. (b) Sakurai, Y.; Takenaka, S.; Miyake, H.; Morita, H.; Ikemoto, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1199−1204.

[20] Ramos, E.; Bosch, J.; Serrano, J. L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc.* **1996**, *118*, 4703−4704.

Scheme 2



(Groups R as defined in Scheme 1)

Results and Discussion

Synthesis and Characterization of the Materials. The synthesis of isocyanide monomers **1** and the corresponding poly(isocyanide)s **5,** which differ in the nature of the tails **a**−**g** attached to the promesogenic cores, described in this work is depicted in Scheme 2.

Treatment of 4-aminobenzoic acid with formic acid and acetic anhydride in ethyl acetate gave 4-formamidobenzoic acid (**2**). The phenol **3a**-(*R*)C1 was prepared from the racemic 1-(4-acetylphenyl)ethanol using a lipase-catalyzed acetylation step[21] to achieve the resolution of the enantiomers. The phenols **3b,c** were prepared by coupling appropriate commercial alkyl alcohols with 4-(benzyloxy)phenol using the Mitsunobu protocol,[22] followed by removal of the protecting group using $Pd(OH)_2/C$ and cyclohexene in ethanol. Williamson ether synthesis using 4-(benzyloxy)phenol and the appropriate alkyl tosylates,[23−25] followed by debenzylation, provided the phenols **3d**−**g**. The coupling[26] of **2** with the phenols **3** using dicyclohexyl carbodiimide (DCC) in the presence of 4-(dimethylamino)pyridine (DMAP) afforded the intermediate formamides **4**, whose dehydration was achieved[27] employing diphosgene. The conversion of the formamides to the unstable isocyanides **1** was evidenced by symmetrization in NMR spectra[28] as well as by the characteristic IR band (at approximately 2120 cm^{-1}) arising from the isocyanide moiety. None of the isocyanides, nor their formamide precursors, presented thermotropic mesophases.

The homopolymers **5** were prepared (Scheme 2) in dry CH_2Cl_2, using $NiCl_2 \cdot 6H_2O$ as catalyst, at a concentration of freshly prepared isocyanide monomer of approximately 200 mM. Air was allowed to be present during the reactions, as it has been shown to be involved during the catalysis in polymerizations of this type.[29,30] The polymerizations proceeded in good to excellent yields, ranging from 68% up to 96%, the majority being in excess of 80%. The conversion of the monomers into the polymers was confirmed by IR, ^1H, and ^{13}C NMR spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarimetry, UV−vis spectroscopy, and circular dichroism (CD) spectrometry.

The IR spectra of the solids showed no signal corresponding to the isocyanide moiety, but were dominated by signals from the promesogenic units. Weak broad bands from the imine groups constituting the polymer backbone were observed at approximately 1655 cm^{-1}. The ^1H NMR of the polymers show extremely broad resonances in the aromatic region from approximately 8.0 to 5.5 ppm corresponding to the phenyl benzoate moiety, their high-field positions indicating the proximity of these groups in the polymer. The hydrogen atom(s) attached to the aliphatic carbon atoms in close proximity to the phenyl ring is also broad, but the resonances of the aliphatic chain become increasingly well-resolved with increasing distance from the polymer backbone. The ^{13}C NMR spectra reveal similar characteristics to the ^1H NMR spectra, in that the resonances arising from the carbon atoms close to the polymer backbone are very broad, while those from the carbon atoms in the aliphatic side chains of the macromolecules are quite well-resolved, reflecting the higher mobility of the atoms at the end of the side chain.

In common with other polymers generated using the $NiCl_2 \cdot 6H_2O$ catalyst,[12] the samples had polydispersities (GPC)[31] between 1.1 and 1.7, with a mean value of 1.4, in accord with the nonliving nature of the polymerization.[29] Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the polymers showed no significant phase transitions in the range of 40−200 °C, but they decomposed (weight loss from sample witnessed by TGA) above approximately 275 °C. None of the polymers presented thermotropic mesophases, presumably because of their rigid nature. All of the homopolymers were very soluble in organic solvents such as toluene, methylene chloride, chloroform, THF, and DMF, while they show low solubility in hexane, acetonitrile, and short-chain alcohols, and remain insoluble in water.

Circular Dichroism Studies

A. Circular Dichroism Spectra of the Polymers. The chiroptical data of the polymers **5** reveal some interesting trends

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[21] Naemura, K.; Fukuda, R.; Konishi, M.; Hirose, K.; Tobe, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1253−1256.

[22] (a) Mitsunobu, O. *Synthesis* **1981**, 1−28. (b) Hughes, D. L. In *Organic Reactions*; Paquette, L. A., et al., Eds.; Wiley: New York, 1992; Vol. 42, pp 335−656.

[23] Sierra, T.; Ros, M. B.; Omenat, A.; Serrano, J. L. *Chem. Mater.* **1993**, *5*, 938−942. This paper describes the preparation of the 2,6-naphthalene analogue.

[24] Decobert, G.; Dubois, J.-C. *New J. Chem.* **1986**, *10*, 777−782.

[25] Decobert, G.; Dubois, J.-C. *Mol. Cryst., Liq. Cryst.* **1984**, *114* (1−3), 237−247.

[26] See, along with references therein: (a) Williams, A.; Ibrahim, I. T. *Chem. Rev.* **1981**, *81*, 589−636. (b) Balcom, B. J.; Petersen, N. O. *J. Org. Chem.* **1989**, *54*, 1922−1927.

[27] Skorna, G.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 259−260.

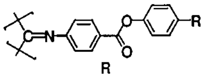
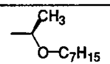
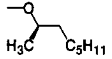
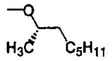
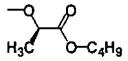
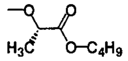
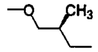
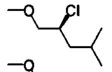
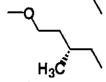
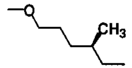
[28] The NMR of the formanilide derivatives described here are complicated by the presence of unequal populations of the cis and trans isomers about the amide bond, a phenomenon noted previously: Bourn, A. J. R.; Gillies, D. G.; Randall, E. W. *Tetrahedron* **1964**, *20*, 1811−1818. This asymmetry vanishes from the NMR spectrum upon conversion of the formamide to the isocyanide.

[29] (a) Deming, T. J.; Novak, B. M. *Macromolecules* **1993**, *26*, 7092−7094. (b) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101−9111.

[30] Euler, W. B.; Huang, J.-T.; Kim, M.; Spencer, L.; Rosen, W. *Chem. Commun.* **1997**, 257−258.

[31] The polymers all had molecular masses in excess of 30 kDa and up to 60 kDa, with a mean of 45 kDa, when determined by GPC against polystyrene standards using THF as eluant. When determined by vapor phase osmometry, the molecular masses were considerably lower, the mean value being of the order of 20 kDa. This discrepancy probably arises from the rigid-rod nature of the polymers, which are known to exhibit exageratedly large molecular masses by GPC when compared against random-coil polymers. The lower limit of molecular mass corresponds to approximately 70 monomer units (if the backbone conformation were a 4_1 helix this molecular mass would correspond to approximately 18 turns).

Table 1. Chiroptical Data for Monomers **4** and the Corresponding Polymers **5**,[32] the Configuration of the Chiral Tail (with the *all-trans* Conformation) Showing the Position of the Methyl Group with Respect to the Promesogenic Core, the Helical Senses of the Polymer Backbones, and the Helical Senses of the Mesophases Induced by the Monomers **4** in Nematic and Smectic C Liquid Crystals

Code	$[\alpha]^{25}_{546}$ Monomer **4**	$[\alpha]^{25}_{546}$ Polymer **5**	$\Delta\varepsilon_{363}$ Polymer **5**		Helical Sense of Polymer **5**	Helical Sense of N* induced by **4**	Helical Sense of S_C* induced by **4**
a-(*R*)C1	+48.3	+336	+2.21		*M*	*P*	*P*
b-(*R*)C2	-5.2	+236	+3.05		*M*	*M*	*M*
b-(*RS*)C2	0	0	0		—	—	—
b-(*S*)C2	+5.2	-216	-3.13		*P*	*P*	*P*
c-(*R*)C2	+33.0	+526	+5.86		*M*	*P*	*M*
c-(*RS*)C2	0	0	0		—	—	—
c-(*S*)C2	-26.3	-564	-5.77		*P*	*M*	*P*
d-(*S*)C3	+6.7	+53	+0.06		*M*	*M*	*M*
e-(*S*)C3	-10.0	+36	+0.60		*M*	*M*	*P*
f-(*S*)C4	+5.1	+4.0	-0.01		*P*	*P*	ins.
g-(*S*)C5	+8.2	+12.0	≈0		—	*M*	ins.

[a] ins. indicates that the monomers were insoluble in this phase. Specific optical rotations in units of deg cm^2·g^{-1} were measured in a 1 cm cell at concentrations of 6−10 mg mL^{-1} in $CHCl_3$ at ambient temperature. CD spectra ($\Delta\epsilon$ in L mol^{-1} cm^{-1}) were recorded in THF at a controlled temperature of 25 °C. No signal could be detected for this polymer **5g**-(*S*)C5.

as can be seen in Table 1, where they are compared with the corresponding precursor formamides **4**.[32] First, there are some parallels between the orders of the specific optical rotations $[\alpha]^{25}_{546}$ and the degrees of the differential molar absorptivities ($\Delta\epsilon_{363}$) from the CD spectra. The molar optical rotation is greatest for the polymer with tail **c**, the value for the polymers being an order of magnitude greater than the corresponding monomers. Polymers with tail **b** also exhibit large molar optical rotations; however, as the chiral center in the promesogenic unit is positioned further away from the relatively rigid aromatic core to which the alkyl chain is connected (i.e., chiral tails **f**-(*S*)-C4 and **g**-(*S*)C5), the optical rotations of the resulting polymers approach those of the monomers. The racemic modifications of **5b**-(*RS*)C2 and **5c**-(*RS*)C2 exhibited no optical rotation.

The CD spectra[33] of the polymers and monomers are more informative than the specific optical rotations, since this technique allows observation of Cotton effects associated with the component chromophores in the macromolecules and molecules, respectively. The most optically active polymers reported here have two bands centered on 252 and 363 nm which have opposite signs and different widths. In the monomers, the former band has a very low intensity and the latter is nonexistant. It is generally accepted that the Cotton effect in the broader absorption centered on 363 nm arises from the imino chromophore's n−π* transition, whose sign and relation with *P* or *M* helicity has been established in related poly(isocyanide)s,[12,15,34] and presents clear evidence that the polymer backbone has an optically active conformation. The more intense and narrow band centered on 252 nm is consistent with a ^1L_b absorption arising from the aromatic chromophore attached to the imino group. The spectra bear a more than passing resemblance—with appropriate displacement to longer wavelength because of the presence of aromatic chromophores—to calculated CD spectra for helical conformations of aliphatic poly(isocyanide)s.[14]

Polymers **5c**-(*R*)C2 and **5c**-(*S*)C2 exhibit mirror-image spectra with differential molar absorptivities of greatest intensity, paralleling the associated molar optical rotations. The largest $\Delta\epsilon$ values observed for the Cotton effects centered on 252 and 363 nm are −8.80 and +5.86 L mol^{-1} cm^{-1}, respectively, for **5c**-(*R*)C2 (Figure 2). In addition, there is a weaker Cotton effect centered on 282 nm, arising from the n−π* absorption of the carbonyl group adjacent to the stereogenic carbon atom. Indeed, the monomer precursor **4c**-(*R*)C2 exhibits a Cotton effect of weaker intensity in its CD spectrum near this wavelength (Figure 2). It is interesting to note that the incorporation of the ester group close to the stereogenic center increases the preference for one helical form of the polymer since the Cotton effects at 252 and 363 nm associated with the polymers **5b**-(*R*)C2 or **5b**-(*S*)C2 are considerably weaker.[35] In liquid crystals the ester

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[32] The molar optical rotations and differential molar absorptivities for the polymers are based on the molecular mass of a monomer unit (identical molecular mass to the corresponding isocyanide precursor), hence they are directly comparable with those of the precursor formamides, since the isocyanides are relatively unstable. This comparison is made and considered valid, given the specific optical rotations for **1b**-(*R*)C2 and **4b**-(*R*)C2 are the same.

[33] For discussions on CD, see: (a) *Analytical Applications of Circular Dichroism*; Purdie, N.; Brittain H. G., Eds.; Techniques and Instrumentation in Analytical Chemistry; Elsevier: Amsterdam, The Netherlands, 1994; Vol. 14. (b) *Circular Dichroism, Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: Weinheim, 1994. (c) Rodger, A.; Nordén, B. *Circular Dichroism and Linear Dichroism*; Oxford University Press: Oxford, 1997.

[34] The CD of related chiral poly(quinoxaline-2,3-diyl)s display similar bands, see: (a) Ito, Y.; Ihara, E.; Murakami, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1509−1510. (b) Ito, Y.; Kojima, Y.; Murakami, M. *Tetrahedron Lett.* **1993**, *34*, 8279−8282. (c) Ito, Y.; Ohara, T.; Shima, R.; Suginome, M. *J. Am. Chem. Soc.* **1996**, *118*, 9188−9189.

[35] It is unlikely that the chiral group attached to one extreme of the promesogenic unit could influence the electronic transition associated with the Cotton effect of the iminomethylene chromophore of the polymer backbone.

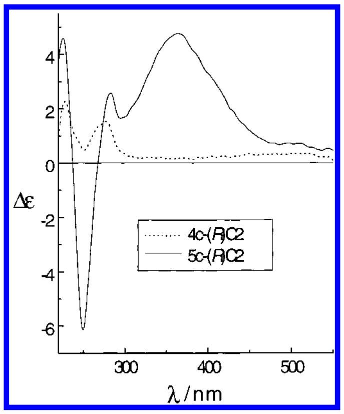

Figure 2. Comparison of the circular dichroism spectra of the monomeric precursor formamide **4c**-(*R*)C2 (dashed line) and the poly(isocyanide) **5c**-(*R*)C2 derived from it (solid line) both recorded in THF.

group linked directly to the stereogenic center in columnar liquid crystals leads to an enhanced rigidity in the tail relative to purely alkyl derivatives, such as those derived from 2-octanol.[36] In the solution state, this less mobile moiety may rigidify the asymmetric part of the monomer, leading to greater chiral induction in the polymers with tails **c** derived from butyl lactate.

The results gathered in Table 1 indicate that the CD absorptions at 363 nm (sign and order of the differential molar absorptivity) associated with the polymer backbone—and hence the sense and predominance of a given atropoisomer—are affected dramatically by the position of the stereogenic center. Indeed, the differential molar absorptivities diminish rapidly and alternate in sign as the chiral center in the promesogenic unit is positioned away from the isocyanide group. The reduced induction can be rationalized by considering the greatly increased rotational freedom of the stereogenic center relative to the promesogenic core with increasing numbers of intervening methylene groups. The sense of the conformation induced in the polymer backbone follows odd−even alternance as the stereogenic center is positioned sequentially along the alkyl tail if the same configuration is maintained. Thus, **5b**-(*S*)C2 and **5c**-(*S*)C2 have predominantly *P*, while **5d**-(*S*)C3 and **5e**-(*S*)C3 have predominantly *M*, and **5f**-(*S*)C4 is inclined toward *P* helical conformations. The only apparent exception to this general behavior is the polymer with the stereogenic center in position 1 (**5a**-(*R*)C1). This apparent discrepancy results from the misleading nomenclature *R* for this center when compared with the other compounds. The Cahn−Ingold−Prelog rules describe the relative positions of ligands relative to the stereogenic carbon rather than to the promesogenic core which is our reference point.

The dominant factor in determining the helical sense of the polymers appears to be steric, since when the conformation of the tails relative to the phenyl benzoate is fixed in an *all-trans* conformation, a given configuration of the stereogenic center (with methyl group above or below the plane of the paper in Table 1) always leads to the same handed backbone. In the particular case of **5a**-(*R*)C1, the enantiomer conformationally related with the (*S*) configuration in an odd position, in comparison with tails **d**-(*S*)C3, **e**-(*S*)C3, and **g**-(*S*)C5), is the (*R*) enantiomer.

It should be noted that while aromatic imines are known to have absorption spectra which change both in intensity and position of maxima,[37] no significant solvent dependence of either the intensity or form of the CD spectra of the poly(isocyanide)s reported here has been observed when they have been recorded in chloroform, THF, or 2:1 ethanol:THF. This result also contrasts with the solvent-dependent CD spectra observed for poly(thiophene)s[38] or poly(isocyanate)s,[8b,c] both of which are conformationally mobile, and suggests that our poly(isocyanides) are conformationally rigid.[39] Indeed, when polymer **5b**-(*S*)C2 was refluxed in toluene for 24 h, no change in its CD spectrum could be detected confirming a prodigious conformational stiffness. This result also indicates (along with the polymerizations performed at various concentrations, vide infra) that the polymers have structures whose conformation is determined largely during their formation and which are not free to reorient dramatically once they are formed, in contrast with other more flexible helical polymers.[8b,c,38,39]

We considered that the inductions observed over unusually large distances in these polymerizations might be a result of the promesogenic nature of the core linking the stereogenic center to the polymerizable group. Therefore, since none of the monomers (or the polymers) exhibit liquid crystalline phases, we investigated their helix-inducing properties in mesophases.

B. Liquid Crystal Induced Circular Dichroism (LCICD) Spectra of the Promesogenic Monomers. Among the mesophases exhibiting helical organization, the two most deeply studied are the cholesteric (N*) and chiral smectic C (S_c*). We thus selected nematic and smectic C "hosts" exhibiting their mesophases at room temperature in order to study the ability of our promesogenic monomer "guests" to induce N*[40] and S_c*[41] phases by virtue of stereoselective noncovalent interactions with the host. To ensure a good transfer of chiral "information" from the guest to the host, we sought host mesogens with relatively close structural features to those of the promesogenic monomers, such as a twist between aromatic rings in the core. As room-temperature nematic hosts, both *p*-methoxybenzylidine-*p*′-(*n*-butyl)aniline (MBBA), which in common with the phenyl benzoate-derived monomers[42] possesses a single alkyl chain and a twist between its two component aromatic rings,[37] and the eutectic mixture (2:1 by weight) of 4-(pentylphenyl)-4-methoxy

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[36] Barberá, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 2908−2918.

[37] For discussions concerning the twist between the component aromatic rings in benzylidineaniline derivatives, see: (a) Brocklehurst, P. *Tetrahedron* **1962**, *18*, 299−304. (b) Smith, W. F. *Tetrahedron* **1963**, *19*, 445−454. (c) Bürgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747−1764. (d) van der Veen, J.; Grobben, A. H. In *Liquid Crystals 3*; Brown, G. H., Labes, M. M., Eds.; Gordon & Breach: New York, 1972; Vol. II, pp 589−595. (e) Bar, I.; Bernstein, J. *Tetrahedron* **1987**, *43*, 1299−1305. (f) Clegg, W.; Elsegood, M. R. J.; Heath, S. L.; Houlton, A.; Shipman, M. A. *Acta Crystallogr. C.* **1996**, *52*, 2548−2552. (g) Navon, O.; Bernstein, J. *Struct. Chem.* **1997**, *8*, 3−11. For an example of an X-ray crystal structure of a mesogen incorporating both phenyl benzoate and benzylideneaniline moieties, see: (h) Baumeister, U.; Hartung, H.; Gdaniec, M. *Acta Crystallogr. C.* **1987**, *43*, 1117−1119.

[38] Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157−160.

[39] This view contrasts with that expressed concerning much lower molecular mass poly(phenylisocyanide) prepared in MeOH. See: Huang, J.-T.; Sun, J.; Euler, W. B.; Rosen, W. *J. Polym. Sci. A. Polym. Chem.* **1997**, *35*, 439−446.

[40] (a) Stegemeyer, H.; Mainush, K. J. *Chem. Phys. Lett.* **1970**, *6*, 5−6. (b) Stegemeyer, H.; Mainush, K. J. *Naturwissenschaften* **1971**, *58*, 599−602. (c) Saeva, F. D.; Sharpe, P. E.; Olin, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 7656. (d) Gottarelli, G.; Samori, B.; Marzocchi, S. *Tetrahedron Lett.* **1975**, 1981−1984.

[41] (a) Li, J.; Takezoe, H.; Fukuda, A.; Watanabe, J. *Liq. Cryst.* **1995**, *18*, 239−250. (b) Yamada, K.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Fukuda, A.; Osipov, M. A. *Phys. Rev. E* **1997**, *56*, R43−R46.

[42] For discussions concerning the twist between the component aromatic rings in benzoate derivatives, see: (a) Schweizer, W. B.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1547−1554. (b) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 585−597. (c) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 597−603. (d) Coulter, P.; Windle, A. H. *Macromolecules* **1989**, *22*, 1129−1136. (e) Emsley, J. W.; Furby, M. I. C.; de Luca, G. *Liquid Crystals* **1996**, *21*, 877−883.

benzoate and 4-(pentylphenyl)-4-(hexyloxy) benzoate[43] (phase ZLI-1052) were employed. The senses of the cholesteric phases induced in the nematic phases formed by addition of the monomers were identical in both host mesogens. As S_c host, a phenylpyrimidine mesogen,[44] known as phase MX8056, which shows a broad phase around room temperature was employed.

First, two enantiomerically pure stereoisomers as well as the racemate of isocyanide monomer **1b**-C2 were studied individually for their ability to induce chiral nematic phases. The racemate **1b**-(*RS*)C2 caused no bulk induction of twisted nematic phases, and the CD of the resulting solution showed no optical response. Conversely, when either **1b**-(*S*)C2 or **1b**-(*R*)C2 were incorporated into the nematic phases, they induced cholesteric phases with large chiroptical effects of opposite sign centered on approximately 380 nm in the case of MBBA and 300 nm in ZLI-1052. The (*S*) stereoisomer induces a *P* helical sense in the nematic phase while the (*R*) enantiomer induces an *M* helical sense.[45] Concerned about the stability of the isocyanide compounds in the nematic phases, we established that the corresponding formamides **4b**-(*S*)C2 and **4b**-(*R*)C2 induce the same helicities in the nematic phases as the derived isocyanides.

Subsequently, the formamides **4** were all studied for their ability to induce N* and S_c* phases in the host mesogens. The results are collected in Table 1. The N* phases induced by the monomers **4a,b**,**d**−**g**—in which a methyl group (and a chlorine atom in **4e**-(*S*)C3) associated with the stereogenic center is increasingly remote from the promesogenic core of the guest along an alkyl chain for the series of *S* enantiomers—show helicities of alternating sense, in accordance with the odd−even rules[16] developed for the prediction of the helicities present in mesophases.[17] Contrastingly, the monomers **4c**-(*S*)C2 and **4c**-(*R*)C2 incorporating the butyl lactate chain induce cholesteric phases of opposite helicity to those of the corresponding enantiomers of **4b** in which the 2-octyloxy chain has the same absolute configuration, despite the fact that the chains have approximately the same conformation with respect to the phenyl ring.[46] This behavior is thought to be a result of the differing dipole moments resulting from the two groups (the ester group in **4c** has a dipole moment directed mainly through the long axis of the promesogenic monomer. This type of longitudinal dipole can influence dramatically the calamitic nematic behavior,[47] overruling the steric factors as the principle cause for the observance of the alternance rules.

The monomers **4** induce S_c* phases with helicities in full agreement with a rigorous application of the odd−even rules to smectogens.[17,48] Indeed, when a methyl group is one of the groups attached to the stereogenic center, in **4a**−**d**, an alternance is seen in the helices for a given configuration. The sense of the helix induced in the S_c phase when a chlorine atom is attached to the stereogenic center (**4e**) is opposite to that resulting from that of the corresponding monomer with a methyl group (**4d**), because of the opposite inductive effect of the groups and consequent opposed transversal dipole moments of the molecules as Goodby et al. proposed in similar chlorine-containing derivatives.[48] Again, dipolar characteristics of the chiral tail are superimposed on pure steric factors in determining the helicity induced in the mesophase.

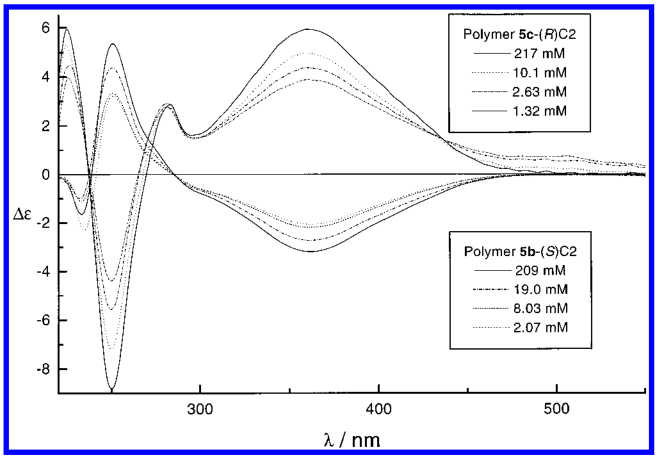

Figure 3. The circular dichroism spectra (recorded in THF) of the poly(isocyanide)s **5c**-(*R*)C2 (positive Cotton effect at 363 nm) and **5b**-(*S*)C2 (negative Cotton effect at 363 nm) prepared at the concentrations indicated.

It is worth emphasizing that, contrary to the situation in the polymers, monomer **4a**-(*R*)C1 obeys the odd−even rules in the induction of both N* and S_c* phases, although its longitudinal dipole is different to the rest of the promesogenic monomers where an oxygen atom is the link between the phenyl ring and the tail. This result, together with the behavior of **c**-C2 in N* and **e**-C3 in S_c* helical phases, supports the hypothesis that the most important factor in the induction of a given helical sense in the polymers is a steric one. The operation of steric effects over such a large distance implied that other noncovalent interactions may be playing a role in the polymerizations and led us to study the influence of certain external factors on this reaction.

Influence of External Factors in Polymerizations of Promesogenic Monomers

A. Variable Concentration. To investigate the possible role that noncovalent interactions play in the transfer of the chiral message from the remote stereogenic center to the polymer backbone, we designed a series of experiments such that the initial concentrations of the monomer and catalyst (at fixed stoichiometry) were varied under otherwise identical conditions. Monomers **1b**-(*S*)C2 and **1c**-(*R*)C2 were polymerized at concentrations ranging from that used for all polymerizations described above (200 mM) to 2mM, and after 2 days of reaction (when all traces of monomer were absent) the polymers were isolated and characterized by GPC and CD. The GPC data revealed that the molecular weights or sizes of the polymers produced at different concentrations were essentially the same for a given monomer. Contrastingly, the CD spectra of the resulting polymers are strikingly different. Spectra for four of the polymers **5b**-(*S*)C2 and **5c**-(*R*)C2 generated under these conditions are shown in Figure 3.

The CD spectra clearly reveal that as the polymers are formed under increasingly dilute conditions, so the induction from the stereogenic center in the monomer to the growing polymer backbone is reduced. This fact is witnessed most strikingly for the CD spectra of the polymers derived from **5c**-(*R*)C2, in which the Cotton effect at 282 nm arising from the carbonyl group

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[43] This nematic phase has been used previously in the study of induced cholesteric phases, see: Nacari, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4352−4357.

[44] Smectic C host phase MX8056 from Displaytech Inc., Boulder, Colorado.

[45] Significantly, the sign of the Cotton effect arising from the aromatic chromophores in the CD spectra of the polymers and induced cholesteric and smectic C liquid crystalline phases are the same, and defines their helical sense, which has been assigned *M* or *P* on the basis of comparison with previous studies of polymers and induced phases. See ref 40.

[46] Iglesias, R.; Serrano, J. L.; Sierra, T. *Liq. Cryst.* **1997**, *22*, 37−46.

[47] Barberá, J.; Marcos, M.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 225.

[48] (a) Goodby, J. W.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175−203. (b) Terashima, K.; Ichihashi, M.; Kikuchi, K.; Furukawa, K.; Inukai, T. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 237−249.

Table 2. Comparison of the Differential Molar Absorptivities from CD in $CHCl_3$ for the Polymers **5b**-(*S*)C2 Prepared in Different Solvents

solvent	hydrogen-bond donor term (α)[52]	hydrogen-bond acceptor term (*β*)[52]	dipolarity−polarizability term[52] (π^*)[a]	cavitational parameter (Ω/100)[53]	$\Delta\epsilon_{363}$ (L mol^{-1} cm^{-1})
n-C_6H_{14}	0.00	0.00	−0.08	0.50	−0.93
C_6H_{14}	0.00	0.00	0.00	0.65	−1.36
(*i*-Pr)$_2$O	0.00	0.49	0.27	0.47	−0.74
CCl_4	0.00	0.00	0.28	0.71	−1.11
n-C_4H_9OH	0.79	0.88	0.47	1.25	−0.33
EtOAc	0.00	0.45	0.55	0.77	−1.53
MeOH	0.93	0.62	0.60	1.98	−0.60
MeCOEt	0.06	0.48	0.67	0.82	−1.56
Me_2CO	0.08	0.48	0.71	0.88	−1.82
C_6H_5Cl	0.00	0.07	0.71	0.91	−2.22
CH_2Cl_2	0.30	0.00	0.82	0.93	−3.03
DMF	0.00	0.69	0.88	1.33	−0.56
DMSO	0.00	0.76	1.00	1.64	−0.91
$C_6H_5NO_2$	0.00	0.89	1.01	1.18	−1.11

[a] The correction factor δ for this term in the LSER expression was 0.001 except for CH_2Cl_2 and CCl_4 (0.5) and C_6H_5Cl and $C_6H_5NO_2$ (1.0).

adjacent to the stereogenic carbon atom in the side-chain is virtually constant, while those at 252 and 363 nm, which correspond to the backbone of the polymer, vary dramatically. In an effort to ascertain whether this effect was just a result of monomer aggregation prior to the polymerization, the isocyanide **1b**-(*S*)C2 was subjected to a variable concentration ^{1}H NMR study in CD_2Cl_2, which showed no chemical shift changes consistent with an aggregation phenomena.[49] The noncovalent interactions driving the stereoselectivity in these reactions are therefore not a result of intrinsic recognition between unreacted monomers, but apparently require covalent modification of the isocyanide moiety to imine in the growing polymer, perhaps being mediated by the metal ion catalyst.

B. Solvent. A noncovalent contribution to the transfer of chirality in the polymerization process should also be influenced by the solvent in which the reaction is performed. We therefore carried out the polymerization of **1b**-(*S*)C2 in some 14 different solvents,[50,51] evaluating the chiroptical properties of the resulting polymer **5b**-(*S*)C2. The $\Delta\epsilon_{363}$ values from the CD spectra of the polymers are collected in Table 2, along with relevant physicochemical characteristics of the solvents in which the polymerizations were performed. At first sight, there was no obvious relation between the polarity of the solvent and the chiral induction observed. However, a linear solvation energy relationship (LSER)[52] analysis of the results reveals the physicochemical features of the solvents which influence the induction. Treatment of the results with the multiparameter expression (eq 1)

$$\mathrm{XYZ} = \mathrm{XYZ_o} + a\alpha + b\beta + s(\pi^* + d\delta) + c\Omega/100 \quad (1)$$

from LSER theory, where XYZ is the observable (here the $\Delta\epsilon_{363}$ of the polymer) and $\mathrm{XYZ_o}$ is the value of this observable in the absence of any solute−solvent interaction, and hydrogen-bond donor (α) and acceptor abilities (*β*), dipolarity−polarizability (π^*, and associated correction factor δ), and cavitational[53] (Ω) terms of the solvents are associated with the coeficients *a*, *b*, *s*, *d*, and *c*, repectively, afforded a fit with regression coefficient $(r) = 0.948$ and a significance level $(P) = 0.001$. The most important terms determining the $\Delta\epsilon_{363}$ of polymer **5b**-(*S*)C2 are those associated with the dipolarity−polarizability and hydrogen-bond acceptor terms ($s = -2.6$, $b = +2.1$), followed by those associated with the cavitational and hydrogen bond donor terms ($c = +1.2$, $a = -1.0$), while the dipolarity−polarizability term correction factor is not significantly influential ($d = 0.2$). The value of $\mathrm{XYZ_o}$ (equivalent to $(\Delta\epsilon_{363})_o$) is −1.88 L mol^{-1} cm^{-1}.

This result indicates that as the dipolarity−polarizability term increases, greater induction of chirality is observed, in support of the proposed influence of noncovalent interactions (aggregation) between polymer and incoming monomer. Contrastingly, as the hydrogen-bond accepting ability of the solvent increases, so induction of chirality is disfavored. The significance of this term may be a result of competing coordination of the solvent and the isocyanide monomers with the nickel ion which catalyzes the polymerization. The counteracting influences of the hydrogen-bond donating and cavitational terms are unclear at this stage. The latter might be related with the large molar volume associated with the aggregate between the polymer and incoming monomer or with the nature of the intermolecular forces—dispersive and van der Waals—in the assembly.

Therefore, overall, the stereoselectivity of the polymerization involves a subtle balance in the intermolecular interactions where, on one hand, high dipolarity−polarizability and hydrogen-bond donating terms and, on the other hand, low hydrogen-bond accepting and cavitational terms favor a high chiral induction.

Conclusion

Induction of chirality over large distances in the formation of covalent bonds is remarkable and rare.[54] The stereogenic group present in the monomers is able to transmit its chiral message over at least 14 atoms (∼16 Å) to the polymerizable carbon atom. The results presented here are therefore important for the understanding of chiral induction in general and, in

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(49) Small chemical shift changes in the resonances arising from the hydrogen atoms attached to the aromatic ring adjacent to the isocyanide group were observed. It is likely that these changes resulted from the presence of small quantities residual water (also present in the polymerizations from the Ni(II) complex). Isocyanides are known to act as a hydrogen-bond acceptors. See: (a) Schleyer, P. v. R.; Allerhand, A. *J. Am. Chem. Soc.* **1962**, *84*, 1322−1323. (b) Ferstandig, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 1323−1324. (c) Ferstandig, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 4, 3553−3557. (d) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 866−870. In addition to the ^{1}H NMR results, UV−vis spectra of the monomers at various concentrations and temperatures showed no significant differences.

(50) (a) Ramos, E. Ph.D. Thesis, Universitat Autonoma de Barcelona, Spain, 1996. Selection of the 14 solvents, representative of the most relevant solute−solvent interactions, was made on the basis of solvent classification guidlines. See: (b) Ventosa, N. Ph.D. Thesis, Universitat Ramon Llull, Spain, 1997. (c) Ventosa, N.; Ruiz-Molina, D.; Rovira, C.; Tomás, X.; André, J.-J.; Veciana, J. Manuscript in preparation.

(51) As far as we are aware, only King and Borodinsky (ref 11c) have performed a limited study of the effects of solvent on the polymerization of achiral isocyanides.

(52) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J.; Abraham, M. H. *J. Soln. Chem.* **1985**, *14*, 153−186.

(53) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Dover Publications: New York, 1964.

particular, in the diastereoselective formation of synthetic polymers and helical liquid crystalline phases.

The parallels and differences between the odd−even effects[16,17,55] concerning the helical preferences in the polymers and LC phases indicate that the steric influence of the chiral tail accounts for the diastereoselectivities observed in the polymerizations. The relative conformation of the chiral tails with respect to the promesogenic phenyl benzoate core is decisive in the induction of a given helical sense in the polymers, overcoming the influence of the electronic environment of the stereogenic center, which also contributes in governing the thermodynamically determined helicities in mesophases. The helical preference in the kinetically controlled polymerization reactions[15] reported here appears to be influenced by stereoselective noncovalent interactions between the promesogenic cores. Indeed, the influence of noncovalent interactions in stereoselective reactions is precedented.[56] This effect has been identified by performing the polymerizations at various concentrations and in different solvents. We hypothesize that in the absence of dipolar effects these same interactions result in the observed induction of N* and S_c* phases[57] and which may be active in the transmission of chiral messages throughout mesophases and related organized media.[58]

All our evidence presented points to polymers with stable optically active helical conformations which are rather rigid and are determined largely during their creation, not being free to reorient once they are formed, in contrast to other more flexible helical polymers.

To shed more light on the steroselective mechanism through which such long-range chiral induction is produced, we are currently exploring the effect of changing the spacer between the benzene rings in the monomer unit. In addition, poly(isocyanide)s have been shown to exhibit interesting material properties,[59] and we are presently studying the unique characteristics of the variety of polymers presented here. For now, they stand as a rare and extraordinary example of long-range chiral induction in covalent bond formation in polymers and highlight the parallels of this phenomenon with long-range chiral induction propagated by noncovalent interactions in liquid crystals.

Experimental Section

Materials and Methods. Chemicals were used as purchased from the Aldrich Chemical Co. and Fluka Chemie AG. The enantiomeric purity of the enantiomers of 2-octanol (Flukabrand) was assayed by polarimetry prior to use. Solvents (SDS) were purified according to literature procedures. (*S*)-3-Methylpentanol,[24] and (*S*)-(−)-4-methylhexanol[25] were prepared according to literature procedures. Column chromatography was performed using silica gel (60 ACC Chromagel (SDS), with particle diameters of 70−200 μm for atmospheric pressure, and 35−70 μm for medium pressure). Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Mass spectra were obtained on a VG TS-250 mass spectrometer using the electron impact method (70 eV) operating in the positive mode. NMR spectra were recorded on a Bruker ARX300 (300 MHz ^{1}H, 75 MHz ^{13}C) spectrometer using the deuterated solvent as lock and tetramethylsilane as the internal reference.

Polarimetry was performed using a Dr. Kernchen Optik+Electronik Propol polarimeter in a 1 cm cell. Circular dichroism spectra were recorded using spectrometric grade solvents (Romel) in a 1 cm cell at sample concentrations of 10^{-3} to 10^{-5} M using a Jasco J-720 Spectropolarimeter and were analyzed using the associated J700 software. GPC was performed using two TOSOHAAS TSK-gel columns, G4000HXL and G3000HXL (7.8 mm id × 30 cm) from Supelco Inc., in series protected by a TSK guard column. Injections of 50 μL of the polymers dissolved in THF (1 mg/mL) were introduced and the THF eluant was pumped at 1 mLmin^{-1} with a Perkin-Elmer 410LC pump. The eluant was monitored simultaneously using a Perkin-Elmer LC-235 diode array detector and the polarimeter described above equipped with an HPLC flow cell.

Mesophase Preparation and Characterization. The induced twisted nematic phases studied by circular dichroism were prepared by dissolving the monomers (in the form of either their isocyanide **1** or their formamides **4**) in either MBBA (Aldrich) or phase ZLI-1052 (Merck, phase sequence X-15-N-48-I) in their isotropic states at 60 °C, then introducing the sample to a 4 μm cell, which had been pretreated with aligning agent, by capillary action. The mixtures were composed of 1−2 wt % of the chiral dopant for MBBA and 4−6% in ZLI-1052. When the mixture had cooled, the presence of cholesteric phases was confirmed outside the cells by the presence of the typical oily streak texture under a microscope equipped with cross-polarizers. The CD spectra of the resulting phase was performed by placing the sample in the spectropolarimeter cavity perpendicular to the direction of the source light.

The induced chiral smectic C phases were prepared by dissolving 3−5 wt % of the monomers **4** in a commercial phenylpyrimidine S_c host (MX8056, phase sequence: X-0.5-S_c-57-S_A-76-N)[44] in its isotropic state at 150 °C. The mixtures exhibit three different mesophases: upon cooling the isotropic liquid a fingerprint texture appeared indicating the cholesteric phase; further cooling resulted in the formation of a smectic A phase in a homeotropically oriented form with small areas of fan-shaped texture; finally, the room temperature smectic C phase was identified by the appearance of gray-blue marbled and Schlieren textures which correspond to a pseudohomeotropically oriented sample. In addition, dechiralization lines appeared in the fan shape texture indicating the helical organization of the smectic C. All of the mixtures were studied in 5 μm ITO cells with polyimide coating for a planar alignment (purchased from LINKAM), and showed optical switching when an a.c. external field was applied to the chiral smectic C phase, confirming its ferroelectric nature. The P_s values could not be accurately determined as they were below the sensitivity of the measuring system. The CD spectra were recorded on free-standing films[38] of the mixtures in the smectic C phase.

(*R*)-4-(1-(Hexyloxy)ethyl)phenol (3a-(*R*)C1). A solution of (*R*)-4-(1-(hexyloxy)ethyl)acetophenone (100 mg, 0.4 mmol) in dry $CHCl_3$ (0.5 mL) was added to a solution of *m*-chloroperbenzoic acid (142 mg, 0.79 mmol) in dry $CHCl_3$ (2 mL), and the mixture was stirred for 10 days. The mixture was diluted with $CHCl_3$, and this solution was extracted with $NaHCO_3$ (aqueous, saturated) and water and dried ($MgSO_4$), and the solvent was removed. The crude product was subjected to flash column chromatography (SiO_2, hexanes:ethyl acetate

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(54) For two recent articles, see: (a) Heinemann, C.; Demuth, M. *J. Am. Chem. Soc.* **1997**, *119*, 1129−1130. (b) Linwane, P.; Magnus, N.; Magnus, P. *Nature* **1997**, *385*, 799−801. The latter example is a result of a folded conformation brought about by cation binding. For a very recent report has detailed long distance transfer of chirality in the formation of poly(isocyanide)s derived from helicenes, see: Chen, J. P.; Gao, J. P.; Wang, Z. Y. *Polym. Int.* **1997**, *44*, 83−87.

(55) Odd−even effects in aliphatic chains have also been observed in amphiphilic assemblies, see: (a) Yamada, N.; Okuyama, K.; Serizawa, T.; Kawasaki, M.; Oshima, S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2707−2713. (b) Shimizu, T.; Mitsutoshi, M. *J. Am. Chem. Soc.* **1997**, *119*, 2812−2818.

(56) The influence of $\pi-\pi$ interactions in synthesis has been discussed. For a review, see: (a) Jones, G. B.; Chapman, B. J. *Synthesis* **1995**, 475−497. For concrete examples, see: (b) Corey, E. J.; Becker, K. B.; Varma, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 8616−8618. (c) Norrby, P.-O.; Becker, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1996**, *118*, 35−42. (d) Quan, R. W.; Li, Z.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 8156−8157. (e) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 11038−11053.

(57) Dipole−dipole interactions leading to helical structures induced in nematic liquid crystals has been proposed. See: Khachaturyan, A. G. *J. Phys. Chem. Solids* **1975**, *36*, 1055−1061.

(58) Walba, D. M.; Stevens, F.; Clark, N. A.; Parks, D. C. *Acc. Chem. Res*. **1996**, *29*, 591−597.

(59) (a) Teerenstra, M. N.; Klap, R. D.; Bijl, M. J.; Schouten, A. J.; Nolte, R. J. M.; Verbiest, T.; Persoons, A. *Macromolecules* **1996**, *29*, 4871−4875. (b) Teerenstra, M. N.; Hagting, J. G.; Schouten, A. J.; Nolte, R. J. M.; Kauranen, M.; Verbiest, T.; Persoons, A. *Macromolecules* **1996**, *29*, 4876−4879.

90:10). Complete separation of the acetate from the starting material proved impractical. The impure material (70 mg) was dissolved in a mixture of MeOH (3 mL) and H_2O (1 mL), $LiOH{\cdot}H_2O$ (70 mg, 1.7 mmol) was added, and the mixture was stirred for 2 h. The mixture was poured onto a mixture of ice and HCl (aq), and the mixture was extracted with ethyl acetate. The organic phase was washed with water and brine and dried over $MgSO_4$, and the solvent was removed. The crude phenol was purified by flash column chromatography (SiO_2, hexanes:ethyl acetate 85:15): white solid, 90%; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, $J = 6.6$ Hz, 3H, CH_2CH_3), 1.14−1.48 (m, 6H, CH_2), 1.39 (d, $J = 6.5$ Hz, 3H, $CHCH_3$), 1.52 (m, 2H, CH_2), 3.25 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.32 (q, $J = 6.6$ Hz, 1H, $CHCH_3$), 5.40 (s, 1H, O*H*), 6.79 (d, $J = 8.5$ Hz, 2H, H_o to OH), 7.16 (d, $J = 8.5$ Hz, 2H, H_o to CH); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.0, 22.6, 24.0, 25.8, 29.8, 31.6, 68.6, 77.4, 115.2, 127.5, 136.1, 155.0; $[\alpha]^{25}_{546}$ ($CHCl_3$) +54.8 deg $cm^2\ g^{-1}$.

General Procedure for Synthesis of Phenols 3b−g. The appropriate benzyl-protected phenol was dissolved in CH_2Cl_2, and 10% Pd/C (Degussa type, 20 wt % of substrate) was added. An atmosphere of H_2 (1 atm) was introduced, and the mixture was allowed to stir at ambient temperature for 4 h. The crude mixture was filtered through Celite, the solvent was stripped, and the product was subjected to flash column chromatography (SiO_2, hexane:ethyl acetate, using a composition from 97:3 to 9:1 by volume depending on the product). Representative analytical data is given for (*R*)-4-(1-(methylheptyl)oxy)phenol (**3b**-(*R*)C2): colorless oil, 93%; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, $J = 7$ Hz, 3H, CH_2CH_3), 1.23 (d, $J = 6$ Hz, 3H, $CHCH_3$), 1.29−1.75 (m, 10H, $(CH_2)_5$), 4.17 (q, $J = 6$ Hz, 1H, $CHCH_3$), 4.69 (s, 1H, O*H*), 6.72 (d, $J = 9$ Hz, 2H, OArO), 6.76 (d, $J = 9$ Hz, 2H, OArO).

General Procedure for Synthesis of Phenyl Benzoate Formamide Derivatives 4a−g. The appropriate phenol **3a−g** (1 mol equiv) was combined in dry CH_2Cl_2 (typically 6 mL for 1.5 mmol of product) with 4-formamidobenzoic acid (1 mol equiv), DCC (1 mol equiv), and DMAP (catalytic quantity), and the mixture was stirred in dry at ambient temperature for 16 h. Filtration of the reaction mixture (to remove precipitated dicyclohexylurea) afforded a solution which was diluted with CH_2Cl_2 and extracted with NaOH (aqueous, 2%, 2 × 50 mL) and H_2O (50 mL). Drying (Na_2SO_4) and removal of solvent afforded white solids which were subjected to flash column chromatography (SiO_2, 1:1 ethyl acetate:hexane by volume) leaving the products as white solids. Representative analytical data is given for (*R*)-4-(1-(methylheptyl)oxy)-phenyl 4-formamidobenzoate (**4b**-(*R*)C2): white solid, 85%; mp 128−129 °C; EIMS 369 $[M^+]$; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, $J = 7$ Hz, 3H, CH_2CH_3), 1.1−2.0 (m, 13H, $CHCH_3$ and $(CH_2)_5$), 4.32 (quintet, $J = 6$ Hz, 1H, $CHCH_3$), 6.90 (d, $J = 9$ Hz, 2H, H_o to OR), 7.08 (d, $J = 9$ Hz, 2H, H_m to OR), 7.10 (d, $J = 9$ Hz, 0.7H, H_o to NH), 7.68 (d, $J = 9$ Hz, 1.3H, H_o to NH), 8.13 (d, $J = 9$ Hz, 1.3H, H_m to NH), 8.18 (d, $J = 9$ Hz, 0.7H, H_m to NH), 8.33 (s, 0.65H, HCO in cis), 8.47 (s, 0.65H, NH in cis), 8.92 (d, $J = 11$ Hz, 0.35H, HCO in trans), 9.07 (d, $J = 11$ Hz, 0.35H, NH in trans); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.5, 74.6, 116.6, 117.2, 119.3, 122.4, 125.2, 125.8, 131.4, 132.1, 141.8, 142.0, 144.1, 156.1, 159.6, 162.2, 165.1, 165.3; $[\alpha]^{25}_{546}$ (CH_2Cl_2) −5.2 deg $cm^2\ g^{-1}$. Anal. Calcd. for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.84; H, 7.54; N, 4.05. The (*S*) enantiomer (79% yield) has identical physical and spectroscopic characteristics and $[\alpha]^{25}_{546}$ (CH_2Cl_2), +5.2 deg $cm^2\ g^{-1}$. The corresponding racemic material (82% yield) has identical physical and spectroscopic characteristics and exhibits no rotation of plane-polarized light.

General Procedure for Synthesis of Phenyl Benzoate Isocyanide Derivatives 1a−g. The appropriate formamide **4a−g** (1 mol equiv) was combined in dry CH_2Cl_2 (typically 6 mL for 1.5 mmol of product) with dry NEt_3 (2 mol equiv), and the mixture was cooled in an ice/salt mixture under an atmosphere of Ar. Trichloromethylchloroformate (diphosgene, 0.55 mol equiv) in dry CH_2Cl_2 was added dropwise by syringe, and the mixture was stirred while warming to ambient temperature for 1 h. Aqueous $NaHCO_3$ (10%) and CH_2Cl_2 were added, and the separated organic phase was washed with $NaHCO_3$ (aqueous, 10%) and H_2O, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude products were purified by flash column chromatography (SiO_2, hexane:EtOAc, 3:1). The products were stable in CH_2Cl_2 solution under Ar at reduced temperatures for months, but in general were unstable at room temperature in their pure state as isolated. Representative analytical data is given for (*R*)-4-(1-(methylheptyl)oxy)-phenyl 4-isocyanobenzoate (**1b**-(*R*)C2): off-white solid, 78%; EIMS 351 $[M^+]$; IR (NaCl plate) 2123 (NC), 1736 (CO) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, $J = 7$ Hz, 3H, CH_2CH_3), 1.1−1.8 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.33 (q, $J = 6$ Hz, 1H, $CHCH_3$), 6.92 (d, $J = 9$ Hz, 2H, CH_o to $OCHCH_3$), 7.10 (d, $J = 9$ Hz, 2H, CH_m to $OCHCH_3$), 7.51 (d, $J = 9$ Hz, 2H, CH_o to NC), 8.24 (d, $J = 9$ Hz, 2H, CH_m to NC); $[\alpha]^{25}_{546}$ (CH_2Cl_2) −5.2 deg $cm^2\ g^{-1}$. The (*S*) enantiomer (69% yield) has identical physical and spectroscopic characteristics and $[\alpha]^{25}_{546}$ (CH_2Cl_2) +5.2 deg $cm^2\ g^{-1}$. The corresponding racemic material (87% yield) has identical physical and spectroscopic characteristics and exhibits no rotation of plane-polarized light.

General Procedure for the Preparation of Polymers 5a−g. The appropriate isocyanide **1a−g** was dissolved in dry CH_2Cl_2 at a concentration of freshly prepared isocyanide monomer of approximately 200 mM, and 0.01 mol equiv of $NiCl_2{\cdot}6H_2O$ in MeOH (42 mM) was added, air being present. The mixture, which immediately turned dark brown, was stirred at ambient temperature in a sealed vial for 2 days. The solvent was evaporated, MeOH was added, and the resulting tan-colored solid was filtered at the pump, washed with two aliquots of MeOH, and dried in vacuo. The chiroptical data for the polymers are collected in Table 1 in the text. Representative analytical data is given for (+)-poly-{(*R*)-4-(1-(methylheptyl)oxy)phenyl 4-iminobenzoate} (**5b**-(*R*)C2): 87%; IR (KBr) 1740 (CO), 1656 (C═N) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.65−0.94 (bm, 3H, CH_2CH_3), 0.96−1.80 (bm, 13H, $CHCH_3$ and $(CH_2)_5$), 3.95−4.33 (bm, 1H, $CHCH_3$), 5.45−6.30 (bm, 2H), 6.31−7.25 (bm, 4H), 7.26−8.15 (bm, 2H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.6, 22.6, 25.5, 29.4, 31.8, 36.7, 74.1, 116.1, 116.5 (vb), 122.3, 128.4 (b), 130.0 (vb) 143.8 (b), 150.9 (b), 155.6, 160.7 (b), 162.3 (b), 164.0 (b). The (−)-(*S*) diastereomer and the corresponding racemic modification were isolated in 93 and 89% yields, respectively, and had identical spectroscopic characteristics.

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Supporting Information Available: Complete experimental procedures for the preparation of 4-formamidobenzoic acid, 1-(4-acetylphenyl)ethanol, (*R*)-1-(4-acetylphenyl)ethyl acetate, (*R*)-1-(4-acetylphenyl)ethanol, (*R*)-4-(1-(hexyloxy)ethyl)acetophenone, (*R*)-1-(1-(methylheptyl)oxy)4-(benzyloxy)benzene, (*R*)-2-[(4-benzyloxy)phenoxy]-*n*-butyl propionate, and (*R*)-2-[4-hydroxyphenoxy]-*n*-butyl propionate, and analytical data for **1a**-(*R*)C1, **1c**-(*R*)C2, **1d**-(*S*)C3, **1e**-(*S*)C3, **1f**-(*S*)C4, **1g**-(*S*)C5, **4a**-(*R*)C1, **4c**-(*R*)C2, **4d**-(*S*)C3, **4e**-(*S*)C3, **4f**-(*S*)C4, **4g**-(*S*)C5, **5a**-(*R*)C1, **5c**-(*R*)C2, **5d**-(*S*)C3, **5e**-(*S*)C3, **5f**-(*S*)C4, **5g**-(*S*)C5, as well as Figures S1−S4 showing the CD spectra of the induced cholesteric and smectic C mesophases, and the dipoles responsible for effects on the helical induction in the LCs (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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