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Chiral teleinduction in the polymerization of isocyanides

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Abstract

The effect of the length, constitution and conformation of rod-like spacers between an isocyanide group and a chiral substituent on the diastereoselectivity of the polymerization of these monomers has been studied. The chiral induction has been monitored using circular dichroism spectroscopy as well as polarimetry, and the polymers have also been characterized using NMR, gel permeation chromatography, and MALDI-TOF mass spectrometry. Of the different spacers that have been studied, the benzoate moiety is the most efficient in propagating the chiral information from stereogenic center to the polymer backbone. Remarkably, when this moiety is included in a spacer which separates the stereogenic center from the reactive carbon atom in the monomer by 21 Å an appreciable induction of activity is still observed in the resulting polymer.

Keywords: Chirality induction; Circular dichroism; Diastereoselectivity

1. Introduction

The mechanisms by which chirality is transmitted over large distances are intriguing and important in a number of research areas [1–9]. Three general types of chiral induction exist: (i) during the formation of covalent bonds in which stereoelectronic and steric effects determine the enantio- or diastereo-selectivity kinetically [10–13]; (ii) in the development of non-covalent interactions in chiral aggregates wherein non-covalent interactions determine the thermodynamically most stable assembly [14–22] and; (iii) processes in which the enantio- or diastereo-selectivity of the formation of covalent bonds is influenced by non-covalent bonds [23–29]. It is in this latter group that non-covalent interactions can lead to a kinetically stable product by chiral induction over a large distance, or *chiral teleinduction*.

When either enantiomer of **1A** (Scheme 1), in which a stereogenic center is separated from an isocyanide moiety by a phenyl benzoate spacer, is polymerized a significant diastereoselectivity in the formation of the chiral backbone of the poly(isocyanide) **2A** is recorded [30,31]. This chiral induction takes place over a distance of approximately 16 Å through the phenyl benzoate group between the isocyanide moiety and the asymmetrically-substituted carbon atom. Because of this long-range effect, we refer to it as teleinduction. The phenomenon is subject to odd–even effects, as observed by the alternating helicities of the polymer backbone when the stereogenic center is moved sequentially down the aliphatic chain. Unlike other chiral polymers which display equilibria [32–37], the poly(isocyanide)s [38–48] of type **2A** have atropoisomeric helical conformations generated during their synthesis with the aid of non-covalent interactions and which are kinetically stable with respect to changes in temperature and solvent [31]. They can even be forced to adopt other chiral conformations by kinetic trapping using appropriate co-monomers [49,50].

The observation of diastereoselectvity over such a long monomer **1A** raises a number of interesting questions, such as: How does the diastereoselectivity vary with changes in (i) the length of the rod-like spacer; (ii) the rigidity of the spacer and; (iii) the conformation of the rod-like spacer? These questions are fundamental in order to formulate a hypothesis which explains the unusual chiral induction

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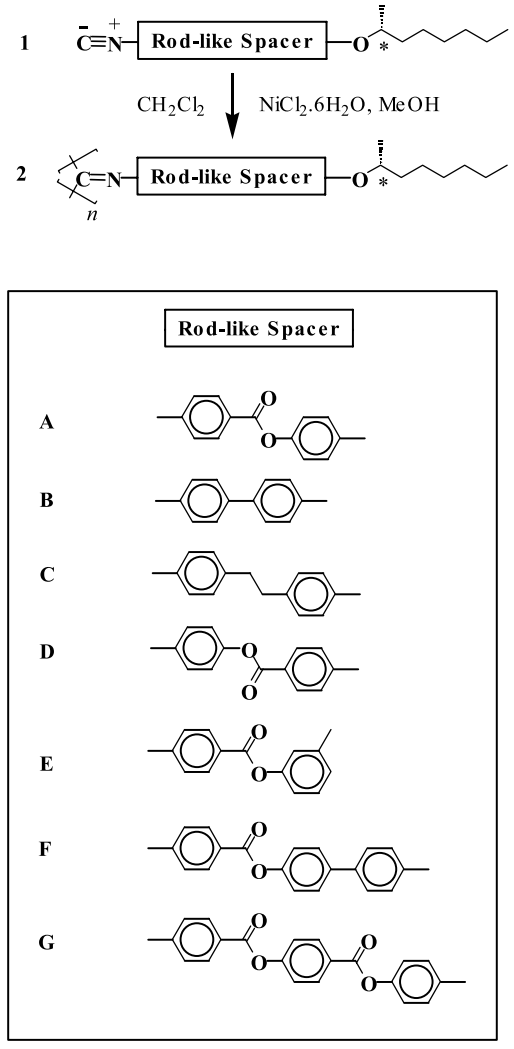


Scheme 1. Synthesis of the poly(isocyanide)s reported in this paper from the corresponding isocyanides. **A** was reported in [31].

phenomena taking place in this system. In this article we address these aspects by studying the diastereoselectivity of the nickel(II)-catalyzed polymerization of the isocyanides incorporating rod-like spacers depicted in Scheme 1 with a common chiral 'tail', (*R*)-2-octyl.

The main objective of this work is to investigate widely the influence of the rod-like unit upon the chiral induction during the polymerization process. For this reason, all the polymers in this study bear the same chiral chain derived from 2-octanol. This group has been proven already to be a well-behaved part of the molecules [30,31].

The polyisocyanide **2A**, studied in our previous work [31] incorporates a phenyl benzoate-derived monomer in which the phenyl group was substituted at its 4-position with the chiral tail (Scheme 1). In the present work, we probe subtle changes in the constitution of the spacer aimed at establishing the effect on the induction of (i) the distance between the stereogenic center and the isocyanide group and, simultaneously, the conformational twisting possibilities of the rod-like spacer (in **B**, **F** and **G**), (ii) the rigidity of the spacer, making it more flexible (in **C**), (iii) the electronic characteristics of the aromatic ring incorporating the chiral tail by changing the orientation of the carboxylate group, so that the chiral group is attached to the benzoate moiety (change of dipole moment, in **D**), and the type of substitution of the benzene ring adjacent to the stereogenic center is changed from *para* to *meta* (in **E**).

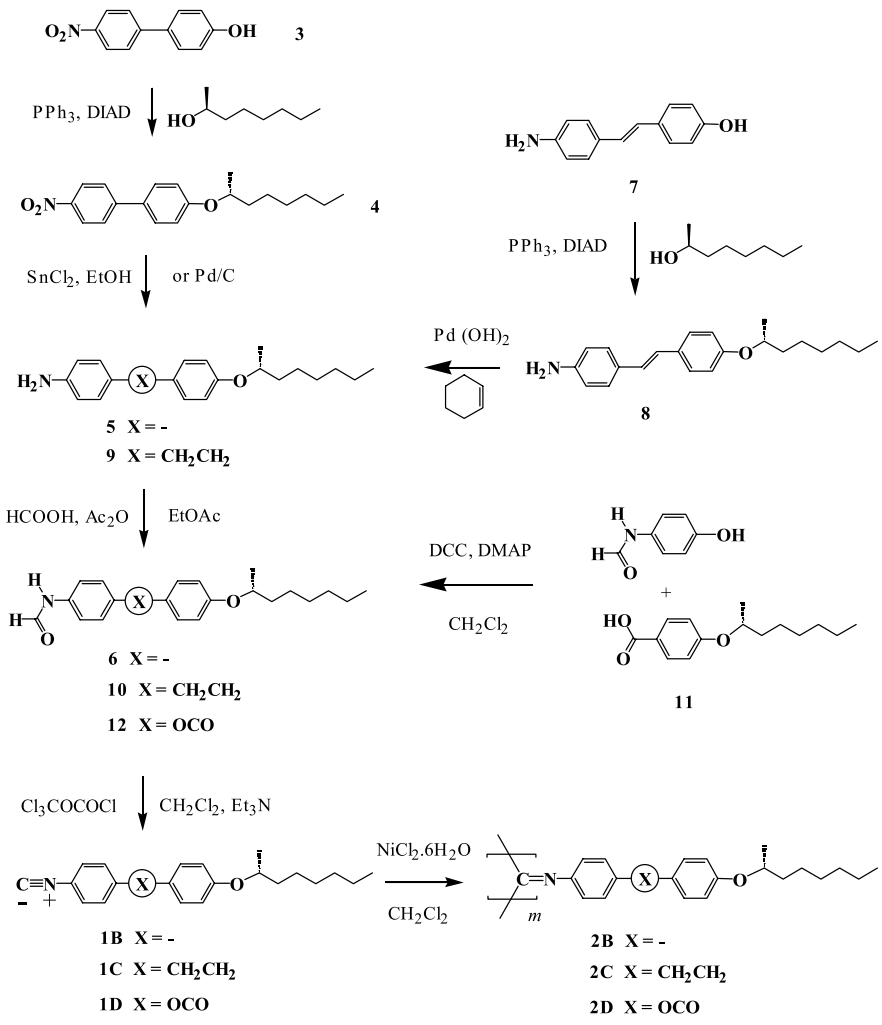
2. Results

2.1. Monomer and polymer synthesis

The series of compounds leading to polymer **2B** incorporating the biphenyl moiety were prepared according to the route outlined in Scheme 2, and has common synthetic steps to the preparation of the other polymers. The phenol **3** [51] was reacted with the (*S*)-2-octanol using the Mitsunobu method [52,53] (which proceeds with inversion of configuration) to afford the (*R*) nitrophenol ether **4**. The nitro-group was reduced to the aromatic amine **5** with $SnCl_2$ in ethanol [54], and converted practically quantitatively into the formamide **6** with the mixed acetic/formic anhydride. Dehydration of the formamide with diphosgene [55] gave rise to the isocyanide **1B** in high yield. The conversion of the formamides to the isocyanides was evidenced clearly by NMR spectroscopy, which reveals much simpler spectra for the latter [56], as well as by the characteristic IR band (at approx. 2120 cm^{-1}) arising from the isocyanide moiety. The polymerization, as in all those carried out here, was performed under the standard conditions originally developed by Drenth, Nolte and co-workers [57–64], in which a methanolic solution of $NiCl_2 \cdot 6H_2O$ is added to a solution of the monomer in dry CH_2Cl_2 at a controlled concentration (an important factor, see [31]) of freshly prepared isocyanide monomer of 200 mM under air [65–67]. The poly(isocyanide) **2B** was isolated as a dark brown powder.

In order to study the influence of the rigidity of the spacer on the chiral transmission we prepared the monomer **1C**, incorporating the 1,2-diphenylethyl spacers (Scheme 2). This possibility was available from compound **7** and following a synthetic route similar to the previously mentioned compound. In particular, reduction of **8** with $Pd(OH)_2/C$ in cyclohexene in the presence of a hydrogen source (cyclohexene) gave the aniline derivative **9**, which, following the steps outlined for **2B**, allowed the preparation of poly(isocyanide) **2C**. Once (*R*)-4-(1-methylheptyloxy)-benzoic acid **11** had been coupled to 4-formamidophenol with dicyclohexyl carbodiimide (DCC) [68,69] (Scheme 2) the poly(isocyanide) **2D** was prepared in similar fashion.

The synthesis of polymer **2E** was achieved starting from commercial resorcinol monobenzoate (Scheme 3), using a route analogous to that involved previously [31]. Statistical monoalkylation of 4,4′-biphenol followed by chromatographic separation of the phenol **15** and subsequent DCC



Scheme 2. Synthesis of the **B**, **C** and **D** isocyanides and the corresponding polymers.

coupling and so on produced polymer **2F**. The macromolecule **2G** was similarly prepared from **17** which had been prepared using benzyl protection–deprotection protocol from (*R*)-4-(1-methylheptyloxy)phenol [31] and 4-benzyloxybenzoic acid (Scheme 3). All these polymers are light yellow solids.

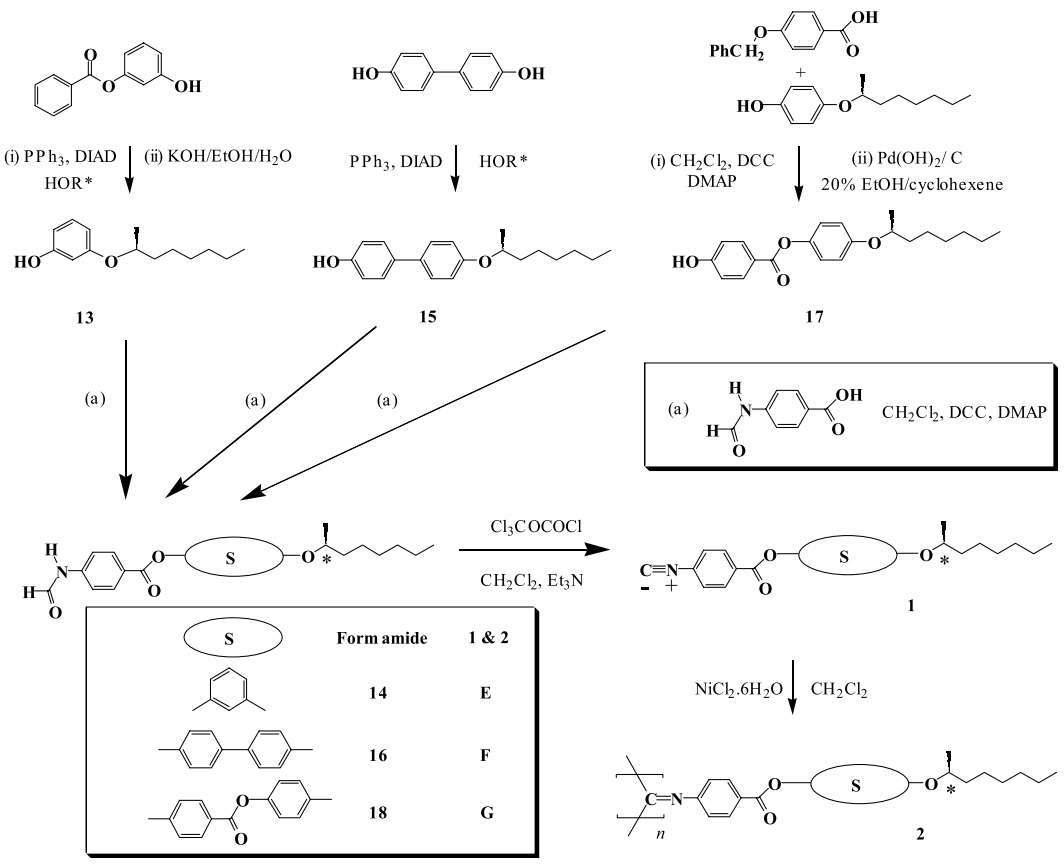
Polymerization yields, molecular weight characteristics, and chiroptical data for all the polymers are given in Tables 1 and 2 in the next section. All the polymers are very soluble in organic solvents such as toluene, methylene chloride, chloroform, THF and DMF, while in general they show low solubility in hexane, acetonitrile, and short-chain alcohols, and are water insoluble.

2.2. Structural and chiroptical characterization of the polymers

All the polymers presented here have ^{1}H NMR spectra which present a very broad set of resonances between approximately 5.5 and 8 ppm on account of the hindered

Table 1
Molecular weight and polydispersity index (as determined by GPC against polystyrene standards) for the polymers along with their yields

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	DP ($\bar{M}_n$)	PDI	Yield (%)
2A	32,000	52,494	71,350	91	1.64	87
2B	8500	20,250	42,100	28	2.38	96
2C	14,600	27,600	50,220	43	1.89	92
2D	18,000	26,000	35,000	51	1.46	81
2E	38,700	58,200	70,200	110	1.51	78
2F	23,200	63,700	129,600	56	2.7	81
2G	32,000	52,500	71,350	65	1.64	83



Scheme 3. Synthesis of the **E**, **F** and **G** isocyanides and the corresponding polymers.

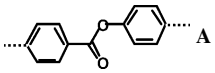
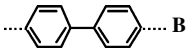
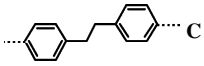
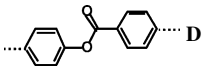
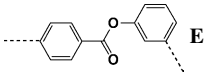
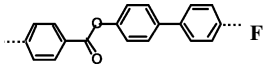
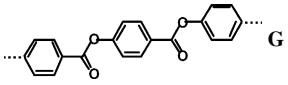
motion and probable conformational stereoirregularity of the polymers (vide infra) [70–74], while the alkyl chain substituents are more narrow but still poorly resolved compared with the isocyanide precursors. These spectral characteristics make impossible any detailed conclusion to be drawn concerning the structure of the polymers, although they do allow identification of any low molecular weight impurities which appear as well resolved peaks. In contrast, the ^{13}C NMR spectra are somewhat more informative.

While the spectra of the monomers are perfectly resolved, those of the polymers reveal resonances corresponding to the alkyl chain's carbon atoms which are clearly resolved, but aromatic carbon atom resonances show increasing chemical shift dispersion the nearer they are to the polymer backbone (Fig. 1). The chemical shift dispersion is to be expected in these polymers given the more hindered environment as well as the possibility stereoirregularity arising from *syn* and *anti* conformers (Fig. 2) which are possible in the helical and non-helical chain conformations proposed for these compounds. In particular, the resonance arising from the iminomethylene carbon atom of the skeleton shows both dispersion and even appearance as two separate peaks (between 160 and 165 ppm), as shown in Fig. 1 for **2E**.

The molecular weights and polydispersities of the polymers as determined by GPC [75] are presented in Table 1. In common with other polymers generated using the $NiCl_2 \cdot 6H_2O$ catalyst [57–64], the poly(isocyanide)s reported here have polydispersities of the order of between 1.4 and 2.7, in accord with the non-living nature of this polymerization method [31,66,71]. The isocyanides incorporating the benzoate attached to the isocyanide give polymers with highest molecular weights, in accord with the greater reactivity of the isocyanide group in these compounds when compared those in **1B** and **1C**.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry has, to our knowledge, never been reported as a characterization technique for poly(isocyanide)s. We used the method here, and while spectra of the high molecular weight polymers (more than 15 kDa) were not obtained in a wide range of matrices, the spectra of the lower molecular weight **2B** gave a spectrum (Fig. 3) with molecular weights which are largely in accord with the mass ranges observed using GPC. The mean mass differences between the peaks correspond to the monomer mass. Addition of silver triflate to this sample (spectrum not shown) also aided the sensitivity of the measurement, with the masses observed being shifted to higher values. Analysis of the spectrum recorded without additive give an $\bar{M}_w$ value of approximately 12,600 Da, slightly lower than that obtained by GPC. This observation supports the idea of a rigid structure for the poly(isocyanide)s, whose mass is

Table 2
Chiroptical data for the formamides and the corresponding polymers **2**

Spacer (number)	Formamide $[\alpha]_{546}^{25}$	Polymer $[\alpha]_{546}^{25}$	Polymer $\Delta\varepsilon_{363}$
 **A**	−5.2	+236	+3.05
 **B**	+4.2	+39.5	+0.52
 **C**	−1.8	−2.6	0
 **D**	−33	+102	+0.90
 **E**	−8.2	−109	−1.51
 **F**	−10	+23.6	+0.78
 **G**	−4.4	+23.1	+0.30

Specific optical rotations (deg $cm^2\ g^{-1}$) were measured in 1 cm cell ($c = 10$–20 mg ml^{-1} in $CHCl_3$) at ambient temperature. CD spectra ($\Delta\varepsilon$ in l $mol^{-1}\ cm^{-1}$) were recorded in THF.

slightly exaggerated by GPC measurements on account of their non-globular structure.

The optical activity of both the monomers and the polymers [76] were investigated in solution using polarimetry as well as circular dichroism spectroscopy (CD), and the data are shown in Table 2. There are some parallels between the orders of the specific optical rotations ($[\alpha]_{546}^{25}$) and the degrees of the differential molar absorptivities ($\Delta\varepsilon_{363}$) from the CD spectra. However, the CD spectra of the polymers and monomers are much more enlightening 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 results obtained will be discussed in more detail below.

3. Discussion

In the CD spectra, the most optically-active polymers presented here have two bands centered at approximately 252 and 363 nm. In the monomers, the former band has a very low intensity and the latter is non-existent. 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 is related with the P or M helicity of the poly(isocyanide) backbone in one sense [57–64,77–79] or another [80]—and presents clear evidence that the polymer backbone has an optically active conformation. The narrower 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(isocyanides) [81]. The results gathered in Table 2 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 length and constitution of the spacer between the carbon atoms which form part of the polymer skeleton and the stereogenic center.

The induction of chirality to the polymer backbone in poly(isocyanide) **2A** has been studied deeply [30,31]. The phenyl benzoates, the spacer in this polymer, generally present a twisted conformation between the RC_6H_4COO unit (which is basically planar [82]) and the phenolic ring, their corresponding dihedral angle being in the range 30 to 90° in the solid state, with a maximum population at around 80° [82,83]. This twisted conformation seemed to favor the possibility of chirality transfer from the stereogenic center in the terminal chain into the poly(isocyanide) backbone, through this semi-rigid spacer. In the present work, this polymer has been taken as a model, and also as the starting point of a comparative study based on modifications of the structure of the rigid spacer between the stereogenic center and the reactive isocyanide group.

We have evaluated the effect of the spacer length using biarylic as well as triarylic systems as a rod-like spacer. To perform this study we prepared monomers **1B**, **1F** and **1G**.

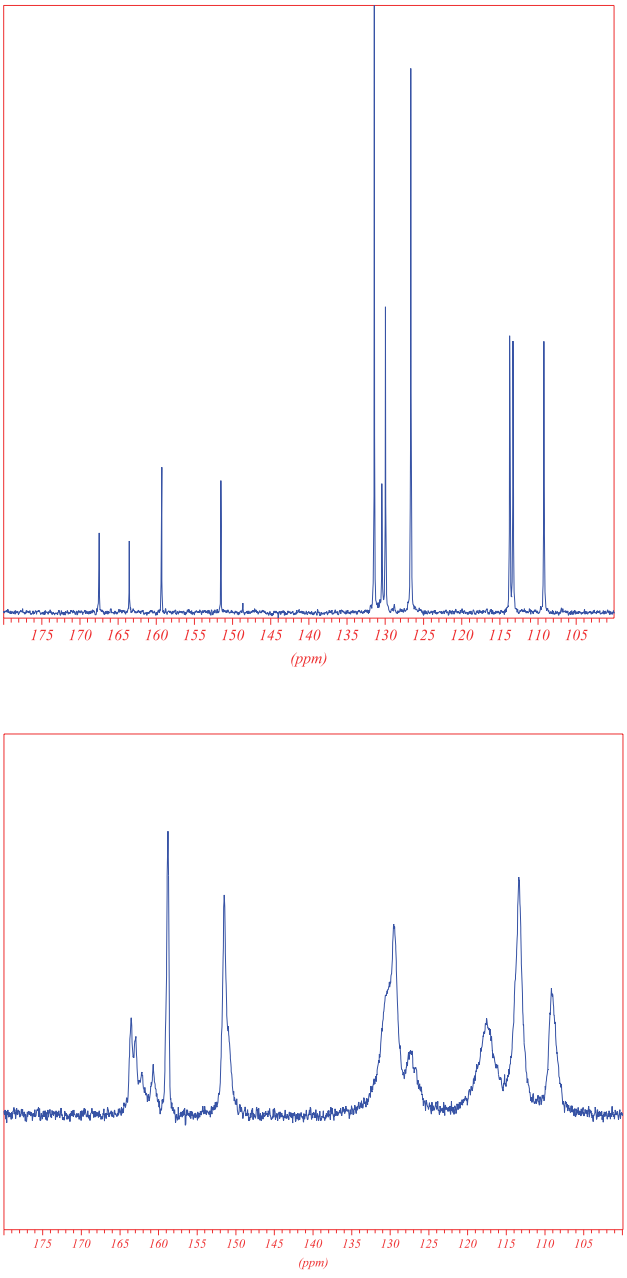


Fig. 1. An example of the aromatic region of the ^{1}H-decoupled ^{13}C NMR spectrum of isocyanide monomer **1E** and the corresponding poly(isocyanide) **2E** in $CDCl_3$.

Their helical induction upon polymerization has been compared with that of **1A**. By using different types of linking group between aromatic rings we have been able, simultaneously, to establish the above-mentioned efficiency of a biased twisting within the rod-like spacer on chirality-transfer efficiency.

When a biphenyl unit is used as spacer between the isocyanide and the chiral chain the corresponding polymer **2B** presents a positive Cotton effect located at 363 nm (Fig. 4) in a position of the ultraviolet corresponding to the polymer backbone. The biphenyl spacer is capable of

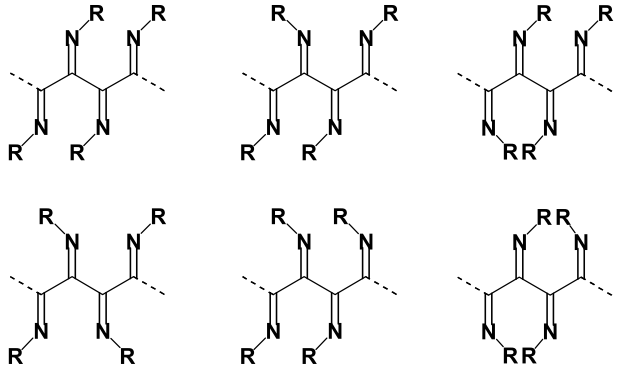


Fig. 2. The possible conformers of an oligo(isocyanide) comprised of four monomers.

adopting twisted and therefore chiral conformations [84–89]—as does the phenyl benzoate group which induces the same sign of Cotton effect—which could be influenced by the chiral groups attached to them transmitting the chiral information to the reactive isocyanide group. However, the possible twisted conformation seems to be not as efficient since the magnitude of the chiral induction in the formation of **2B** ($\Delta\varepsilon = 0.52$ deg cm^2 g^{-1}) is not as marked as in that of **2A** ($\Delta\varepsilon = 3.05$ deg cm^2 g^{-1}). Besides, this occurs in spite of the stereogenic center being closer to the isocyanide group. Moreover, a poorly defined backbone conformation, as hinted at in the ^{13}C NMR spectrum of the former poly(isocyanide) can also disfavor chirality transfer. Two very broad resonances corresponding to the imino carbon atom in the skeleton of the macromolecule are observed (Fig. 5) which may point to an intermediate situation between that of the well-defined backbones in which two clear resonances are observed and those where an extremely broad resonance is present in the spectrum.

Polymerization of the monomers incorporating three benzene rings in between the isocyanide group and the chiral substituent gives polymers which both show optical activity arising from their backbone, as revealed in their CD spectra (Fig. 6). In both cases the spacers induce a chirality i.e. polymer backbone which affords a positive Cotton effect. The observation of induction of chirality in these polymerizations is particularly remarkable given that the distance between the carbon atom that forms part of the polymeric chain and the stereogenic center is approximately 18 Å in **2F** and 21 Å in **2G**.

The induction through the two triarylic spacers, **F** and **G**, built through the formal addition of a benzoate group to **1B** and **1A**, respectively, confirms the efficiency of the phenyl benzoate group as a conveyor of chiral information. The addition of a benzoate group to the biphenylic system (**1F**) promotes greater induction than that observed in **1B**, a truly remarkable observation given that the distance between stereogenic center and polymer backbone is shorter in the former by around 5 Å. The chiral induction during the formation of polymer **2G** is somewhat lower than **2F**, but the distance between stereogenic center and backbone is

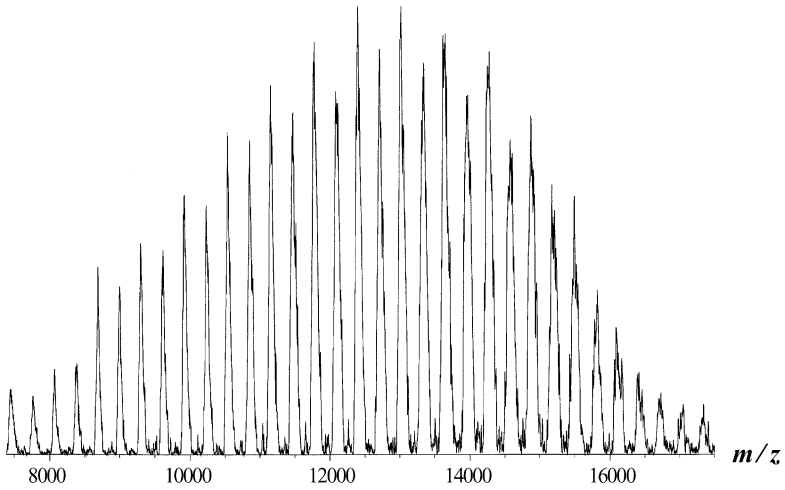


Fig. 3. MALDI-TOF mass spectrum of **2B**, recorded in positive ion mode using indole acrylic acid as matrix.

larger in the former, and in addition **1G** can present conformational isomers in their rod-like structure, a '*cis*' and '*trans*' pair (Fig. 7), whose mismatch during the growth of the polymer would lead to lower diastereoselectivity.

The rigidity of the spacer between the stereogenic center and the isocyanide group is essential, as proved here when the 1,2-diphenylethylene linking group was employed. No chiral transmission takes place at all. The polymer **2C** has a CD spectrum (not shown) devoid of optical activity in the area corresponding to the polymer backbone, which can be interpreted as a result of the high flexibility and the conformational freedom of the linking unit which gives no preferential transfer of chirality.

On the other hand, changing the orientation or connectivity of the ester group in the phenyl benzoate is a 'mutation' to **1A**, which is tolerated in its ability to undergo diastereoselective polymerization. When **1D**—with the ester group 'reversed'—is polymerized the optical activity of **2D** is lower than that of **2A**.

When the chiral group is located at the 3-position of the closest phenyl ring to it, the induction of chirality is maintained but reversed respect to the former cases. This observation is consistent with an odd–even effect, previously observed when changing the position of the stereogenic center in the terminal alkyl chain [31]. The polymer **2E** shows appreciable optical activity with the Cotton effect at 363 nm (Fig. 4) characteristic of a well defined polymer backbone, a hypothesis backed up by the ^{13}C NMR spectrum (Fig. 1).

4. Summary and conclusions

All the polymers prepared here are chiral—they all contain the (*R*)-2-octyl chain—yet their overall chirality, transmitted through the rod-like spacer to the polymer backbone, shows dramatic differences. The results demonstrate that during the polymerization the spacer plays an active and crucial role in the transmission of stereochemical information. We have shown that chirality transfer active during diastereoselective reactions is possible over extremely large distances—remarkably, as far as 21 Å. Polymers **2F** and **2G** have significant optical activity arising from the polymer backbone conformation as a result of chiral teleinduction operating during their synthesis.

Some chiral semi-rigid twisted conformation must be adopted by the spacer in between the stereogenic center and the reactive group, giving dihedral angles which could be biased towards a given sense according to the influence of the stereogenic center. Although in a less efficient way than phenyl benzoate (**1A**), the biphenyl spacer within the monomer **1B** behaves similarly to the benzoate spacer introducing a dihedral angle between the benzene rings, which is responsible for a twisted conformation capable of transmitting the chiral information to the reactive group. When the transmission of the chiral information is broken because of the conformational freedom of the spacer, as occurs for monomer **1C** incorporating an ethylene moiety, no teleinduction is observed. The semi-rigid spacer is crucial.

It is striking that the Cotton effect associated with the backbone of the polymer at 363 nm is greater in **2F** than it is in **2B**, even though the chiral message has been passed over 6 Å more. The contrary occurs for **2A** and **2G**, in which a second benzoate group has been added. The intensity of the Cotton effect is much lower for the polymer with three rings within the spacer than for this derived from phenyl benzoate. It seems that a benzoate group reinforces chirality transfer in any case, and two benzoate groups weaken it because of conformational mismatch.

The results reported here show that even when kinetics rule predominantly in the generation of a chiral conformation which is determined during the formation of the polymers—as has been confirmed in previous studies

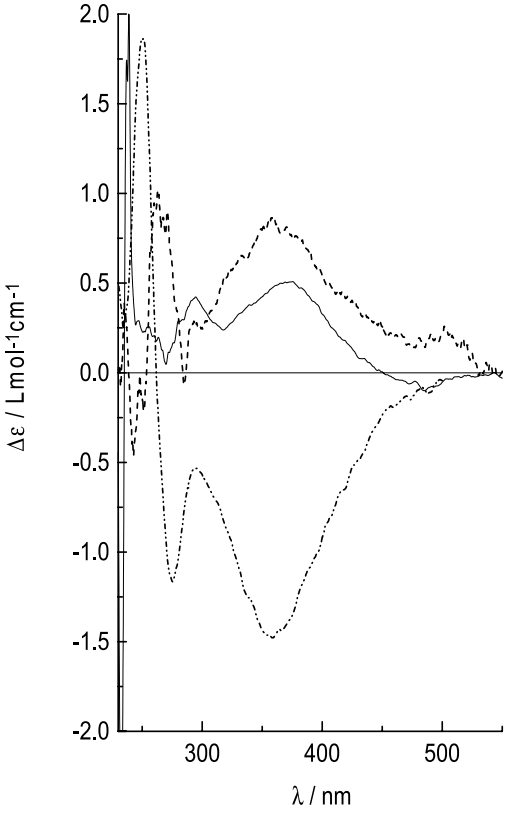


Fig. 4. The CD spectra (in THF at RT) **2B** (solid line), **2D** (dashed line) and **2E** (dotted line).

[50,90]—a kinetic stereoselection can be seen over extremely large distances.

5. Experimental section

5.1. Materials and methods

Chemicals were used as purchased from the Aldrich Chemical Company and Fluka Chemie AG. The enantiomeric purity of the enantiomers of 2-octanol (Flukabrand) was assayed by polarimetry prior to use. 4-Hydroxy-4′-nitrobiphenyl [51], and 4-formamidobenzoic acid [31] were prepared according to literature methods. 4-benzyloxybenzoic acid and resorcinol monobenzoate were commercially purchased from Aldrich and were used without further purification. Solvents (SDS) were purified 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.

Electron impact mass spectra (EIMS) were obtained on a VG TS-250 mass spectrometer operating in the positive mode (70 eV). The MALDI mass spectra were recorded using a KRATOS ANALYTICAL (Manchester, UK) KOMPACT MALDI-2 K-PROBE instrument, which uses a 3 ns pulse from a nitrogen laser ($\lambda = 337$ nm) at a target area of 100 μm diameter, and pulse extracts the ions down a linear flight tube (2 m). Spectra were run in positive high mass mode, which employs a 20 kV pulsed extraction of the ions, typically accumulating 500 shots for each spectrum. The matrices were used as purchased from Aldrich Chemical Co. The samples were prepared by dissolving the polymer and matrix (at a concentration of 10 mg ml^{-1}) in an approximate 1:100 ratio or lower in dichloromethane and then applying a 2 μl sample of the solution onto the stainless steel sample holders used in the instrument. The samples were run immediately after air-drying at room temperature. 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. Determination of the helix sense in cholesteric mixtures was carried out as described in Ref. [31].

GPC was performed using two TOSOHAAS TSK-gel columns, G4000HXL and G3000HXL (7.8 mmID × 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 ml min^{-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.

The chiroptical data for the polymers and formamides are collected in Table 1 in the text, and the GPC data for the polymers in Table 2.

5.2. General synthetic procedures

Conversion of nitro aromatics into amines. An ethanolic solution of the nitro-aromatic compound was purged with nitrogen, then $SnCl_2$ was added as a solid, and the mixture was brought to reflux immediately under nitrogen. After 1.5 h, the mixture was poured onto ice (50 g), and K_2CO_3 was added until the solution became basic. The mixture was extracted with diethyl ether, and the organic layers were dried ($MgSO_4$) and stripped of solvent. The materials were subject to column chromatography, where appropriate.

Conversion of aromatic amines into formamides. The aniline derivative (1 mol equiv.) was dissolved in dry EtOAc (typically 25 ml for 5 mmol of product) and the mixture was cooled to 0 °C under a $CaCl_2$ guard. A mixture of formic acid and acetic anhydride (1.8 ml of a 10.8:4.35 solution previously stirred together for 1 h) was added

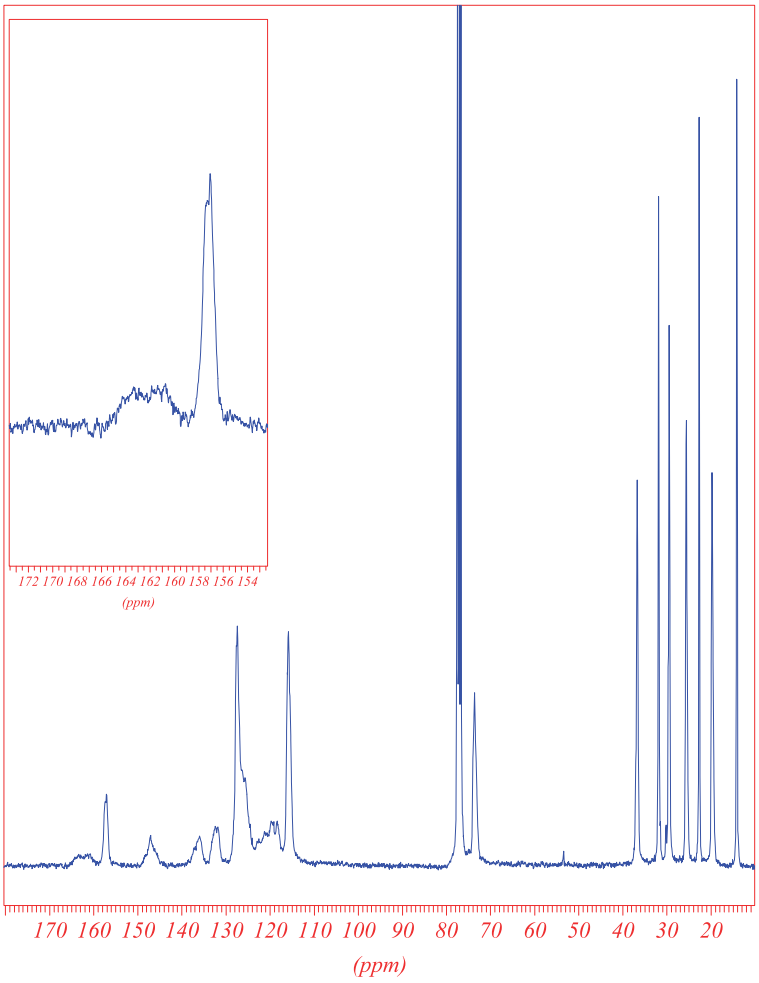


Fig. 5. ^{1}H-decoupled ^{13}C NMR spectrum of poly(isocyanide) **2B** in $CDCl_3$. Inset: an enlargement of the area of the imino carbon atom resonances.

dropwise, and the reaction was allowed to proceed for 2 h. An aqueous solution of $NaHCO_3$ was added, and the product was extracted with ethyl acetate, and chromatographed on a column (SiO_2, CH_2Cl_2/MeOH 2%).

General procedure for coupling of 4-formamidobenzoic acid with phenols. The appropriate phenol (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.), dicyclohexyl carbodiimide (1 mol equiv.) and 4-dimethylamino pyridine (catalytic quantity), and the mixture was stirred in the dry at ambient temperature (16 h). Filtration of the reaction mixture (to remove precipitated dicyclohexyl urea) afforded a solution which was diluted with CH_2Cl_2 and extracted with NaOH (aq., 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).

Conversion of formamides into isocyanides. The appropriate formamide (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 $NaHCO_3$ (aq., 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.

Preparation of poly(isocyanide)s. The isocyanide was dissolved in dry CH_2Cl_2 at a concentration of freshly prepared 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 and washed with two aliquots of MeOH, and was dried in vacuo.

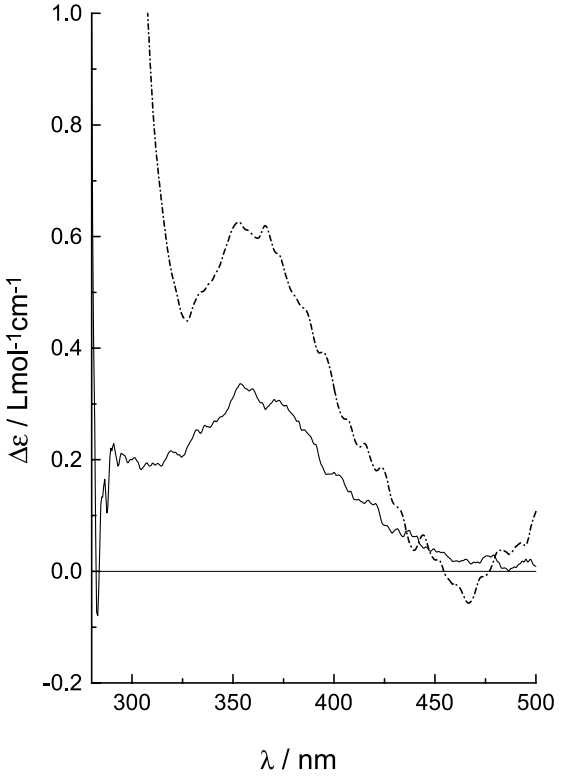


Fig. 6. The CD spectra (in THF at RT) of polymers **2F** (dotted line) and **2G** (solid line).

*(R)-4-(1-Methylheptyloxy)-4′-nitrobiphenyl (**4**)*. A mixture of (*S*)-2-octanol (3.46 mmol), 4-hydroxy-4′-nitrobiphenyl [51] (**3**, 732 mg, 3.40 mmol) and triphenylphosphine (1.11 g, 4.24 mmol) in dry THF under an Ar atmosphere was cooled in an ice/salt mixture and a solution of diethylazodicarboxylate (DEAD, 0.75 ml, 4.24 mmol) in THF was added dropwise over 30 min, and the resulting red solution was stirred at ambient temperature for 14 h. The resulting yellow mixture was quenched with water (10 ml), and the mixture was stripped of THF, and the residue was partitioned between CH_2Cl_2 and brine. The dried organic fraction was stripped of solvent, and the residue was subjected to column chromatography (SiO_2, hexane/CH_2Cl_2 2:1). The product was isolated as a yellow oil, 93%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.15–1.85 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.41 (sext., $J=6$ Hz, 1H, $CHCH_3$), 6.98 (d, $J=8.8$ Hz, 2H, H_o to OR), 7.54 (d, $J=8.8$ Hz, 2H, H_m to OR), 7.66 (d, $J=8.8$ Hz, 2H, H_m to NO_2), 8.23 (d, $J=8.8$ Hz, 2H, H_o to NO_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.4, 74.0, 116.3, 124.1, 126.9, 128.6, 130.6, 146.4, 147.2, 159.2. $[\alpha]^{25}_{546}$ (CH_2Cl_2), +6.9 deg cm^2 g^{-1}.

*(R)-4-(1-Methylheptyloxy)-4′-formamidobiphenyl (**6**)*. (*R*)-4-(1-Methylheptyloxy)-4′-nitrobiphenyl was reduced with $SnCl_2$ using the standard procedure. Thin layer chromatography (SiO_2, CH_2Cl_2) indicated that the reaction to give the aromatic amine **5** had proceeded to completion, and given the likely toxicity of the product, it was used in the next step without further handling. The amine was reacted with a mixture of formic acid and acetic anhydride using the standard method, and were chromatographed (SiO_2, CH_2Cl_2/MeOH 4%) giving the product a as white solid. 96%. Mp 136–138 °C. MALDI-TOF-MS (sinapinnic acid) 325.1 [M$^-$]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.25–1.82 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.38 (sext., $J=6$ Hz, 1H, $CHCH_3$), 6.92 (d, $J=8.8$ Hz, 1H), 6.94 (d, $J=8.8$ Hz, 1H), 7.13 (d, $J=8.8$ Hz, 1H), 7.43–7.54 (m, 4H), 7.58 (d, $J=8.8$ Hz, 1H), 7.96 (bd, 0.5H, NH in *cis*), 8.35 (d, $J=1.9$ Hz, 0.5H, HCO in *cis*), 8.72 (d, $J=11.2$ Hz, 0.5H, HCO in *trans*), 8.84 (bd, $J=11.2$ Hz, 0.5H, NH in *trans*); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.5, 29.3, 31.8, 36.5, 74.0, 116.1, 119.1, 120.4, 127.1, 127.8, 127.9, 132.2, 132.6, 135.4, 135.6, 137.4, 138.0, 157.8, 157.9, 159.3, 162.9. Anal. Calcd for $C_{21}H_{27}NO_2$: C, 77.50, H, 8.36, N 4.30. Found: C, 77.53, H, 8.40, N 4.27.

*(R)-4-(1-Methylheptyloxy)-4′-isocyanobiphenyl (**1B**)*. Prepared using the standard procedure from **6**. Clear oil, 78%. MALDI-TOF-MS (DHB) 307.1 [M$^+$]; IR (NaCl plate) 2121 (NC) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, $J=6.9$ Hz, 3H, CH_2CH_3), 1.25–1.83 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.39 (sext., $J=6.0$ Hz, 1H, $CHCH_3$), 6.95 (d, $J_{AB}=8.8$ Hz, 2H, H_o to OR), 7.38 (d, $J_{AB}=8.8$ Hz, 2H, H_m to NC), 7.46 (d, $J_{AB}=8.8$ Hz, 2H, H_m to OR), 7.53 (d, $J=8.8$ Hz, 2H, H_o to NC); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.5, 74.0, 116.2, 126.7, 127.4, 128.2, 131.3, 142.0, 158.6, 164.4. $[\alpha]^{25}_{546}$ ($CHCl_3$), +5.0 deg cm^2 g^{-1}.

*(+)-Poly-{(R)-4-(1-Methylheptyloxy)-4′-iminobiphenyl} (**2B**)*. Prepared from **1B** using the standard procedure. Black solid 96%; IR (KBr) 1638 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75–1.96 (bm, 16H, CH_3, and $(CH_2)_5$), 3.55–4.60 (bm, 1H, $CHCH_3$), 5.60–7.85 (bm, 8H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.7, 25.6, 29.4, 31.9, 36.7, 73.6 (b), 115.8 (b), 119.8 (vb), 125.9 (vb), 127.3 (b), 132.2 (vb), 136.0 (vb), 147.0 (vb), 157.1 (vb), 161.0 (vb), 163.3 (vb).

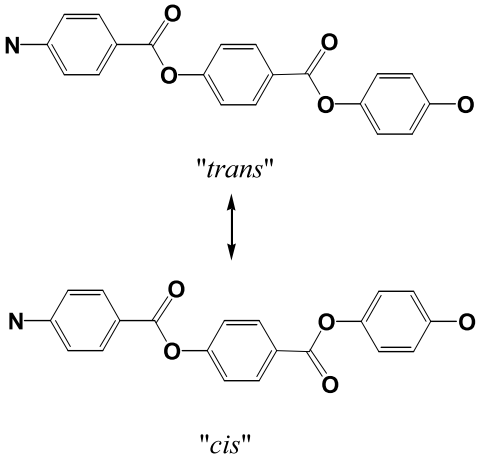


Fig. 7. Conformational isomers of the spacer in **1G** and **2G**.

*(R)-4-(1-Methylheptyloxy)-4′-aminostilbene (**8**).* To a mixture of (*S*)-2-octanol (2.16 g, 17 mmol), 4-amino-4′-hydroxystilbene (**7**, 3.51 g, 17 mmol) and triphenylphosphine (5.44 g, 21 mmol) in dry THF under an Ar atmosphere, a solution of diethylazodicarboxylate (DEAD, 3.62 g, 21 mmol) in THF (5 ml) was added dropwise over 30 min. The resulting red solution was stirred at ambient temperature for 24 h. The reaction mixture was quenched with water (10 ml), and the mixture was stripped of THF, and the residue was partitioned between CH_2Cl_2 and brine. The dried organic fraction was stripped of solvent, and the residue was subjected to column chromatography (SiO_2, hexane/ethyl acetate 9:1). The product was isolated as a yellow solid. Yield: 93%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.25–1.45 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 3.66 (s, 2H, NH_2), 4.35 (m, $J=6$ Hz, 1H, $CHCH_3$), 6.65 (d, $J=8.1$ Hz, 2H, H_o to OR), 6.83 (this signal appears as a singlet, 4H), 7.28 (d, $J=9.1$ Hz, 2H), 7.60 (d, $J=9.1$ Hz, 2H).

*4-{2-[4′-(R)-(1-Methylheptyloxy)phenyl]ethyl}aniline (**9**).* To a solution of (*R*)-4-(1-methylheptyloxy)-4′-aminostilbene (**8**, 2.80 g, 9 mmol) in 70 ml of ethanol and 70 ml of cyclohexene, 600 mg of $Pd(OH)_2$/C 20% were added in small portions. The mixture was refluxed for 10 h. Then the mixture was filtered through a pad of celite®. After removing the solvent, a yellow oil was obtained that was chromatographed (SiO_2, hexane/ethyl acetate 9:1). Yield: 74%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, $J=6.6$ Hz, 3H, CH_2CH_3), 1.25–1.60 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 2.80 (s, 4H, –CH_2–CH_2-), 4.28 (m, $J=6$ Hz, 1H, $CHCH_3$), 6.60 (d, $J=8.4$ Hz, 2H), 6.78 (d, $J=8.4$ Hz, 2H), 6.96 (d, $J=8.4$ Hz, 2H), 7.06 (d, $J=8.4$ Hz, 2H).

*4-{2-[4′-(R)-(1-Methylheptyloxy)phenyl]ethyl}-formamidobenzene (**10**).* Prepared from **9** using the mixed acetic–formic anhydride method. Pale yellow oil. Yield: 94%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.25–1.82 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 2.83 (s, 4H, CH_2CH_2), 4.30 (sext., $J=7$ Hz, 1H, $CHCH_3$), 6.80 (d, $J=9.4$ Hz, 2H), 6.85–7.17 (m, 5.1H), 7.35–7.46 (m, 1.35H), 8.21 (bd, $J=13.7$ Hz, 0.55H, NH in *trans*), 8.33 (d, $J=1.9$ Hz, 0.45H, HCO in *cis*), 8.65 (d, $J=13.7$ Hz, 0.55H, HCO in *trans*); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.6, 37.0, 37.4, 74.1, 116.0, 119.1, 120.0, 129.1, 129.4, 129.8, 133.3, 133.5, 138.6, 139.2, 156.5, 158.9, 162.6. Anal. Calcd for $C_{23}H_{31}NO_2$: C, 78.15, H, 8.84, N 3.96. Found: C, 77.89, H, 8.60, N 3.68. $[\alpha]^{25}_{546}$ (CH_2Cl_2), -1.8 deg cm^2 g^{-1}.

*4-{2-[4′-(R)-(1-Methylheptyloxy)phenyl]ethyl}-isocyanobenzene (**1C**).* Prepared from **10** as a clear oil in 88% yield: IR (NaCl plate) 2118 (NC); MALDI-TOF-MS (sinapinnic acid) 336.2 $[M+H^+]$;^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, $J=6.6$ Hz, 3H, CH_2CH_3), 1.10–1.90 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 2.84 (s, 4H, CH_2CH_2), 4.34 (m, $J=6.3$ Hz, 1H, $CHCH_3$), 6.80 (d, $J=8.6$ Hz, 2H), 6.90 (d, $J=8.6$ Hz, 2H), 7.21 (d, $J=8.6$ Hz, 2H), 7.46 (d, $J=8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.6, 37.0, 37.4, 74.1, 116.0, 119.1, 129.2, 129.5, 133.2, 134.6, 138.9, 156.6, 163.2.

*Poly-{4-[2-[4′-(R)-(1-methylheptyloxy)phenyl]ethyl]-iminobenzene} (**2C**).* Prepared from **1C** under the standard polymerization conditions. Dark tan solid, 76%. IR (KBr) 1654 (NC) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.72–1.85 (bm, 16H, CH_2CH_3, $CHCH_3$, and $(CH_2)_5$), 2.70 (bs, 4H, CH_2CH_2), 3.80–4.30 (bm, 1H, $CHCH_3$), 5.60–8.10 (bm, 8H, aromatics); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.6, 37.0, 37.4, 74.1, 116.4 (b), 120.0 (vb), 128.9 (vb), 129.9 (b), 135.2 (vb), 156.9 (vb), 161.3 (vb), 163.2 (vb).

*(R)-4-(1-Methylheptyloxy)phenylbenzoyloxy-4-formanilide (**12**).* Prepared from 4-formamidophenol and 4-(1-methylheptyloxy)benzoic acid (**11**) using the standard DCC coupling reaction as a white solid, 92%. Mp 105–107 °C. EI-MS 369.0 $[M^+]$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.25–1.80 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.48 (sext., $J=6$ Hz, 1H, $CHCH_3$), 6.93 (d, $J=8.8$ Hz, 2H, H_o to OR), 7.08–7.23 (m, 2.8H, H_m to NH and H_o to NH in *trans*), 7.57 (d, $J=8.8$ Hz, 1.2H, H_o to NH in *cis*), 7.63 (s, 0.6H, NH in *cis*), 7.99 (d, $J=11$ Hz, 0.4H, NH in *trans*), 8.12 (d, $J=8.8$ Hz, 2H, H_m to OR), 8.34 (s, 0.6H, CHO in *cis*), 8.62 (d, $J=11$ Hz, 0.4H, CHO 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, 74.5, 117.0, 117.4, 119.2, 122.8, 125.2, 125.8, 131.4, 132.1, 141.7, 142.1, 143.5, 154.9, 157.6, 162.4, 165.2, 165.6. Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52, H, 7.37, N 3.79. Found: C, 71.28, H, 7.33, N 4.12.

*(R)-4-(1-Methylheptyloxy)phenylbenzoyloxy-4-isocyanobenzene (**1D**).* Prepared from **12** as a clear oil, 75%. EI-MS 351.2 $[M^+]$; IR (NaCl plate) 2130 (NC) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, $J=6.9$ Hz, 3H, CH_2CH_3), 1.24–1.84 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.47 (sext., $J=6.0$ Hz, 1H, $CHCH_3$), 6.95 (d, $J_{AB}=8.8$ Hz, 2H, CH *o* to OR), 7.25 (d, $J_{AB}=8.8$ Hz, 2H, CH *o* to NC), 7.44 (d, $J_{AB}=8.8$ Hz, 2H, H *m* to CN), 8.10 (d, $J=8.8$ Hz, 2H, CH *o* to CO); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.6, 22.6, 25.5, 29.2, 31.8, 36.4, 74.1, 114.2, 113.7, 126.8, 128.9, 130.2, 132.3, 151.4, 157.8, 163.8, 167.4. $[\alpha]^{25}_{546}$ ($CHCl_3$), -34.2 deg cm^2 g^{-1}.

*(+)-Poly-{(R)-4-(1-Methylheptyloxy)phenylbenzoyloxy-4-iminobenzene} (**2D**).* Prepared from **1D** as a brown solid, 80%. IR (KBr) 1741 (CO), 1658 (NC) cm^{-1};^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.72–1.85 (bm, 16H, CH_2CH_3, $CHCH_3$, and $(CH_2)_5$), 3.80–4.30 (bm, 1H, $CHCH_3$), 5.50–8.20 (bm, 8H, aromatics); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.6, 22.6, 25.5, 29.4, 31.8, 36.7, 74.0, 115.3, 116.5 (vb), 122.3, 128.4 (b), 130.0 (vb) 143.8 (b), 148.9 (b), 155.6, 160.6 (b), 162.2 (b), 164.2 (b).

(R)-3-(1-Methylheptyloxy)phenyl benzoate. A mixture of (*S*)-2-octanol (606 mg, 4.65 mmol), resorcinol monobenzoate (999 mg, 4.66 mmol) and triphenylphosphine (1.23 g, 4.65 mmol) in dry THF under an argon atmosphere was cooled in an ice/salt mixture and a solution of diethylazodicarboxylate (DEAD, 0.70 ml, 4.65 mmol) in THF was

added dropwise over 30 min, and the resulting solution was stirred at ambient temperature for 14 h. Water (10 ml) was added and the mixture was stripped of THF, and the residue was partitioned between CH_2Cl_2 and brine. The dried organic fraction was stripped of solvent, and the residue was subjected to column chromatography (SiO_2, hexane/CH_2Cl_2 3:1). The product was isolated as a clear oil in 71% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J= 7 Hz, 3H, CH_2CH_3), 1.25–1.85 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.33 (sext., J=6 Hz, 1H, $CHCH_3$), 6.75–6.80 (m, 3H, H_o to OR), 7.27 (dd, J=8.8 Hz, 1H, H_m to OR), 7.46 (dd, J=7.5 Hz, 2H, H_m to COO), 7.58 (tdd, J=7.5, 2.1 Hz, 1H, H_p to COO), 8.18 (dd, J=7.5, 2.1 Hz, 1H, H_o to COO); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.5, 74.1, 109.4, 113.5, 113.6, 128.5, 129.7, 129.8, 130.1, 133.5, 152.0, 159.3, 165.0. $[\alpha]^{25}_{546}$ (CH_2Cl_2), -12.7 deg cm^2 g^{-1}.

*(R)-3-(1-Methylheptyloxy)phenol (**13**).* (*R*)-3-(1-Methylheptyloxy)phenyl benzoate (1.08 g, 3.31 mmol) was taken up in EtOH (25 ml) and an aqueous solution of KOH (0.723 g in 10 ml) was added dropwise and the mixture was stirred overnight at room temperature. The mixture was diluted with HCl (aq) until pH 1 was reached, and diethyl ether and brine were added. The aqueous phase was extracted once more with ether, and the combined organic layers were dried (Na_2SO_4) and stripped of solvent. The product was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 1:1) and was isolated as a clear oil in 82% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J=7 Hz, 3H, CH_2CH_3), 1.25–1.80 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.29 (sext., J=6 Hz, 1H, $CHCH_3$), 5.45 (s, 1H, O*H*), 6.37–6.45 (m, 2H, H_o to OR), 6.47 (dd, J=8.6, 2.1 Hz, 1H, H_o to OH), 7.09 (dd, J=8.8 Hz, 1H, H_m to OR); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.1, 19.8, 22.6, 25.5, 29.3, 31.8, 36.5, 74.3, 103.5, 107.7, 108.4, 130.1, 156.7, 159.6. $[\alpha]^{25}_{546}$ (CH_2Cl_2), -22.8 deg cm^2 g^{-1}.

*(R)-3-(1-Methylheptyloxy)phenyl 4-formamidobenzoate (**14**).* Prepared from **13** and 4-formamidobenzoic acid using the standard DCC coupling reaction. White solid, 74%. MALDI-TOF-MS (sinapinnic acid) 369.0 [M$^-$]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J=7 Hz, 3H, CH_2CH_3), 1.25–1.80 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.34 (sext., J= 6 Hz, 1H, $CHCH_3$), 6.70–6.82 (m, 3H, H_o to O), 7.18 (d, J= 8.8 Hz, 0.76H, H_o to NH), 7.29 (t, J=7.9 Hz, 1H, H-5 of resorcinol residue), 7.46 (s, 0.62H, HCO in *cis*), 7.70 (d, J= 8.8 Hz, 1.24H, H_o to NH), 7.93 (d, J=11 Hz, 0.38H, HCO in *trans*), 8.15–8.23 (m, 2H, H_m to NH), 8.44 (s, 0.62H, NH in *cis*), 9.07 (d, J=11 Hz, 0.38H, NH in *trans*); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.6, 22.6, 25.5, 29.2, 31.8, 36.4, 74.3, 109.5, 113.5, 117.2, 119.3, 125.0, 125.7, 129.9, 131.5, 132.2, 141.8, 142.0, 151.8, 151.8, 159.3, 159.6, 162.2, 164.7, 164.9. Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52, H, 7.37, N 3.79. Found: C, 71.74, H, 7.43, N 4.02. $[\alpha]^{25}_{546}$ (CH_2Cl_2), -8.2 deg cm^2 g^{-1}.

*(R)-3-(1-Methylheptyloxy)phenyl 4-isocyanobenzoate (**1E**).* Prepared from **14** as an off-white solid, 96%. IR (NaCl plate) 2119 (NC); MALDI-TOF-MS (sinapinnic acid) 352.0 [M+H$^+$]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J=7 Hz, 3H, CH_2CH_3), 1.20–1.80 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.35 (sext., J=6 Hz, 1H, $CHCH_3$), 6.70–6.85 (m, 3H, H_o to O), 7.26–7.35 (m, 3H, H_o to NC and H-5 of resorcinol residue), 7.52 (d, J=8.8 Hz, 1.24H, H_o to NC), 8.25 (d, J=8.8 Hz, 2H, H_m to NH); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.6, 22.6, 25.5, 29.2, 31.8, 36.4, 74.2, 109.2, 113.2, 113.7, 126.6, 129.9, 130.4, 131.4, 151.5, 159.3, 163.5, 167.5. $[\alpha]^{25}_{546}$ (CH_2Cl_2), -8.4 deg cm^2 g^{-1}.

*(−)-Poly-{(R)-3-(1-Methylheptyloxy)phenyl 4-iminobenzoate} (**2E**).* Prepared from **1E** as a yellow solid, 83%. IR (NaCl plate) 1740 (CO), 1647 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.70–1.75 (bm, 16H, CH_2CH_3, $CHCH_3$, and $(CH_2)_5$), 3.80–4.30 (bm, 1H, $CHCH_3$), 5.50–8.20 (bm, 8H, aromatics); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.4, 22.6, 25.3, 29.3, 31.8, 36.4 (b), 73.7 (b), 109.1 (b), 113.3 (b), 117.6 (vb), 127.7 (vb), 130.6 (vb), 150.9 (b), 158.7 (b), 160.7, 162.1, 162.9, 163.5.

*(R)-4-(1-Methylheptyloxy)-4′-hydroxybiphenyl (**15**).* A mixture of the (*S*)-2-octanol (1 equiv.) was mixed with 4,4′-biphenol (1.6 equiv.) and triphenylphosphine (1 equiv.) in dry THF under an argon atmosphere. It was cooled in an ice/salt mixture and a solution of diethyl azodicarboxylate (DEAD, 1 equiv.) in THF was added dropwise over 30 min, and the resulting solution was stirred at ambient temperature for 14 h. The reaction mixture was filtered to remove the triphenylphosphine oxide, evaporated onto SiO_2, and subjected to column chromatography (SiO_2, CH_2Cl_2/0.5% MeOH).White solid, 49%. Mp 99–100 °C; MALDI-TOF-MS (sinapinnic acid) 298.9 [M+H$^+$]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, J=7 Hz, 3H, CH_2CH_3), 1.25–1.90 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.44 (sext., J=6 Hz, 1H, $CHCH_3$), 5.67 (s, 1H, O*H*), 6.94 (d, J_{AB}=8.6 Hz, 2H, OArArO), 7.01 (d, J_{AB}=8.6 Hz, 2H, OArArO), 7.45–7.83 (m, 4H, OArArO); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.5, 74.4, 115.7, 116.3, 127.7, 127.9, 133.3, 133.7, 154.6, 157.2. Anal. Calcd for $C_{19}H_{22}O_4$: C, 80.50, H, 8.83. Found: C, 80.67, H, 8.83. $[\alpha]^{25}_{546}$ ($CHCl_3$), $+0.39$ deg cm^2 g^{-1}.

*(R)-4-(1-Methylheptyloxy)-4′-biphenyl 4-formamidobenzoate (**16**).* Prepared from **15** using the standard procedure as a white solid, 56%. Mp 167–169 °C. MALDI-TOF-MS (sinapinnic acid) 446.0 [M$^-$]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, J=7 Hz, 3H, CH_2CH_3), 1.20–1.90 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.41 (sext., J=6 Hz, 1H, $CHCH_3$), 6.98 (d, J=8.8 Hz, 2H, H_o to OR), 7.22 (d, J=8.8 Hz, 0.74H, H_o to NH), 7.28 (d, J=8.8 Hz, 2H, OArArO), 7.52 (d, J=8.8 Hz, 2.63H, OArArO and HCO in *cis*), 7.60 (d, J=8.8 Hz, 2H, OArArO), 7.72 (d, J=8.8 Hz, 1.26H, H_o to NH), 8.02 (d, J=11 Hz, 0.35H, HCO in *trans*), 8.15–8.28 (m, 2H, H_m to NH), 8.46 (s, 0.63H, NH in *cis*), 8.93 (d, J=11 Hz, 0.37H, NH in *trans*); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.5, 74.0, 116.1, 117.2, 119.2, 121.8, 125.5, 126.0, 127.7, 128.1, 131.6, 132.3, 132.6, 138.8, 138.9, 141.4, 141.5, 149.8,

157.9, 158.9, 161.4, 164.4, 164.6. Anal. Calcd for $C_{28}H_{31}NO_4$: C, 75.48, H, 7.01, N 3.14. Found: C, 75.27, H, 7.44, N 3.20.

*(R)-4-(1-Methylheptyloxy)-4′-biphenyl 4-isocyanobenzoate (**1F**)*. Prepared from **16** using the standard procedure as an off-white solid. MALDI-TOF-MS (dihydroxy benzoic acid) 427.5 [M^+]; IR (NaCl plate) 1740.6 (C=O), 2116 (NC) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.23–1.84 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.39 (sext., $J=6$ Hz, 1H, $CHCH_3$), 6.95 (d, $J=8.8$ Hz, 2H, H_o to OR), 7.23 (d, $J=8.8$ Hz, 2H, H_o to NC), 7.49 (d, $J=8.8$ Hz, 2H, OArArO), 7.52 (d, $J=8.8$ Hz, 2H, OArArO), 7.60 (d, $J=8.8$ Hz, 2H, OArArO), 8.26 (d, $J=8.8$ Hz, 2H, H_o to NC); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.5, 74.0, 116.1, 121.7, 126.7, 127.8, 128.2, 130.4, 131.5, 132.4, 139.2, 149.5, 158.0, 163.7, 167.7.

*(+)-Poly-{(R)-4-(1-Methylheptyloxy)-4′-biphenyl 4-iminobenzoate} (**2F**)*. Prepared from **1F** as a yellow solid, 84%. IR (KBr) 1736 (CO), 1662 (NC) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.72–1.85 (bm, 16H, CH_2CH_3, $CHCH_3$, and $(CH_2)_5$), 4.10–4.50 (bm, 1H, $CHCH_3$), 5.51–8.20 (bm, 12H, aromatics); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.7, 22.7, 25.5, 29.4, 31.9, 36.7, 73.7, 116.0, 117.4 (vb), 121.8 (b), 127.1 (b), 127.9, 130.9 (vb), 132.0 (b), 137.8 (b), 149.4 (b), 150.9 (vb), 157.6, 161.0 (vb), 162.8 (vb), 163.4, 163.9.

*(R)-4-(1-(1-Methylheptyloxy)phenyl 4-hydroxybenzoate (**17**)*. 4-Benzyloxybenzoic acid (1.12 g, 4.9 mmol) was combined in dry diethyl ether (35 ml) with (*R*)-4-(1-methylheptyloxy)phenol (1.20 g, 5 mmol),[6] dicyclohexyl carbodiimide (DCC, 1.12 g, 5.4 mmol) and 4-dimethylamino pyridine (DMAP, 0.06 g, 0.49 mmol), and the mixture was stirred under dry atmosphere at ambient temperature (20 h). The filtered reaction mixture was diluted with CH_2Cl_2 and extracted with NaOH (aq., 2%, 2×50 ml) and H_2O (50 ml). Drying (Na_2SO_4) and removal of solvent afforded a white solid which was subjected to flash column chromatography (SiO_2, ethyl acetate/hexane 9:1). Yield: 30%. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.32–1.75 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.45 (sext., $J=6$ Hz, 1H, $CHCH_3$), 5.03 (s, 2H, CH_2Bz), 6.95–7.00 (m, 4H, H_o to OR, H_o to OH), 7.05 (d, $J_{AB}=8.8$ Hz, 2H, H_m to OR), 7.34–7.47 (m, 5H, CH_2Ar), 8.07 (d, $J_{AB}=8.8$ Hz, 2H, H_m to OH). Cleaving of the benzyloxy moiety to liberate the hydroxy group was undertaken by the same method described for the synthesis of 4-{2-[4′-(*R*)-(1-methylheptyloxy)phenyl]-ethyl}aniline. The product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 8:2). Yield 80%. White solid. Mp 102–103 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.23–1.86 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.30 (sext., $J=6$ Hz, 1H, $CHCH_3$), 5.42 (s, 1H, OH), 6.83–6.92 (m, 4H, H_o to OR), 7.06 (d, $J_{AB}=8.8$ Hz, 2H, H_m to OR), 8.08 (d, $J_{AB}=8.8$ Hz, 2H, H_m to OH); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.5, 74.6, 115.4, 116.6, 122.0, 122.5, 132.5, 144.2, 155.9, 160.4, 165.5; $[\alpha]_{546}^{25}$ ($CHCl_3$), −15.0 deg cm^2 g^{-1}.

*4-[(R)-4′-(1-Methylheptyloxy)phenoxycarbonyl]phenyl 4-formamidobenzoate (**18**)*. Prepared from **17** using the standard DCC coupling. White solid 69%: mp 156–158 °C, IR (KBr) 1743, 1731 (CO) cm^{-1}; MALDI-TOF-MS (sinapinnic acid) 489.1 [M^-]; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, $J=7$ Hz, 3H, CH_2CH_3), 1.1–2.0 (m, 13H, $CHCH_3$, and $(CH_2)_5$), 4.34 (quin., $J=6$ Hz, 1H, $CHCH_3$), 6.92 (d, $J=8.8$ Hz, 2H, H_o to OR), 7.13 (d, $J=8.8$ Hz, 2H, H_m to OR), 7.23 (d, $J=8.8$ Hz, 0.7H, H_o to NH), 7.39 (d, $J=8.8$ Hz, 2H, H_o to 4-formamidobenzoate), 7.72 (d, $J=8.8$ Hz, 1.3H, H_o to NH), 7.83 (s, 0.65H, NH in *cis*), 8.11–8.33 (m, 4H, H_m to 4-formamidobenzoate, H_m to NH), 8.43 (s, 0.65H, HCO in *cis*), 8.48 (d, $J=11$ Hz, 0.35H, NH in *trans*), 8.93 (d, $J=11$ Hz, 0.35H, HCO 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, 122.0, 122.4, 124.7, 125.3, 127.2, 127.3, 131.7, 131.8, 132.1, 132.3, 141.9, 142.0, 144.1, 155.0, 155.1, 156.1, 159.1, 161.6, 163.8, 164.0, 164.9. Anal. Calcd for $C_{29}H_{31}NO_6$: C, 71.15, H, 6.38, N 2.86. Found: C, 71.44, H, 6.53, N 3.05.

*4-[(R)-4′-(1-Methylheptyloxy)phenoxycarbonyl]phenyl 4-isocyanobenzoate (**1G**)*. Prepared from **18**. Off-white solid, 97%. MALDI-TOF-MS (DHB) 494.2 [$M+Na^+$]; IR (NaCl plate) 2120 (NC), 1745, 1730 (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 OR), 7.10 (d, $J=9$ Hz, 2H, CH *m* to OR), 7.39 (d, $J=9$ Hz, 2H, H_o to 4-isocyanoobenzoate), 7.51 (d, $J=9$ Hz, 2H, CH *m* to NC), 8.20 (d, $J=9$ Hz, 2H, H_m to 4-isocyanobenzoate), 8.26 (d, $J=9$ Hz, 2H, CH *o* to NC); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.5, 74.7, 115.9, 121.8, 122.5, 126.8, 127.6, 129.9, 131.6, 131.9, 145.0, 154.7, 155.5, 163.0, 164.4, 168.0.

*(+)-Poly-{4-[(R)-4′-(1-methylheptyloxy)phenoxycarbonyl]phenyl-4-iminobenzoate} (**2G**)*. Prepared from **1G** under the standard polymerization conditions. Yellow solid, 81%. IR (KBr) 1741 (CO), 1657 (NC) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.72–1.85 (bm, 16H, CH_2CH_3, $CHCH_3$, and $(CH_2)_5$), 3.80–4.30 (bm, 1H, $CHCH_3$), 5.50–8.20 (bm, 12H, aromatics); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.1, 19.7, 22.6, 25.5, 29.4, 31.9, 36.7, 74.1, 115.8, 117.5 (vb), 121.3 (b), 122.5, 127.4, 129.0 (b), 144.7 (b), 150.8 (vb), 154.0 (b), 155.3, 162.5 (b), 163.9.

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[76] The molar optical rotations and differential molar absorptivities for

the polymers are based on the molecular weight 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.

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