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A free radical initiated optically active vinyl polymer with memory of chirality after removal of the inducing stereogenic center†

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Free radical polymerization of (+)-2,5-bis[4′-((*S*)-2-methylbutyloxy)phenyl]styrene yields a chiral polymer with memory of optical activity after the initial stereogenic center in the side group of the monomer is chemically removed.

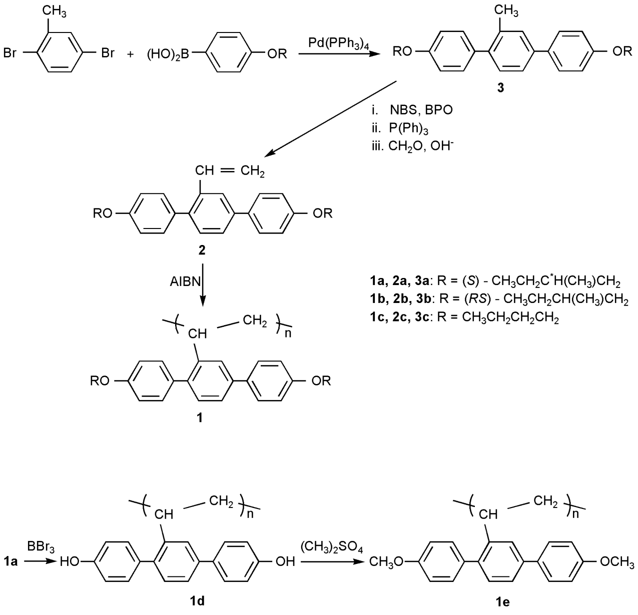
Chiral architectures like helices play important roles in many biological systems and also in technological processes.[1] Natural macromolecules adopt helical conformations with an excess helical sense by self-assembly of building blocks that are chiral and non-racemic. Such chiral information is not uniformly present in the structures of monomers leading to synthetic polymers and therefore the synthesis of optically active polymers, whose chirality is based on a helical conformation, remains a challenge. A few polymers with helical chirality have been synthesized, examples of which include poly(chloral),[2] poly(isocyanate)s,[3] poly(isocyanide)s,[4] poly(triarylmethyl methacrylate)s,[5] and some substituted π-conjugated polymers.[6] Among these helical polymers, Okamoto *et al.* reported that helix-sense selection of a vinyl polymer can be induced both by the chirality of a monomer itself and *via* a chiral additive acting as a spectator to the polymerization process.[5] These approaches to gain an excess helical sense have also been accomplished in the free radical polymerization of some bulky methacrylates based on triaryl methacrylate ester pendant groups.[5,7]

In the present work we have accomplished the free radical synthesis of a vinyl based optically active polymer with a chiral, likely helical, secondary structure of the main chain, in which an excess helical sense arises from a chiral group appended to an aromatic moiety attached laterally to the backbone. In this situation the chiral entity, although covalently attached at a point far removed from the backbone helix, is forced by the nature of the substitution to closely approach and therefore affect the helical sense choice of the backbone. Remarkably, removal of the inducing stereogenic center leaves the chirality in place demonstrating that the pendant group offers a steric impediment blocking helical sense changes in the polymer.

Polymer **1** consists of a vinyl based polyethylene backbone and a 4,4″-dialkoxyterphenyl group laterally attached to every second carbon atom of the main chain. The terphenyl group is chosen as the substituent of the monomer **2** since its bulk serves the fundamental idea of enforcing a helical sense while it is also often used in the construction of thermotropic liquid crystals allowing the possibility in future work of translating our results into a liquid crystal phase. The utmost length of the repeating unit of polyethylene is about 2.5 Å but the length of the side group bonded to each repeating unit is as large as 23.3 Å. The steric repulsion of the highly crowded side groups prevents the polymer backbone from adopting a random conformation. As we will show below this kind of structure leads to a chiral secondary structure, which is controlled by the remote stereogenic chiral groups.

Monomer **2** is synthesized in 4 steps with an overall yield of ~43% as shown in Scheme 1. The free radical polymerization of **2** with 2,2′-azobisisobutyronitrile in benzene at 60 °C gives the corresponding polymer **1**, poly[2,5-bis(4′-alkoxyphenyl)-styrene], in good to excellent yields (Table 1). The specific optical rotation $[\alpha]_{365}^{20}$ (in THF, *c* = 2.0 g L^{-1}) of **2a**, (+)-2,5-bis[4′-((*S*)-2-methylbutyloxy)phenyl]styrene, is +60.4°, but its corresponding polymer **1a** shows an $[\alpha]_{365}^{20}$ value of −71.9°. The opposite sign of **1a** compared to the monomer from which it is formed indicates that the optical activity of **1a** does not arise from the configurational chirality of the side groups and suggests that a higher structure, most likely a secondary helical structure, has been formed. This conclusion is also supported by the optical activity studies of **1a** as a function of molecular weight.[8]

The circular dichroism (CD) spectrum of **1a** exhibits a strong negative non-conservative Cotton effect of π–π* transition of terphenyl group at 304 nm, while both **2a** and **3a** display positive Cotton effects at 283 and 280 nm, respectively (Fig. 1). The presence of non-conservative optical activity in **1a** may be



Scheme 1 Synthesis of chiral vinyl polymer.

Table 1 Summary of polymerization results, chirooptical properties of monomers and corresponding polymers

Polymer	$[\alpha]_{365}{}^{a}$/°	Yield (%)	$M_n \times 10^{-5b}$	PDI	$[\alpha]_{365}{}^{c}$/°
1a	60.4	71.0	1.02	1.74	−71.9
1b	0	86.4	1.41	1.58	0
1c	0	91.2	0.13	1.94	0
1d		98.0	0.70	2.00	−113.6
1e		90.0	0.75	1.89	−93.6

[a] Specific optical rotations of the monomers measured in THF (*c* = 2.0 g L^{-1}) at 20 °C. [b] Determined by GPC on the basis of a calibration of polystyrene standards and using THF as eluent at 35 °C. [c] Specific optical rotations of the polymers measured in THF (*c* = 2.0 g L^{-1}) at 20 °C.

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† Electronic supplementary information (ESI) available: complete experimental procedures; NMR and X-ray spectra; POM photograph; specific optical rotations of the polymers with different molecular weights. See http://www.rsc.org/suppdata/cc/b2/b212916g/

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due to an interaction of a transition with other transitions occurring at a very different wavelength region, although the nature of this interaction is not clear at present. It is a commonly used method to investigate macromolecular conformations of proteins and helical polyolefins with incorporation of aromatic chromophores into the chains of polymers as probes.[9] Due to the asymmetrical microenvironment of the helical main-chain, achiral aromatic groups show strong optical activity of the π–π* transition. Therefore, the chiral optical effect for the pendant terphenyl groups of **1a** is consistent with a chiral secondary structure and for a linear polymer chain such as **1a** the reasonable chiral secondary structure is helical.

In a remarkable feature of this polymer, the removal of the chiral non-racemic 2-methylbutyl group from the pendant terphenyl does not cause loss of the chiral optical characteristics measured in both the circular dichroism spectrum and in the optical activity. This maintenance of the chiral optical character demonstrates that the secondary structure of this polymer, once formed, is held immutable by the steric characteristics of the terphenyl pendant. The resultant atropoisomer, poly[2,5-bis(4′-hydroxyphenyl)styrene] (**1d**), which contains no chiral stereogenicity at all, exhibits an even larger negative optical rotation and an even stronger negative Cotton effect than **1a** as shown in Table 1 and Fig. 1. Consistent with the conformational rigidity of the secondary structure, polymer **1e**, which is derived from **1d** *via* methylation with dimethyl sulfate, displays a CD spectrum very similar to those of polymers **1a** and **1d** and has a specific rotation of −93.6° at 365 nm.

As an interesting additional point, the value of the optical rotation should be the sum of the conformational asymmetry of the main chain and the configurational asymmetries of the alkoxy tails. This is consistent with the increase in the optical activity of **1d**, which may be a result of elimination of the chiral tails, whose optical rotation is suggested to be opposite in sign to the backbone helix by the optical rotation of the monomer. However, such an effect cannot contribute to the circular dichroism intensity in the region of the aromatic chromophore, which may more likely be affected by small conformational changes associated with the helical conformation on achiral alterations to the pendant group. Force field calculation studies are underway to explore these features of the secondary structure.[10]

In conclusion, we have demonstrated that the free radical polymerization of (+)-2,5-bis[4′-((*S*)-2-methylbutyloxy)phenyl]styrene leads to a chiral, likely helical, secondary structure of the vinyl backbone, which is then maintained even after the initial chiral information in the side group of the monomer is chemically removed. Since it is known that a polymer with this kind of architecture shows characteristics of rigid or semi-rigid main-chain liquid crystalline polymers we expect to encounter liquid crystal characteristics,[11] which have already been seen in preliminary work and will be reported in a full paper to follow.[12]

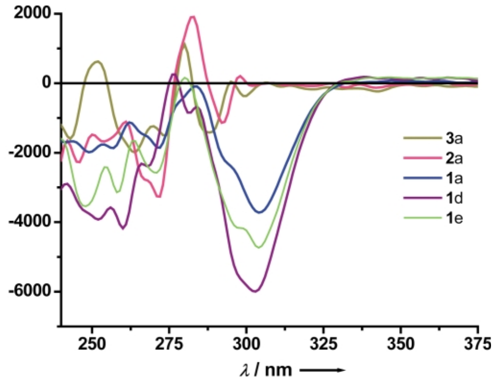

Fig. 1 Comparison of the CD spectra of model compound **3a**, monomer **2a**, and polymers **1a**, **1d**, **1e** (recorded at 20 °Cin THF). [θ] = molar ellipticity with repeating unit: deg cm² dmol⁻¹.

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8 As shown in the ESI, oligomers with low molecular weights show positive optical rotations, while the oligomers/polymers with higher molecular weights display negative optical rotations. The chirooptical properties have a tendency to grow with degree of polymerization (DP) and appear to become constant ($[\alpha]^{20}_{365} = -150$) in the DP range of *ca.* 20–170. This is expected for a helical main-chain conformation (see: (*a*) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, 1960, **82**, 4745; (*b*) P. Pino, C. Carlini, E. Chiellini, F. Ciardelli and P. Salvadori, *J. Am. Chem. Soc.*, 1968, **90**, 5025), and in fact has been seen in studies of the mechanism of formation of a regular helical structure with an excess helical sense in the work of Okamoto and co-workers on the poly(trityl methacrylates) (see: T. Nakano, Y. Okamoto and K. Hatada, *J. Am. Chem. Soc.*, 1992, **114**, 1318).

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12 Experimental details and data: see ESI.