# Odd−Even Effect in Free Radical Polymerization of Optically Active 2,5-Bis[(4′-alkoxycarbonyl)-phenyl]styrene

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Optically active polymers with main-chain helical chiralities have attracted long-standing interest for their wide potential applications in asymmetric synthesis, molecular recognition, and photoelectrical materials.[1−7] Polymerization of chiral, non-racemic monomer is one of the most frequently used strategies to prepare such polymers. With this approach, the stereocenter in monomer molecule plays an important role in induction of a prevailing helical sense.[8−11] In order to increase stereoselectivity, the chiral atom is usually linked directly to (or close to) the polymerizable group, which can be expected to favor the coupling between the asymmetry of the side groups and the helical main chain. For example, in a series of isotactic copolymers of enantiomers,[12] Pino et al. found that the stereocenter separated from the vinyl group by one or two covalent bond(s) was able to pass its chiral information to the growing main chain. Whereas, when the distance between the stereocenter and the vinyl group was three covalent bonds, the chiral side chains had no effect on the backbone.

Serrano, Veciana, and co-workers first achieved long-distance chirality transfer in the preparation of helical polyisocyanides from chiral promesogenic monomers.[13,14] By virtue of the noncovalent steric interaction of rigid phenyl benzoate spacer, the stereocenter, which was at least 14 atoms remote from isocyano group, induced polyisocyanide main chain to take a helical conformation with an excess screw sense. More remarkably, the sense of helical induction in these rigid polymers followed an odd−even alternation rule with increasing the distance of the stereocenter with respect to the mesogenic core. This rule was initially established in cholesteric mesophase (N*) by Gray and MacDonnell[15] and developed by Goodby et al. to apply to chiral smectic C phase (SmC*).[16] A similar phenomenon has also been observed in chiral polythiophene,[17] polysilylene aggregates,[18] and optically active polyfluorenes and poly-*p*-phenylenevinylene in solid films.[19,20] Masuda reported a conflicting system.[21,22] In five helical poly(propiolic ester)s with chiral moieties that possessed identical stereogenic centers, but different numbers of methylene groups between the ester group and asymmetric atom, only one showed weak positive optical rotation ($[\alpha]_D = +4°$) and all the other four displayed strong negative optical rotations ($[\alpha]_D = -340°-612°$). To our knowledge, there has been no work addressing long-distance chirality transfer in radical polymerization yet. In fact, radical polymerization is seldom employed to prepare optically active helical polymer, although it is not as synthetically demanding and can tolerate many polar functional groups, especially compared to ionic or coordination polymerizations. The main reason is that the planarity of propagation species (sp$^2$ hybridization) renders poor control over polymer stereostructure. Only a limited number of successful examples have been known up to now, including (meth)acrylic polymers by Okamoto et al.[23−28] and styrenic polymers by us.[29−31] Herein, we report the first systematic investigation of the effects of the position and configuration of the stereogenic carbon atom in vinyl monomers on the optical activity of their respective polymers obtained via radical polymerization.

Five structurally different vinyl monomers, namely, 2,5-(−)-2,5-bis[4′-(*R*)-*sec*-butyloxycarbonylphenyl]styrene (***R*-(−)-M0**), 2,5-(+)-2,5-bis[4′-(*S*)-*sec*-butyloxycarbonylphenyl]styrene (***S*-(+)-M0**), (+)-2,5-bis{4′-[(*S*)-2-methylbutyloxycarbonyl]-phenyl}styrene (***S*-(+)-M1**), (+)-2,5-bis{4′-[(*S*)-3-methyl pentyloxycarbonyl]phenyl}styrene (***S*-(+)-M2**), and (+)-2,5-bis{4′-[(*S*)-4-methylhexyloxycarbonyl]phenyl}styrene (***S*-(+)-M3**), were designed and synthesized as illustrated in Scheme 1. The molecules, ***S*-(+)-M*m*** (***m*** = 0, 1, 2, and 3), have identical stereocenters, but away from the terphenyl group by different distances. The monomer ***R*-(−)-M0** distinguishes ***S*-(+)-M0** only by the spatial configuration of the chiral carbon atom. In our previous study, (+)-2,5-bis{4′-[(S)-2-methylbutyloxy]phenyl}-styrene, an unsaturated compound similar to ***S*-(+)-M1**, was proven to yield an optically active helical polymer through radical polymerization.[29] The laterally attached bulky *p*-terphenyl group was considered to serve to enforce a helical conformation of the backbone, and the excess helical sense was induced by the chiral tails appended to the *p*-terphenyl moiety.

The monomers were prepared in moderate yields (∼60%) by esterification of chiral alcohols R*OH with 2,5-di(4′-carboxylphenyl)styrene, which was preconverted to highly active acyl chloride by reaction with oxalyl chloride in the presence of trace amount of *N*,*N*-dimethylfomamide (DMF) (see Supporting Information for details). Polymerization was carried out in anisole solution at 90 °C for 24 h using benzoyl peroxide as an initiator. The polymers were obtained with moderately high molecular weights ($(8.8-11.7) \times 10^4$ Da) and in good to excellent yields (>73%). They have good solubilities in many organic solvents such as tetrahydrofuran (THF), chloroform, and DMF. The polymerization results and the chiroptical properties of the monomers and the corresponding polymers are summarized in Table 1.

The specific optical rotation $[\alpha]_{365}^{25}$ (in THF, $c = 0.2$) of ***R*-(−)-M0** is −130.9°, but its polymer shows an $[\alpha]_{365}^{25}$ value of 627.6°. The absolute value of specific rotation for the polymer is about 5 times greater than that of its monomer. The opposite sign of ***R*-(−)-P0** to its monomer and a large increase in chiral optical power indicate that the optical activity of ***R*-(−)-P0** is not solely attributed to the configurational chirality in the side groups and suggest that a higher chiral structure, most likely secondary helical structure, has been formed.[33−36] Changing the configuration of the stereocenters in the chiral tails from *R* to *S* as in ***S*-(+)-M0** leads to an inversion of the sign of optical rotation for both monomer and polymer, suggesting the remarkable role of the stereocenter in induction of helical sense. All the other three monomers, ***S*-(+)-M1** to ***S*-(+)-M3**, have positive optical rotations like ***S*-(+)-M0** since they have similar chemical structures and identical stereogenic centers. However, the sign of optical rotation of the resultant polymers alternates in an odd−even way as in chiral mesophase as the chiral center is removed from terphenyl group. In addition, the closer the stereogenic center is to terphenyl group, the larger the optical rotation of the polymer becomes, an indicative of enhanced

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**Scheme 1. Synthesis and Polymerization of Chiral 2,5-Bis(4′-alkoxycarbonylphenyl)styrene**

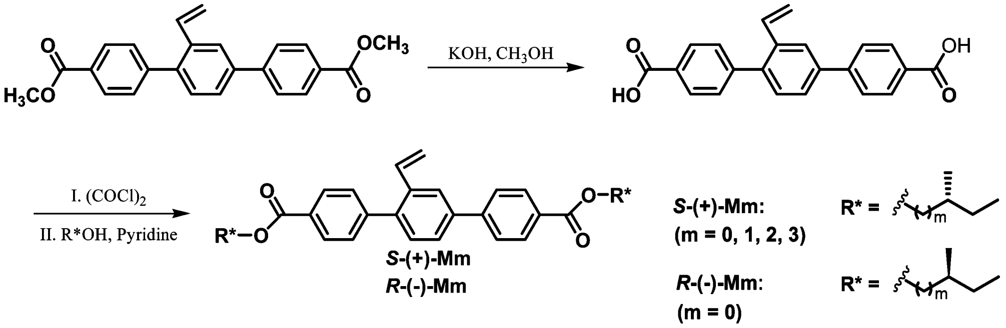

**Table 1. Polymerization Results, Chiroptical Properties of Monomers and Polymers, and the Helical Senses of the Cholesteric Phases of 2,5-Bis(4′-hexyloxycarbonylphenyl)styrene Induced by Chiral Monomers**

| monomer | $[\alpha]_{365}^{25\,a}$ | polymer | yield (%) | $M_n \times 10^{-4\,b}$ | $M_w/M_n^{\,b}$ | $[\alpha]_{365}^{25\,c}$ | parity[d] | helical sense of induced N*[e] |
|---|---|---|---|---|---|---|---|---|
| **R-(−)-M0** | −130.9 | **R-(−)-P0** | 96.0 | 10.8 | 2.06 | +627.6 | odd | RH (rod) |
| **S-(+)-M0** | +131.5 | **S-(+)-P0** | 73.7 | 9.7 | 1.71 | −605.7 | odd | LH (sol) |
| **S-(+)-M1** | +25.9 | **S-(+)-P1** | 92.8 | 10.5 | 1.98 | +244.9 | even | RH (sed) |
| **S-(+)-M2** | +30.9 | **S-(+)-P2** | 88.1 | 8.8 | 1.87 | −19.5 | odd | LH (sol) |
| **S-(+)-M3** | +27.6 | **S-(+)-P3** | 94.9 | 11.7 | 1.74 | +56.8 | even | RH (sed) |

[a] Specific optical rotation of monomer in unit of degree was measured in a 1 dm cell at a concentration of ca. 4.0 mg mL$^{-1}$ in THF at 25 °C. [b] Determined by GPC calibrated against a series of monodispersed polystyrene standards. [c] Specific optical rotation of polymer in unit of degree based on molecular mass of repeating unit. [d] The position of the chiral center relative to *p*-terphenyl core. [e] Right-handed (RH) and left-handed (LH) helical senses determined based on Mauguin's model.[32]

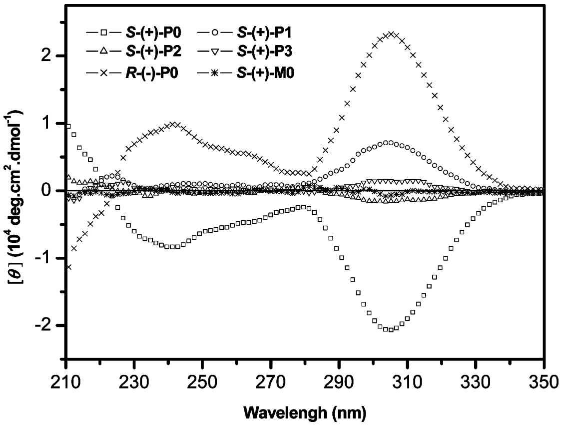

**Figure 1.** CD spectra of **R-(−)-P0**, **S-(+)-P0**, **S-(+)-P1** **S-(+)-P2**, **S-(+)-P3**, and **S-(+)-M0** recorded in THF at 25 °C ($c = 4.0 \times 10^{-5}$ M).

asymmetric induction in the twisting sense preference of the polymer chain. This should be relevant with the decreased rotational freedom of the stereogenic center relative to the rigid core.[14]

Figure 1 shows the circular dichroism (CD) spectra of the five polymers, **S-(+)-P*m*** (***m*** = 0−3) and **R-(−)-P0**, and one monomer, **S-(+)-M0**. All the polymers exhibited two intensive absorption bands centered at 220 and 283 nm (Figure S1), which can be assigned to the electronic transitions of the side terphenyl groups.[29,37] The CD spectrum of **S-(+)-P0** exhibits one positive Cotton effect at the wavelength less than 223 nm and two negative Cotton bands in the wavelength ranges of 223−279 and 279−343 nm. Further analysis of the spectrum suggests the presence of two negative Cotton effects with exciton-coupling characteristics, which intersect zero axis at 220 and 283 nm, corresponding to the maximum absorption wavelengths of terphenyl group. The absence of positive area of the first exiton-coupling bands might be due to the overcompensation of the intensive negative signals of the second exiton-coupling bands. Unfortunately, the noise at the wavelength less than 210 nm is so strong that quantitative analysis of CD spectra of the polymers is currently not allowed. The major electronic transitions of **S-(+)-M0** are essentially those of **S-(+)-P0**, except for the absorption of vinyl group (Figure S2). However, its CD spectrum is significantly different. **S-(+)-M0** shows only indiscernible positive Cotton effects in the same absorption region. The absence of the Cotton effect of **S-(+)-M0** is probably due to the fact that its chiral centers are far away from the *p*-terphenyl group. The apparent difference between the CD spectra of **S-(+)-M0** and **S-(+)-P0** demonstrates that the side *p*-terphenyl groups are arrayed in a skewed way along the polymer backbone.[38−41] The chiral perturbation of an aromatic group as in (*S*)-2-phenyl-3,3-dimethylbutane can also give rise to enhanced Cotton effects due to the smaller conformational mobility of phenyl ring.[42] However, the existence of electronic interactions between aromatic groups with a fixed mutual geometrical disposition along the helical chain supplies additional rotatory strength and splits the electronic transitions, particularly to those having larger polarizability.[43] As a result, it is reasonable to think that the generated Cotton effects for the pendant terphenyl groups of **S-(+)-P0** is consistent with the conformational property of the polymer. And for a linear polymer chain such as **S-(+)-P0**, the most likely chiral secondary structure is a helical conformation with a preferred screw sense.

The Cotton effects of **S-(+)-P*m*** decrease significantly in intensity and alternate in sign as the stereocenter appears increasingly far away from the *p*-terphenyl group. Remarkably, the sign alternation of the Cotton effects at 305 nm follows a clear odd−even rule. It implies that the twisting direction of the chiral secondary structure changes alternatively depending on the number of methylene groups between the stereocenter and *p*-terphenyl group. Furthermore, the CD spectra of polymers **R-(−)-P0** and **S-(+)-P0** are nearly mirror images of each other, indicating enantiomeric conformations with opposite helicities adopted by the two polymers.

The shortest distance of the stereocenter relative to the vinyl group in the monomers studied is nine covalent bonds. One may ask why the chiral message in the asymmetric carbon atoms can be passed to the growing polymer chain over such a long distance. Serrano et al. established a connection between the odd−even effects concerning the helical preferences in optically active polyisocyanides derived from chiral premesogenic monomers and chiral mesophases.[13,14] It was thought that the steric influence of chiral tails accounted for the diastereoselectivity observed in polymerization. The monomers concerned here have quite similar structural characteristics with those isocyanides since the vinyl group and the chiral tails are connected by *p*-terphenyl, which is frequently chosen to construct liquid crystals because of its rodlike shape and high thermal and chemical stability. Therefore, we think the long-distance asymmetric induction observed in our polymers is presumably relevant to the mesogenic nature of the *p*-terphenyl group. To prove this point, cholesteric liquid crystal induced circular dichroism (LCICD) was employed to study the driving force of the monomers in inducing chiral mesophase and prevailing helical sense of the optically active polymers.[13,14,32] Since all the monomers are not liquid crystalline, they are doped into an achiral liquid crystalline compound, 2,5-bis(4′-hexyloxyphenyl)-styrene (BHPSt),[44] which displays enantiotropic nematic phase in the temperature range of 64.1 to 85.5 °C (see Supporting Information). BHPSt is selected as a host because its structure is closely similar to those of the studied monomers, which is in favor of noncovalent interaction in mesophase.[45] The results are collected in Table 1. The parities of the chiral carbon atoms with respect to *p*-terphenyl groups in the monomers ***S*-(+)-M0** and ***S*-(+)-M2** are odd. The N* phase of BHPSt induced by these two molecules has left-handed (LH) long axis ordering,[46] whereas the N* phase of BHPSt induced by ***S*-(+)-M1** and ***S*-(+)-M3**, the parities of which are even, displays right-handed ordering. Although the twisting directions of the corresponding polymer backbones remain unknown right now, the parallel in the odd−even effects between the helical sense of induced N* phase and the direction of optical rotation of the polymers is obvious.

On the basis of these results, a mechanism of long-range chirality transfer in radical polymerization of chiral bulky vinyl monomer is proposed. The polymers ***S*-(+)-P*m*** and ***R*-(−)-P*m*** consist of flexible polyethylene backbones with 4,4″-dialkoxy-terphenyl groups laterally substituted at every carbon atom of the main chain. On the one hand, the steric repulsion of the highly crowded side groups gives rise to stereoisomerism due to restricted rotation around single bonds linking main chain carbons (atropisomerism).[47] The polymers with such kind of architecture have long been known to take extended conformation and exhibit stable thermotropic liquid crystalline properties.[31,48,49] Moreover, ***S*-(+)-P*m*** has been reported to have a quite large persistence length of 15.4 ± 0.3 nm in THF.[50] On the other hand, *p*-terphenyl, like phenyl benzoate in helical polyisocyanides,[13,14] helps long-range chirality transfer from stereogenic centers in the side chain to the backbone. The chiral information originated from the stereocenter in the monomer induces *p*-terphenyl group to adopt a chiral conformation and therefore develops two differentiated diastereomeric faces in the surroundings of polymerizable vinyl groups. Driven by a similar noncovalent intermolecular interaction in induced cholesteric phases, the next additional monomer interacts stereoselectively with the growing species leading to an excess of one screw sense in the resulting polymer. Changing the position of the stereocenter along the alkyl chains leads to a change in the conformation of aromatic group relative to the flexible tail in an odd−even way. These give the odd−even alternation in the preferences of the screw sense of the polymers chains and in the helices of the induced N* phases.

In conclusion, we have shown that the stereogenic centers in a series of bulky vinyl monomers, 2,5-bis[(4′-alkoxycarbonyl)-phenyl]styrene, are able to transmit their chiralities to the growing polymer chains during free radical polymerization. The sign of optical rotation of the resulting polymers in THF depends on the absolute spatial configuration of chiral atom and its position relative to *p*-terphenyl group. Inverting the spatial configuration of asymmetric center or changing the parity of covalent bond number between stereocenter and *p*-terphenyl group alternates the direction of the optical rotation of the polymer. This phenomenon parallels the dependence of the helical twist sense of the chiral nematic phase of achiral 2,5-bis(4′-hexyloxyphenyl)styrene induced by the analogous chiral monomers, implying the same driving force for the formation of chiral mesophase and the chiral secondary structure of the polymer. This study provides a facile way to obtain optically active polymers with chiral secondary structure via radical polymerization. Unlike promesogenic isocyanides,[13,14] each monomer studied here has two stereocenters, which have same distance to *p*-terphenyl group but different distance to the polymerizable group and therefore different distance to polymer backbone. The present work cannot tell which one is dominant in inducing a prevailing screw sense of polymer main chain. The monomer with one stereocenter should help answer the question, and the work has been under way.

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**Supporting Information Available:** Synthesis and characterization of monomers and polymers; mesophase formation and characterization of an achiral liquid crystalline compound induced by the chiral monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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