

Helical Poly(aryl isocyanide)s Possessing Chiral Alkoxy carbonyl Groups

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Precise synthesis with structural control of helical polymers is attractive subjects in polymer science from the view point of new chiral materials. Although many stereoregular macromolecules are known to take a helical conformation in the solid state, limited numbers of synthetic polymers that keep a helical structure even in solution have been reported.¹ Polyisocyanides with bulky substituents are a representative example of such helical polymers.² When chiral groups are introduced on isocyanide monomers, resulting polymers with *P* and *M* helices become diastereomeric pairs and are no longer thermodynamically equivalent. Consequently, single-handed helical polymers are predominantly produced if a helical structure is stable in solution. Some attempts to prepare single-handed helical polymers predominantly from chiral alkyl isocyanides have been made.³

Previously we showed a novel living polymerization of aryl isocyanides by using dinuclear μ -ethynediyl complex **1** as an initiator.⁴ This system was successfully applied to a screw-sense selective (SSS) polymerization of achiral isocyanides by a block copolymerization.⁵ Chiral oligomer complexes prepared from **1** with chiral isocyanides effectively initiate the SSS polymerization of achiral isocyanides possessing a bulky substituent to give single-handed helical polymers predominantly. Recently we reported that random copolymerization between chiral and achiral isocyanides also predominantly produced single-handed helical polyisocyanides.⁶ Since adequate choice of chiral monomers is essential to achieve high selectivity of the screw sense in polyisocyanide, systematic investigation on the effect of chiral substituents would provide valuable information to develop helical polymers. Our previous results suggest that the chiroptical properties would be sensitive to not only the kind but also the position of the substituents on an aromatic ring in poly(aryl isocyanide)s.^{5b} Thus, the effect of the position and the environment of the stereogenic center on helical structures might be appraised by using poly(aryl isocyanide)s possessing various chiral substituents with the same functional group. Few examples of such studies on helical polyisocyanide, however, have been found in the literature so far.^{3f} In this communication, we wish to report the precise syntheses of poly(aryl isocyanide)s having several kinds of chiral alkoxy carbonyl groups and the relation between the structure of chiral monomers and the selectivity of screw sense in the

resulting polymers.

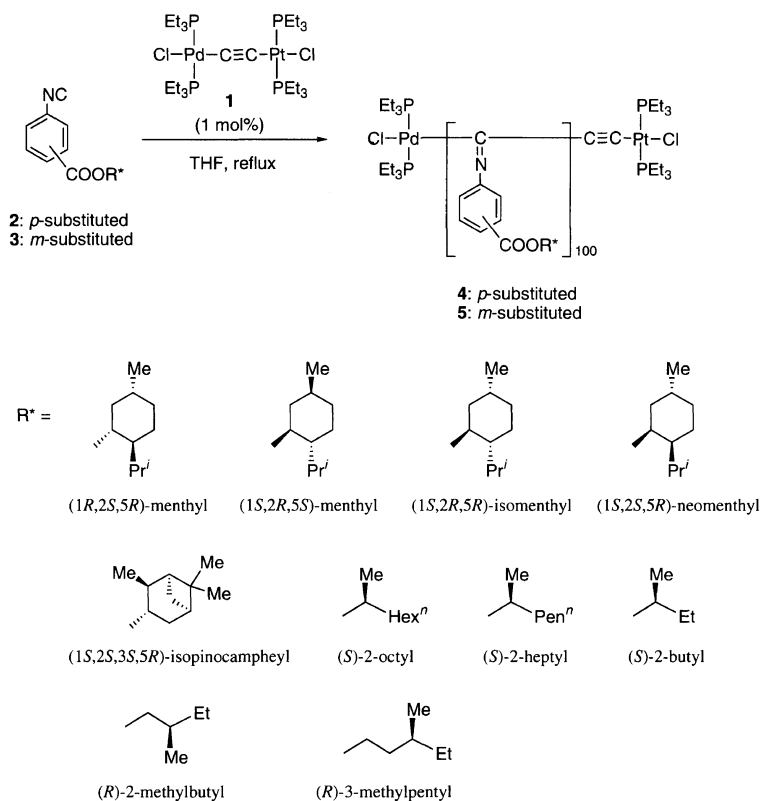
RESULTS AND DISCUSSION

Aryl isocyanides **2** and **3** with chiral alkoxy carbonyl groups at *p*- or *m*-position were easily prepared from chiral alcohols commercially available by the method reported previously.^{5b} These chiral monomers **2** and **3** were smoothly polymerized in the presence of 1 mol% of Pd-Pt μ -ethynediyl complex **1** in refluxing THF for 20h to give brownish-yellow polymers in quantitative yields. The resulting polymers were fully characterized by means of spectral and GPC analyses. Since the present polymerization has an almost ideal living nature, all polymers prepared in this study have a narrow polydispersity index.

Previously we have reported that polymers **4a** and **4b**, prepared from *p*-(1*R*,2*S*,5*R*)- and *p*-(1*S*,2*R*,5*S*)-menthylalkoxy carbonylphenyl isocyanides **2a** and **2b** respectively, show large optical rotations and intense Cotton effects at 364 nm due to the stable helical conformation of their main chains.⁵ Thus, we started our studies on the effect of chiral substituents from polymers **4c** and **4d**, which contain diastereomeric substituents, (1*S*,2*R*,5*R*)-isomenthyl and (1*S*,2*S*,5*R*)-neomenthyl groups. Optical properties of the resulting polymers along with those of monomers are summarized in Table I, where the molar optical rotation $[\phi]_D$ and the molar circular dichroism $\Delta\epsilon_{364}$ of polymers are given on the basis of the isocyanide monomer unit. Both polymers **4c** and **4d** showed large negative optical rotations and similar CD curves to that of **4b** (Figure 1), suggesting that they keep rigid helical structures with the same screw sense of **4b**. Comparison of the stereostructure of the substituents with the signs of the optical rotations and the circular dichroism $\Delta\epsilon_{364}$ indicates that the screw-sense of the resulting polymers depends on the stereochemistry at the 1-position of chiral substituents.

Polymer **4e** having (1*S*,2*S*,3*S*,5*R*)-isopinocampheyl groups also exhibited a large negative optical rotation and an intense Cotton effect at 364 nm, of which absolute values are slightly smaller than those of **4b**. To our surprise, polymers **4f**–**4h** having the smaller chiral groups relative to those of **4a**–**4e** also adopt a helical conformation with one-handed screw sense predominantly since the absolute values of the optical rotation and the circular dichroism are as large as those of **4e**. These results suggest that the steric bulkiness of the

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Scheme 1.

Table I. Poly(aryl isocyanide)s having chiral alkoxy carbonyl groups at *para*- or *meta*-positions

Monomers	R*	$[\alpha]_D^{20b}$ deg	Polymers	$M_n \times 10^{-3a}$	M_w/M_n^a	$[\alpha]_D^{20b}$ deg	$[\phi]_D^{20b}$ deg	$\Delta\epsilon_{364}^c$ dm ³ cm ⁻¹ mol ⁻¹
2a	(1 <i>R</i> ,2 <i>S</i> ,5 <i>R</i>)-menthyl ^d	-75	4a ^e	13.2	1.13	1070	3147	13.0
2b	(1 <i>S</i> ,2 <i>R</i> ,5 <i>S</i>)-menthyl ^d	73	4b ^e	13.3	1.12	-1054	-3100	-12.0
2c	(1 <i>S</i> ,2 <i>R</i> ,5 <i>R</i>)-isomenthyl	9	4c	13.0	1.09	-1060	-3117	-13.2
2d	(1 <i>S</i> ,2 <i>S</i> ,5 <i>R</i>)-neomenthyl	23	4d	13.1	1.18	-1280	-3764	-12.8
2e	(1 <i>S</i> ,2 <i>S</i> ,3 <i>S</i> ,5 <i>R</i>)-isopinocampheyl	31	4e	13.8	1.14	-920	-2687	-9.8
2f	(<i>S</i>)-2-octyl	41	4f	16.4	1.11	-860	-2305	-9.7
2g	(<i>S</i>)-2-heptyl	38	4g	14.3	1.11	-1000	-2540	-9.8
2h	(<i>S</i>)-2-butyl	26	4h	16.0	1.13	-1030	-2183	-8.5
2i	(<i>R</i>)-2-methylbutyl	8	4i	10.9	1.30	34	77	0.3
2j	(<i>R</i>)-3-methylpentyl	6	4j	13.4	1.17	-8	-19	~0
3a	(1 <i>R</i> ,2 <i>S</i> ,5 <i>R</i>)-menthyl ^d	-83	5a ^e	11.5	1.06	270	794	2.8
3b	(1 <i>S</i> ,2 <i>R</i> ,5 <i>S</i>)-menthyl ^d	82	5b ^e	11.9	1.08	-260	-764	-2.9
3c	(1 <i>S</i> ,2 <i>S</i> ,5 <i>R</i>)-neomenthyl	22	5c	12.3	1.14	290	853	3.4
3d	(<i>S</i>)-2-octyl	33	5d	15.5	1.06	-60	-161	-0.6
3e	(<i>S</i>)-2-butyl	26	5e	14.3	1.06	-20	-42	-0.2

^a M_n and M_w/M_n were determined by a GPC analysis based on the calibration of polystyrene standards. ^b $c = 0.1$, CHCl₃. ^c CD spectra were measured in CHCl₃ at ambient temperature. ^d (1*R*,2*S*,5*R*)-menthyl = (*l*)-menthyl, (1*S*,2*R*,5*S*)-menthyl = (*d*)-menthyl. ^e See ref 10.

chiral substituents is not a major factor controlling the selectivity of the screw sense in the present system. It may be of interest that polymers **4e–4h** having an *S* configuration at the 1-position of chiral substituents exhibited the same sign, that is minus, in their optical rotation and circular dichroism $\Delta\epsilon_{364}$ in as observed in **4b–4d**, indicating that all of these polymers take the same screw sense predominantly. Recently the induced helix formation through complexation with chiral substrates, of which the helical sense depends on the absolute configuration of chiral center, has been reported for poly(phenylacetylene) derivatives.⁷ On the other hand, poly-

mer **4i** with (*R*)-2-methylbutyl groups, in which the stereogenic center is located at the next carbon to that bound with the ester oxygen, showed a small optical rotation and a weak Cotton effect. Similar optical properties were observed for polymer **4j** with (*R*)-3-methylpentyl, in which the stereogenic center is located further apart from the ester group. Thus, the selectivities of screw sense in **4i** and **4j** must be much lower than those in **4f–4h**. These results suggest that the position of a chiral center is closely correlated with the selectivity of screw sense of poly(aryl isocyanide)s bearing chiral alkoxy carbonyl groups at a *p*-position. Similar results

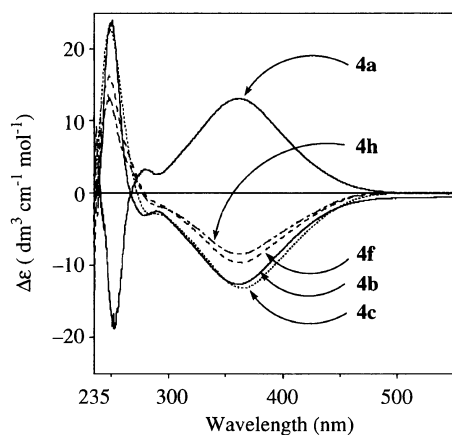


Figure 1. CD spectra of polymers.

have been reported for polyisocyanide with chiral phenyl bonzoates by Serrano,^{3f} while poly(propionic ester)s with chiral groups through an appropriate spacer take a helical conformation predominantly.⁸

In contrast, somewhat different phenomena were observed for polymers **5** prepared from *m*-substituted aryl isocyanides **3**. We have already shown that optical properties of poly(aryl isocyanide)s are strongly affected by the position of substituents on the aromatic ring even if they exhibit the same selectivity of screw sense as *p*-substituted analogs. Polymers **5a** and **5b** keep a one-handed helical structure with almost the same selectivity as **4a** and **4b** in spite of their smaller absolute values of the optical rotation and the circular dichroism relative to those of **4a** and **4b**.^{5b} Thus, we appraised the selectivity of screw sense of **5c–5e** having chiral alkoxy carbonyl groups at *m*-position on the basis of their optical rotation and the circular dichroism by comparison with those of **5a** and **5b**. While polymer **5c** having (1*S*,2*S*,5*R*)-neomenthyl groups exhibited similar optical properties to those of **5a**, the absolute values of the optical rotation and the circular dichroism $\Delta\epsilon_{364}$ of **5d** and **5e** were much smaller than those of **5a** and **5b**. These results indicate two different points in the effects of chiral groups in polymers **5** from *p*-substituted polymers **4**. One is that the bulkiness of chiral group is important to produce one-handed helices and the other is that the screw sense does not depend on the absolute configuration at the 1-position of chiral groups.

In conclusion, we have found that the selectivity of screw sense in poly(aryl isocyanide)s having chiral alkoxy carbonyl groups depends on the some structural factors, that is the position of chiral substituents on aromatic rings, the position of stereogenic center and the bulkiness of chiral groups. These results may provide useful information for design and construction of helical chiral polyisocyanide having novel functions.

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