# Asymmetric Radical Polymerization of Maleimides Using a Chiral Cobalt(II) Complex

**Tamaki Nakano,*,† Daisuke Tamada,† Jun-ichi Miyazaki,† Kiyomi Kakiuchi,† and Yoshio Okamoto‡**

*Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), Takayama-cho 8916-5, Ikoma, Nara 630-0101, Japan, and Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

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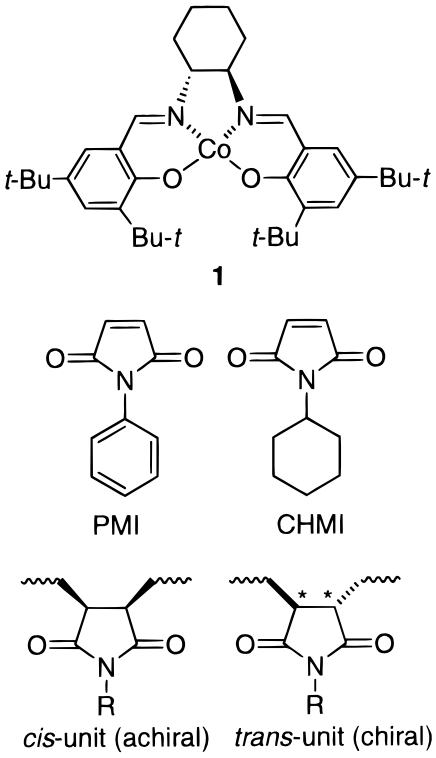
**Introduction.** Control of stereochemistry in free-radical polymerization is an important goal in macromolecular science because many polymers are produced by radical catalysis in industry, and the properties of polymers are often dependent on the main-chain configuration.[1−3] Through our efforts in this field, we recently found that radical polymerization of 1-phenyldibenzosuberyl methacrylate gives a single-handed helical, highly isotactic polymer in the presence of a chiral Co(II) complex (**1**) (helix-sense-selective radical polymerization).[4] The chiral induction was assumed to be based on radical−radical interaction between growing species and the chiral **1**. In this work, to extend the use of **1** to configurational chirality control of radical polymerization, we carried out the radical polymerization of *N*-phenylmaleimide (PMI) and *N*-cyclohexylmaleimide (CHMI) in the presence of **1**. The two monomers are known to afford optically active polymers by asymmetric anionic polymerization using the *n*-BuLi/(−)-sparteine complex.[5,6] The polymers may have achiral *cis*- and/or chiral *trans*-monomeric units, and the chiroptical properties have been ascribed to the excess of (*R*,*R*)- or (*S*,*S*)-*trans*-configuration induced during the polymerization by the effect of (−)-sparteine.

**Experimental Section. Materials.** Complex **1**[7,8] was available from our recent work.[4] PMI and CHMI (TCI) were used as obtained. α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Solvents were purified by distillation and stored under an argon atmosphere.

**Polymerization.** Radical polymerization was performed by heating (60 °C) or UV-irradiating (30, 0 °C) a solution of monomer, AIBN, and **1** under an argon atmosphere. Anionic polymerization was carried out according to the literature.[5,6a] The products were precipitated in methanol and isolated with a centrifuge and further purified by reprecipitation in a methanol−pyridine mixture several times.

**Measurements.** The $^1$H NMR spectra were recorded on a JEOL JNM LA400 spectrometer (400 MHz for $^1$H measurement). Circular dichroism (CD) spectra were obtained with a JASCO J-720L spectrometer. The SEC experiment was performed using a chromatographic system consisting of a Hitachi L-7100 pump, an L-7420 UV detector (254 nm), an L-7490 RI detector, and a JASCO OR990 polarimetric detector equipped with TOSOH TSKgel G3000H$_{HR}$ and G6000H$_{HR}$ columns connected in series (eluent, THF; flow rate, 1.0 mL/min).




**Results and Discussion.** The conditions and results of radical and anionic polymerization are summarized in Table 1. The results of the asymmetric anionic polymerization were consistent with the previous reports,[5,6] resulting in the optically active polymers (runs 7, 12). The radical polymerizations were performed in a solution containing pyridine because **1** showed better solubility in the presence of pyridine than in pure tetrahydrofuran (THF) or toluene. The polymers obtained in the absence of **1** contained a large amount of tetrahydrofuran (THF)- or $CHCl_3$-insoluble part while those prepared in the presence of **1** were soluble in THF or $CHCl_3$ except for the polymer of run 6. This may suggest that **1** has an effect on molecular weight or stereochemistry of the products.

The polymers obtained by radical polymerization using **1** showed optical activity in most cases. To learn the origin of the optical activity, CD spectra of the polymers were taken (Figure 1). As shown in Figure 1A,B, the spectral pattern of the poly(PMI) of run 2 obtained in toluene−pyridine and that of the poly(CHMI) of run 11 obtained in THF−pyridine were quite similar to those of the corresponding polymers prepared anionically. In addition, the sign and the relative intensity of the spectra corresponded fairly well with the sign and the relative magnitude of the optical activity. These results indicate that the chiroptical properties of the poly(PMI) and the poly(CHMI) obtained by radical polymerization are based on configurational chirality of the main chain which is similar to that of the anionically obtained polymers. Thus, **1** was shown to induce main-chain chirality in the radical

* To whom correspondence should be addressed. Phone +81-743-72-6081; fax +81-743-72-6089; e-mail nakano@ms.aist-nara.ac.jp.
† Nara Institute of Science and Technology (NAIST).
‡ Nagoya University.

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**Table 1. Polymerization of Maleimides under Radical and Anionic Conditions[a]**

| run | monomer | reaction mode | initiator | solvent | $[\mathbf{1}]_0$, M | temp, °C | yield,[b] % | $M_n$[c] × $10^3$ | $M_w/M_n$[c] | $[\alpha]_D$ ($\alpha_D$),[d] deg |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PMI | radical | AIBN | toluene−pyridine | 0 | 60 | 59 | n.d.[e] | n.d.[e] | |
| 2 | PMI | radical | AIBN | toluene−pyridine | 0.023 | 60 | 25 | 5.9 | 2.50 | −4 (−0.018)[f] |
| 3 | PMI | radical | AIBN-UV | toluene−pyridine | 0.023 | 30 | 55 | 5.0 | 2.40 | −4 (−0.017)[g] |
| 4 | PMI | radical | AIBN-UV | toluene−pyridine | 0.023 | 0 | trace | | | |
| 5 | PMI | radical | AIBN | THF−pyridine | 0 | 60 | 34 | n.d.[e] | n.d.[e] | |
| 6 | PMI | radical | AIBN | THF−pyridine | 0.023 | 60 | 64 | 4.1[h] | 3.15[h] | ∼0[i] |
| 7 | PMI | anionic | *n*-BuLi-Sp | toluene | 0 | 0 | 11 | 3.5 | 2.23 | −6 (−0.061) |
| 8 | CHMI | radical | AIBN | toluene−pyridine | 0 | 60 | 65 | n.d.[e] | n.d.[e] | |
| 9 | CHMI | radical | AIBN | toluene−pyridine | 0.023 | 60 | 18 | 3.7[j] | 1.38[j] | +7 (+0.075)[k] |
| 10 | CHMI | radical | AIBN | THF−pyridine | 0 | 60 | 49 | n.d.[e] | n.d.[e] | |
| 11 | CHMI | radical | AIBN | THF−pyridine | 0.023 | 60 | 72 | 8.1 | 2.06 | +6 (+0.011)[l] |
| 12 | CHMI | anionic | *n*-BuLi-Sp | toluene | 0 | 0 | 38 | 6.3 | 2.63 | −36 (−0.361) |

[a] Conditions: $[\text{monomer}]_0 = 2.2-2.3$ M (runs 1−6, 8−11), 0.27 M (runs 7, 12). $[\text{pyridine}]_0 = 0.35$ M (runs 1−6, 8−11). $[\text{AIBN}]_0 = 0.023$ M (runs 1−6, 10, 11), 0.23 M (runs 8, 9). $[\text{Li}]_0 = 0.0073$ M (run 7), 0.0063 M (run 12). $[\text{Sp}]_0 = 0.0088$ M (run 7), 0.0075 M (run 12). [b] MeOH-insoluble part. [c] Estimated by SEC (vs polystyrene). [d] Measured in THF (concn = ca. 1.0 g/dL) using a 1 dm quarz cell. The observed range of error for $\alpha_D$ was within ±0.001°. [e] Mostly insoluble in THF or $CHCl_3$. [f] Cell length = 0.5 dm. [g] Concn = 0.40 g/dL. [h] THF-soluble part only (50 wt %). [i] In DMSO. [j] Accompanied with a minor peak at $M_n = 2.74 \times 10^3$ ($M_w/M_n = 2.71$). [k] In $CHCl_3$. [l] Concn = 0.33 g/dL. Cell length = 0.5 dm.

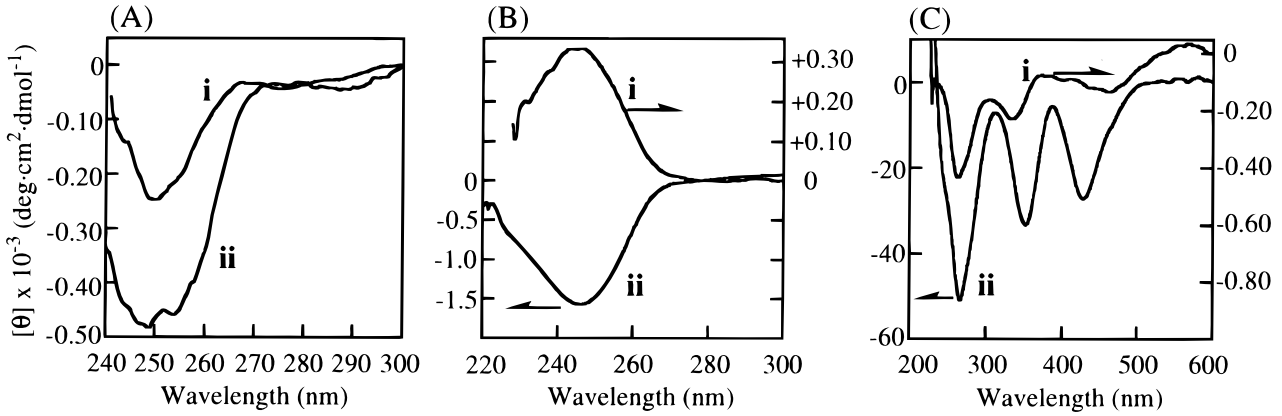



**Figure 1.** CD spectra of poly(PMI)s (A) [run 2 (i) and run 7 (ii)], poly(CHMI)s (B) [run 11 (i) and run 12 (ii)], and poly(CHMI) of run 9 and Co complex **1** (C) [polymer (i) and **1** (ii)]. The spectra were taken in THF at room temperature.

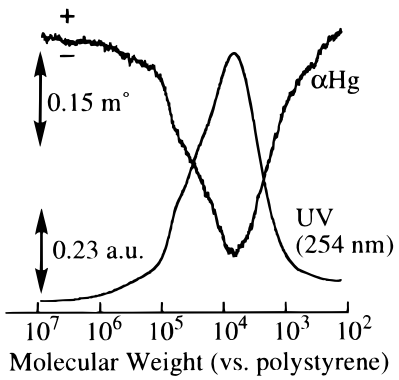


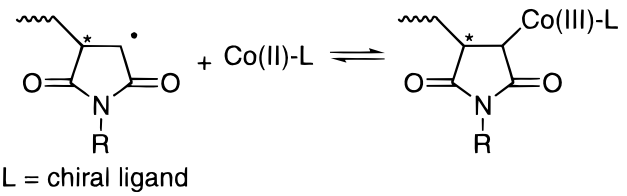

**Figure 2.** SEC curves obtained by polarimetric (top) and UV (bottom) detectors of the poly(PMI) of run 2.

polymerization under the conditions discussed so far. To obtain information on the chiral structure on the polymers, SEC analysis using simultaneous UV and polarimetric detection was performed for the poly(PMI) of run 2 (Figure 2). The UV and polarimetric chromatograms corresponded well. This means that the all polymer chains have statistically similar chiral configuration. In the polymerization of PMI in toluene−pyridine, lowering the reaction temperature from 60 to 30 °C did not increase the optical activity of the product, and only a trace amount of polymer was obtained at 0 °C (runs 3, 4).

The efficiency of chiral induction and polymerization behavior depended on the reaction conditions. The CD spectrum of the poly(CHMI) obtained with **1** in toluene−pyridine (run 9) had a completely different pattern from that of the anionically prepared polymer and was rather similar to the spectrum of **1** (Figure 1C), suggesting that the residue of **1** is attached to the polymer chain probably at the terminal through C−Co(III) bonding. Formation of such a bonding has been proposed for the cobalt-mediated living radical polymerization system of methyl acrylate.[9] To remove the Co residue from the polymer terminal and to know the contribution of main-chain chirality to the CD spectrum, the polymer was treated with an excess amount of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) in a $CHCl_3$−pyridine (2:1) solution under UV irradiation ($[\text{polymer}]_0 = 0.0052$ M, $[\text{TEMPO}]_0 = 0.26$ M, ambient temperature, time 12 h). After this treatment, the polymer showed no clear CD absorption or optical activity, indicating that the Co residue was successfully removed from the chain and that no chiral induction took place in the CHMI polymerization in toluene−pyridine (run 9) in contrast to the reaction in THF−pyridine (run 11). A similar treatment applied to the poly(PMI) of run 2 led to only subtle changes in the CD spectrum and optical activity, confirming that the treatment does not seriously racemize the main-chain asymmetric centers. The results described so far indicate that the function of **1** differs depending on monomer and reaction conditions.

The chiral induction by **1** is probably based on the interaction of the Co(II) radical with the growing polymer radical. Although the mechanism of maleimide

**Scheme 1**




polymerization in the presence of **1** is not immediately clear, it is assumed that the growing radical and **1** interact with each other as proposed for the living radical polymerization system of methyl acrylate[9] (Scheme 1), and the incoming monomer has some steric interaction with the cobalt species. Although several Co(II) complexes are known to act as chain-transfer agents in methacrylate polymerization giving polymers with an $\omega$-end unsaturated structure through $\beta$-hydrogen elimination,[10−13] an $\omega$-end unsaturated moiety was not clearly confirmed for the optically active polymer of run 11 by $^1$H NMR analysis. This indicates that chain transfer is not a primary function of **1** in the present systems.

Another possible mechanism of chiral induction could involve Lewis acid−Lewis base interaction between monomer and **1**. However, preliminary polymerizations in toluene using equimolar reaction products of (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, the ligand of **1**, with $Ti(OPr^i)_2Cl_2$ and with $AlEt_3$ as additives in place of **1** did not give optically active polymers. This result implies that the acid−base interaction does not significantly contribute to the chiral induction mechanism although it does not completely rule out the possibility that **1** acts as a Lewis acid.

The chiral induction based on **1** observed here is in contrast to the fact that no clear influence of the metallic radical species on the tacticity has been found for the radical polymerization of vinyl monomers mediated by transition-metal complexes including cobalt, ruthenium, nickel, iron, rhenium, and copper.[9,10,14] However, the present results could mean that stereochemical control using a radical species may be possible when one designs reactions properly.

In addition, it is not clear at this point whether the proposed metal−radical interaction (Scheme 1) is best achieved with a Co(II) complex. Examination of chiral complexes having a different metallic radical center will be necessary to answer this question.

**Conclusions.** A catalytic amount of chiral cobalt complex was shown to induce configurational chirality in a radical polymerization for the first time. The induction of configurational chirality to the polymer chain by radical polymerization using a chiral radical species is unprecedented though there are examples based on chiral monomer structure,[15] chiral additives that presumably work as Lewis acids,[16,17] and a chiral inclusion complex.[18] Further work is in progress in order to clarify the mechanism, to enhance the induction efficiency, and to find a way to control tacticity in the polymerization of more versatile monomers using a radical species.

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