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Metal-Induced Supramolecular Chirality in Optically Active Polymers of Oxazoline-Substituted *N*-Phenylmaleimides

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ABSTRACT Polymerization of *N*-phenylmaleimide derivatives bearing a chiral oxazoline substituent at *ortho*-position on the phenyl group (namely, *N*-[*o*-(4,5-dihydro-1,3-oxazol-2-yl)phenyl]maleimides, OPMI) was carried out with diethylzinc (Et_2Zn) as an initiator. The resulting polymers exhibited a quite high specific rotation and a unique split-type circular dichroism. Furthermore, an induced Cotton effect was observed in the π–π* transition region of the chromophores upon complexation of these polymers with copper(II) salt in tetrahydrofuran solution, indicating the formation of chiral supramolecular aggregates. The induced supramolecular chirality was found to be dependent on the absolute configuration of monomer units, that is, the polymers with (*R*)-configurational oxazolinyl chromophores tended to form chiral aggregates with levorotatory handedness, while polymers obtained from the (*S*)-monomer offered dextrogyrate one upon the addition of Cu(II) salt. *Chirality 19:521–527, 2007.*

KEY WORDS: anionic polymerization; supramolecular chirality; induced circular dichroism; poly(*N*-phenylmaleimides); oxazoline; aggregate

INTRODUCTION

In recent decades, great interest has been focused on exploring and extending the chirality by helical polymers[1–3] and supramolecular assemblies,[4–8] because these systems can be applied to developing novel chiroptical devices and chiral materials as enantioselective catalysts.[9–12] On the other hand, the oxazoline derivatives have attracted much attention because of their proved utility in different chemical fields, for example, in asymmetric catalysis,[13–17] supramolecular system,[18,19] and the synthesis of optically active compounds.[20–23] Yashima et al. designed and synthesized a type of polythiophene containing an optically active oxazoline residue in the side group, which self-assembled into supramolecular chiral aggregates, with intermolecular π-stacking interactions in a poor solvent or in a film. Also, they found metal-induced chirality in a chiral polythiophene aggregate originated from intermolecular complexation between the oxazoline residue and the metal ions.[19,24,25]

Recently, we synthesized a new type of oxazoline-substituted *N*-phenylmaleimides bearing different substituents (i.e., phenyl, *iso*-propyl, and methyl) on the oxazoline moiety (referred to as (*R*)-PhOPMI, **a**; (*S*)-Pr^iOPMI, **b**; and (*S*)-MeOPMI, **c**; respectively) to prepare the optically active polymers, as shown in Scheme 1.[26,27] The poly(OPMI)s were designed on the assumption that the chiral oxazoline residues could coordinate to various metal ions to form chiral supramolecular aggregates, which should have potential uses as a polymeric catalyst for asymmetric synthesis, because many metal complexes with chiral oxazoline derivatives have been used as highly enantioselective catalysts.[13–17] In addition, the polymerization of *N*-substituted maleimide-type monomers proceeds through only *trans*-opening reaction of double bond in the imide ring to produce stereogenic centers (*S*, *S*) and (*R*, *R*).[28] Thus, an excess (*S*, *S*) or (*R*, *R*) configurational pair in the main chain based on *threo*-di-isotactic structure is expected to endows the polymer with optical activities. When the same configurational pairs are successively connected in the *threo*-diisotactic sequences, the main chains can form a helical conformation. In contrast, the polymer with *threo*-disyndiotactic structure does not exhibit chirality because stereogenic centers (*S*, *S*) and (*R*, *R*) in each repeating unit equally exist.

We previously reported that the poly(OPMI)s obtained with *n*-BuLi initiating system showed relatively low molecular weights ($M_n = 2 \times 10^3 - 6 \times 10^3$) and small specific rotations, which may be relative to the rigidity of cyclic imide units in the main chain.[26,27] Also, it was found that the polymeric materials do not show a significant complexing ability as we expected. The addition of metal salts, such as $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(OTf)_2$ or $Zn(OTf)_2$, into the solution of poly-**a** in THF resulted in the formation of precipitation.

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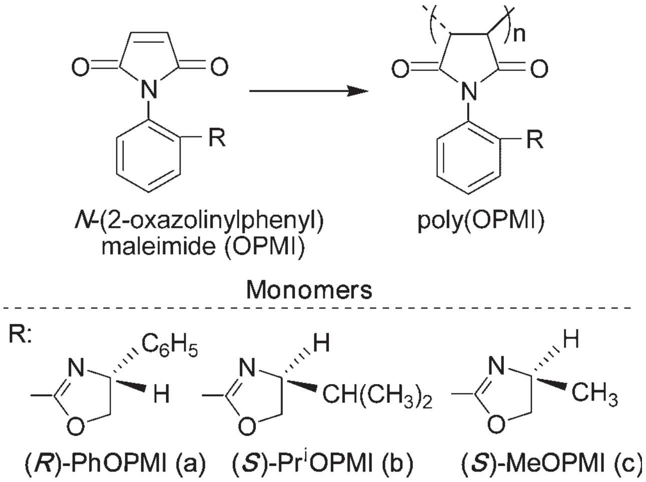

Scheme 1. Chiral *N*-phenylmaleimide monomers for polymerization.

In the present work, diethylzinc (Et_2Zn) was applied to induce the anionic polymerization of OPMI. The resulting polymers, in contrast to the reported poly(OPMI)s with *n*-BuLi or radical initiators, exhibited a quite high optical activity and a unique circular dichroism (CD) fashion. Furthermore, the addition of Cu(II) salts caused a dramatic enhance in the specific rotation of the polymers and unusual effects on the chiroptical property as evidenced by UV–vis and CD spectroscopy. This supramolecular assembly phenomena derived from the metal complexation were also investigated by means of atomic force microscopy (AFM) measurements.

MATERIALS AND METHODS

Chemicals and Reagents

Commercially available Et_2Zn and *n*-BuLi in an *n*-hexane solution (Acros) were used without further purification. (−)-Sparteine (Sp, purity 99%), purchased from Aldrich Chemical, was distilled under reduced pressure over calcium hydride and stored under nitrogen atmosphere at 4°C in the dark. Solvents were purified by the usual methods before use. Zinc(II) trifluoromethanesulfonate (Zn$(OTf)_2$) and copper(II) trifluoromethanesulfonate (Cu$(OTf)_2$) was synthesized according to the reported methods.[29] $CuCl_2{\cdot}2H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ (Shanghai Reagent, Shanghai, China) were used as received. The chiral monomer (OPMI) shown in Scheme 1 was synthesized according to the reported procedures.[26,27]

Measurements

^{13}C NMR spectra were recorded on a Bruker Avance AMX-500 NMR spectrometer with TMS as internal standard. Absorption and CD spectra were measured on a Jasco V-570 spectrophotometer and a Jasco J-820 spectropolarimeter, respectively, in a 1.0-cm quartz cell. A Bruker Vector 22 Fourier Transform Infrared spectrometer was applied for recording spectra in KBr pellets. D-line specific rotations ($[\alpha]_D^{25}$) were measured in THF at 25°C, using a Wzz-2s Automatic Digital Polarimeter (Shanghai Pudong Optics Apparatus). The molecular weights of the polymers were determined by gel permeation chromatography (GPC), using a Waters 2414 GPC apparatus equipped with a set of Styragel® columns (HT-3, HT-4) and a differential refractometer (eluent, THF; a flow rate of 1.0 ml/min). The GPC chromatogram was calibrated against standard polystyrene samples. AFM measurements were carried out on a SPI3800N atomic force microscope in the tapping mode. Topography and phase images were simultaneously measured at the resonance frequency of the silicon tips with cantilevers 100 μm in length. The analysis of zinc element remaining in the polymer samples was made on a IRIS IntrepidIIXSP full spectrum plasma emission spectrometer (America Thermoelectricity).

Polymerization

Anionic polymerizations were initiated by injecting Et_2Zn via a syringe to a monomer solution in dry Schlenk tubes under dry nitrogen atmosphere. After passage of prescribed time, the reaction mixture was poured into a large amount of *n*-hexane to precipitate the polymer. The product was filtered off and dried. The obtained samples were purified by reprecipitation from THF-*n*-hexane system in five cycles and dried under reduced pressure at 40°C for 2 days before measurements.

Experiments on the Complexing Reaction of Polymers with Cu(II) Salts

Typical experimental procedure: Adding Cu(II) salts to poly-**a** solution (1.2 mg/ml, 3.8 mM monomer units) in THF according to the prescribed ratio of Cu(II) to polymer. The resulting solution suffered directly the measurement of specific rotation and then was diluted to 0.4 mg/ml for CD and UV testing. All the operations were finished in ambient atmosphere.

AFM Measurements on Supramolecular Aggregates of Poly-b with $Cu(NO_3)_2{\cdot}3H_2O$

A stock solution of poly-**b** (25 ml, 0.2 mg ml^{-1}, 0.7 mM) in THF was prepared. And then $Cu(NO_3)_2{\cdot}3H_2O$ (2.1 mg, 8.8×10^{-3} mmol) was added to the solution. The solution was allowed to stand for a predetermined interval of time, and then cast on freshly cleaved mica substrates. The solvents were evaporated in a stream of nitrogen, and AFM images were recorded.

RESULTS AND DISCUSSION

Table 1 summarizes the results on the anionic polymerization of OPMI (**a**, **b**, and **c**) initiated by Et_2Zn. In all cases, the polymerization gave low yields, probably because of the low activity of Et_2Zn. A remarkable change in optical activity was observed during the transformation from (*S*)-Pr^{i}OPMI (**b**) ($[\alpha]_D^{25} = -60.6°$) to the corresponding polymer ($[\alpha]_D^{25} = +23.6° \sim +134.7°$). The reversal in optical direction indicates that the optical activity of the polymer does not only arise from the chiral oxazoline moieties and suggests that a higher-ordered structure, most likely a secondary helical structure, had been formed.[30,31] Interestingly, poly-**a** and poly-**b** prepared at 30°C exhibited much higher absolute value of specific rotations than

TABLE 1. Anionic polymerization of OPMI using Et_2Zn as an initiator at different conditions[a]

		Reaction conditions[c]		Polymer				
Run	Monomer[b]	Solvent	Temp (°C)	Yield (%)[d]	Zn (mol-%)[e]	M_n[f] (10^3)	M_w/M_n[f]	$[\alpha]_D$[b] (°)
1	**a**	THF	0	8.3	24.5	1.8	1.1	−92.4
2	**a**	Toluene	0	8.4	21.1	1.6	1.5	−62.6
3	**a**	THF	30	18.2	35.4	1.5	2.0	−169.3
4	**b**	THF	0	–[g]	–	–	–	–
5	**b**	Toluene	0	15.2	20.5	0.9	1.4	+23.6
6	**b**	Toluene	30	12.0	33.8	1.8	2.3	+134.7
7	**c**	THF	30	14.2	28.9	1.6	1.6	−35.7
8	**c**	Toluene	30	24.8	22.0	1.2	1.6	−17.2

[a] $[M]_0 = 0.5$ mol/l.

[b] Specific rotation ($[\alpha]_D$) of monomers: −58.0° (**a**), −60.6° (**b**), and −131.7° (**c**), which measured in THF ($c = 0.3$ g/dl, $l = 10$ cm) at 25°C.

[c] $[Et_2Zn]_0/[monomer]_0 = 0.1$ (molar ratio).

[d] Insoluble part in *n*-hexane/THF (2:1, v/v).

[e] Mole percent of Zn remaining in the polymer relative to monomer units: Zn (mol-%) = ([Zn]/[Zn] + monomeric unit) × 100%.

[f] By GPC.

[g] No product.

those of the polymers obtained at 0°C, which is different from the previous observation in the case of *n*-BuLi-initiated polymerization of OPMI.[26,27]

To obtain the structural information and thereby to elucidate the chiroptical property for the present polymers, NMR spectroscopic study is necessary. Figure 1 depicts ^{13}C NMR spectrum of poly-**a** obtained with Et_2Zn (the spectra of poly-**b** and poly-**c** are available in Supporting Information). The broad NMR peaks were attributed to the multiconfigurations in the polymaleimide derivatives.[21–23] According to Oishi and coworkers,[20,22,23] the signals around 41 and 43 ppm in ^{13}C NMR spectra are assigned to *threo*-diisotactic and *threo*-disyndiotactic configurations, respectively. They also demonstrated that the magnitude of specific rotation increases with an increase in the ratio of *threo*-diisotactic structures in the polymers even though they also include main chain carbons with the other configurations. Comparison of Figure 1 and our previous results indicates that poly-**a** obtained in this study possessed a lower *threo*-diisotactic content in the main chain on the basis of the relative intensities of the peak at 41 ppm. However, the problem is poly-**a** showed a much higher specific rotation when compared with its analogs

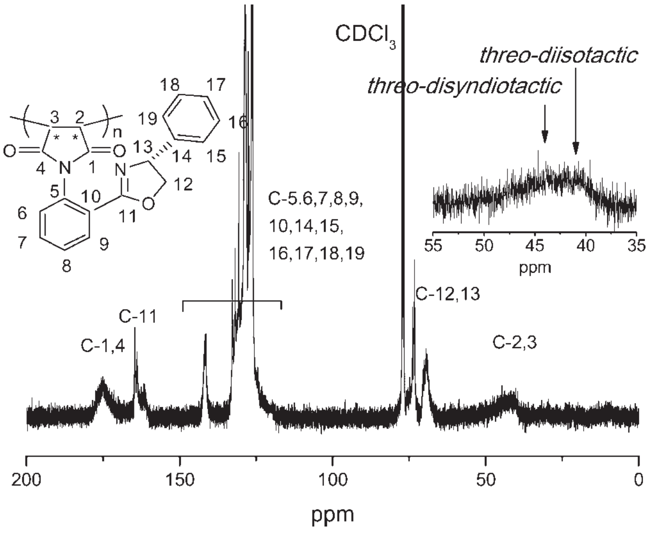

Fig. 1. ^{13}C NMR spectrum for poly-**a** obtained with Et_2Zn in THF ($[\alpha]_D^{25} = -92.4°$, Run 1 in Table 1).

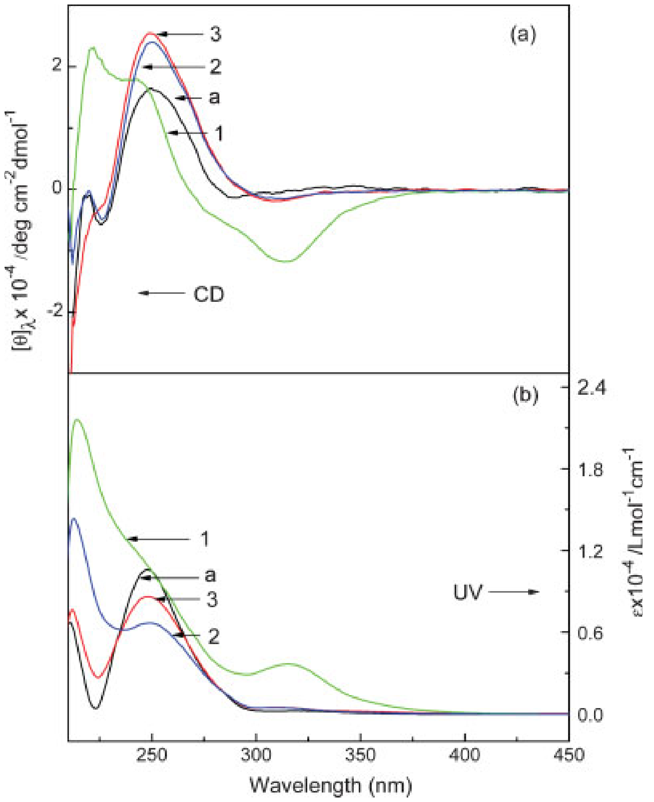

Fig. 2. CD (**a**) and UV–vis spectra (**b**) for poly-**a** samples: (1) Run 3 in Table 1, $[\alpha]_D^{25} = -169.3°$; (2) obtained with Et_2Zn/(−)-Sp in toluene at −35°C, $[\alpha]_D^{25} = +29.7°$; (3) obtained with *n*-BuLi in THF at 0°C, $[\alpha]_D^{25} = +4.0°$; (**a**) momomer (*R*)-PhOPMI $[\alpha]_D^{25} = -58.0°$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

having *threo*-diisotactic-rich structure obtained in *n*-BuLi system.[26,27] In fact, a sample obtained with Et_2Zn reached a $[\alpha]^{25}_{D}$value as high as −169.3° (Run 3 in Table 1), which seems to be inconsistent with the conclusion educed by Oishi and coworkers.[20] Considering the complexing capacity of oxazoline pendants, we presume that the present polymerization produced chiral polymer complexes incorporating Zn(II) ions, which is likely responsible for its high optical activity.

As shown in Figure 2, poly-**a** obtained with Et_2Zn displayed a unique split-type CD in the $\pi-\pi^*$ transition region, which contrasts to the other samples with *n*-BuLi or Et_2Zn/(−)-Sp. Similar phenomena were also observed for poly-**b** and poly-**c** (see: Supporting Information). Apparently, the intense CD signal at near 315 nm should be related to the coordination of Zn(II) ions with oxazoline moieties of poly(OPMI)s. It is noteworthy that the chiral initiator Et_2Zn/(−)-Sp did not give the corresponding polymeric complex. This can be explained by the fact that sparteine as a bidentate ligand may very tightly coordinate to Zn(II) ions, which prevents the incorporation of metal ions into the polymer. Although a complete structural interpretation of chiral poly(OPMI)s with Et_2Zn for the induced optical activity still remains unclear, the polymers should be in-situ transformed to the metal complexes via the coordination between catalyst residues with oxazoline pendants during the polymerization.[†]

Interestingly, the present polymers are capable of further ligating other kinds of metal ions to build up chiral complexes/aggregates on a supramolecular scale. We found that the specific optical rotation ($[\alpha]^{25}_{D}$) was enhanced dramatically upon the addition of $Cu(NO_3)_2 \cdot 3H_2O$ to the solution of poly(OPMI)s in THF, and the solution spontaneously changed from pink to olivine.[‡] Moreover, the variation in $[\alpha]^{25}_{D}$ depended on the amount of Cu(II) added (Fig. 3). In all cases, the magnitude of the specific rotation initially rises as [Cu(II)]/[monomer units of polymer] increases, reaches a maximum at about 1/5 of the ratio and then the value almost keeps constant as more salt is added into the solution. On the other hand, the amplitudes of $[\alpha]^{25}_{D}$ are different for the three poly(OPMI)s, indicating that the steric bulk of the substituents at the chiral center have an important influence on the chiroptical properties of resulted aggregates.

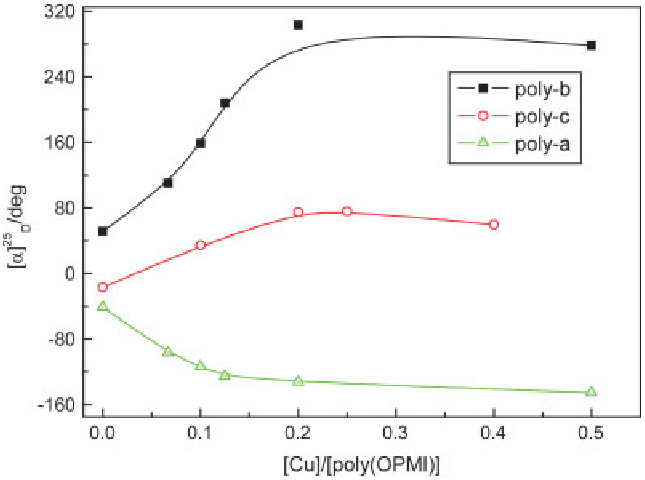

Fig. 3. Dependence of specific optical rotation ($[\alpha]^{25}_{D}$) on the amount of $Cu(NO_3)_2 \cdot 3H_2O$ added the solution of polymers in THF ([Cu]/[monomer units of polymer]): (■) poly-**b** ($[\alpha]^{25}_{D}$ = +51.3°), (○) poly-**c** ($[\alpha]^{25}_{D}$ = −17.2°), and (△) poly-**a** ($[\alpha]^{25}_{D}$ = −41.1°); an initial polymer concentration = 1.2 mg ml^{-1}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Note also that the specific rotations increased in dextrogyrate direction upon the addition of Cu(II) salt for both poly-**b** and poly-**c** having (*S*)-configurational oxazolinyl chromophores in the side-chain, although the former is dextrogyrate and the latter levorotatory. In contrast, the addition of Cu(II) salt made the specific rotation increase in levorotatory direction in the case of poly-**a** containing (*R*)-configurational oxazoline residues. These results suggest that the absolute configuration of the pendant groups had a significant effect on the supramolecular chirality of poly(OPMI)s with Cu(II) ions. That is, poly(OPMI)s bearing (*R*)-configurational oxazoline pendants tended to form chiral aggregates with levorotatory handedness in a complicated manner, while the polymer with (*S*)-configurational lateral groups produced a dextrogyrate one upon the addition of Cu(II) salt.

The formation of Cu(II)-induced aggregates has been evidenced by the CD and absorption spectroscopic studies. It can be seen that Cu(II) salts brought about remarkable changes in the ICD and UV–vis patterns of poly-**a** obtained with Et_2Zn (Fig. 4). Upon the addition of $Cu(NO_3)_2 \cdot 3H_2O$ to the solution of poly-**a**, the original CD signal around 315 nm sharply weakened and a broad ICD appeared at longer wavelengths (380−450 nm). These variations in the CDs were accompanied by a significant change in the absorption spectra; furthermore, the absorption intensity increased with an increase in [Cu(II)]/[monomer units of polymer]. Similar spectral variations were also observed for other poly(OPMI) systems. However, the change in CD intensity of poly-**c** was smaller as compared with the other two polymers, which corresponds with the magnitude in change of their specific rotations (see: Supporting Information).

It should be emphasized that the Zn-containing polymer generated during the Et_2Zn-initiated polymerization plays a key role for the formation of Cu(II)-induced chiral aggre-

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[†] To clarify this point, we prepared poly(Pr^{i}OPMI) via a radical polymerization method, this sample being chosen because it was rich in *threo*-disyndiotactic structure like the Et_2Zn-synthesized one, and then carried out a post-synthetic treatment on it. That is, the polymer was mixed with $Zn(OTf)_2$ or Et_2Zn in THF solution and then was stirred for a sufficient time. As a result, no difference could be detected between the two samples (i.e. poly(Pr^{i}OPMI)s with and without the treatment) in both optical rotation and in IR spectral fashion (see: Supporting Inf.). In fact, the infrared spectra showed a shift of the characteristic C=N stretching peak from oxazoline residue to a lower wavenumber (1638 cm^{-1}) for poly(OPMI)s obtained with Et_2Zn. Whereas the polymers synthesized by the radical, *n*-BuLi, or Et_2Zn/(−)-Sp systems showed the absorption at nearly same position (1644 cm^{-1}). The result further confirmed the formation of polymer–Zn(II) complexes.

[‡] The hydrated Cu(II) salt was directly used for the complexing reaction, which is different from the procedure reported by Yashima and coworkers (Ref. 19). In their experiments, the complexing reaction of poly[3-{4-((*R*)-4-ethyl-2-oxazolin-2-yl)phenyl}thiophene] (PTs) with Cu(II) was very sensitive to water. They considered that hydration hinders the coordination of copper(II) ions to the oxazoline residues of PTs.

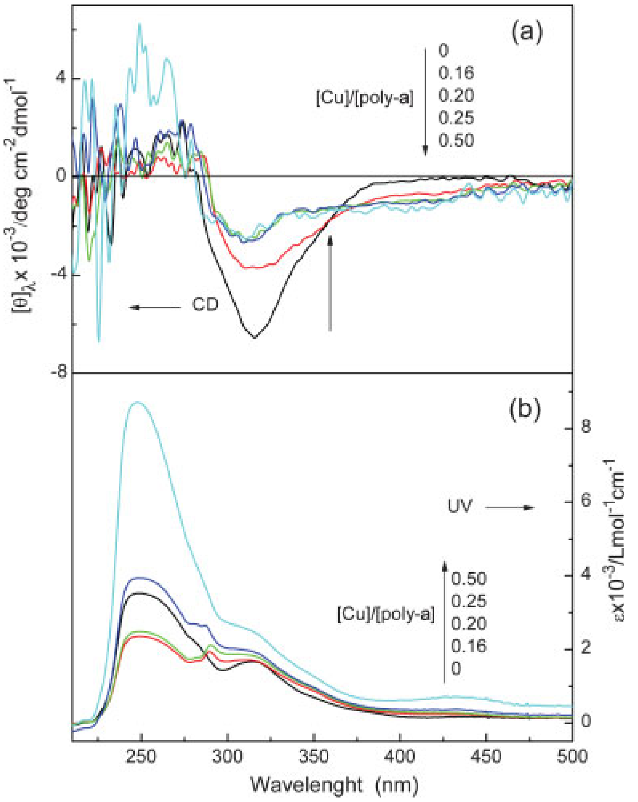
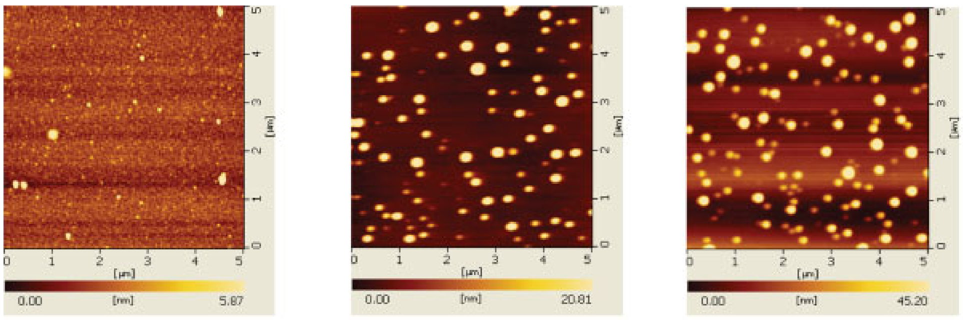


Fig. 4. CD (**a**) and UV–vis (**b**) spectral changes of poly-**a** obtained with Et_2Zn in toluene at 40°C ($[\alpha]_D^{25} = -96.4°$) in the presence of $Cu(NO_3)_2{\cdot}3H_2O$ in THF at ambient temperature with a polymer concentration of 0.4 mg ml^{-1} (1.3 mM monomer units). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gates. For the poly(OPMI)s obtained with AIBN, *n*-BuLi, or Et_2Zn/(−)-Sp initiators, the addition of $Cu(NO_3)_2{\cdot}3H_2O$ did not bring any changes to their optical rotation, CD, and absorption spectra. Furthermore, adding $Zn(OTf)_2$ together with $Cu(NO_3)_2{\cdot}3H_2O$ to the solution of the polymers caused almost no changes in chiroptical properties. Based on the elemental analysis, the mole percent of zinc remaining in these samples ranged from 20 to 35% (Table 1). This means that the number of coordinated Zn(II) ion per 10 repeating units is 3–4 on average. Thus, it may be concluded that the chiral supramolecular aggregates have an asymmetric arrangement via Cu/Zn cooperation complexation. The addition of other copper(II) salts, such as $Cu(OTf)_2$ and $CuCl_2{\cdot}2H_2O$, into the solution of poly(OPMI)s may also cause chiral aggregations with a handedness.

AFM provided direct evidence for the supramolecular aggregation of poly(OPMI)s with Cu(II) salts. As shown in Figure 5A, the AFM image of poly-**b** displays a number of small, anomalous particles with an average diameter and height of 80 ± 20 nm and 10 ± 8 nm, respectively. On addition of $Cu(NO_3)_2{\cdot}3H_2O$ to the solution, the particle size markedly increased (Fig. 5B), and the average diameter and height reached 140 ± 10 nm and 40 ± 20 nm, respectively. The combination of the changes of both the particle size and chiroptical property indicates that upon complexation with Cu(II) ions the polymer probably formed chiral aggregates on a supramolecular scale. However, no distinct variation in the particle size was observed with a prolongation of complexation reaction, which is different from the results described by Yashima and coworkers.[19]

Supramolecular chirality implies asymmetric arrangement of molecular compounds to constitute an assembly taking advantage of weak interactions. On the basis of the earlier observations, a possible supramolecular structure of the poly(OPMI)–metal complexes is shown in Figure 6. We consider that the unusual induced chirality of poly(OPMI)s obtained with Et_2Zn may be derived from the chirality of asymmetrically helicated fractions in the main chain that in-situ generated by the intramolecular coordination of oxazoline residues to Zn(II) ions during the polymerization. A *threo*-disyndiotactic structure of the main chain may facilitate the adjacent oxazoline moieties coordi-



A
average height 10 ±8 nm
average size 80 ± 20 nm

B
average height 40 ± 20 nm
average size 140 ± 10 nm

C
average height 40 ± 20 nm
average size 160 ± 20 nm

Fig. 5. Changes in AFM images of poly-**b** and poly-**b**/$Cu(NO_3)_2{\cdot}3H_2O$ complexes, prepared from a THF solution of poly-**b** and poly-**b** in the presence of $Cu(NO_3)_2{\cdot}3H_2O$; the initial poly-**b** concentration and the molar ratio of $Cu(NO_3)_2{\cdot}3H_2O$ to poly-**b** were 0.2 mg ml^{-1} (0.7 mM monomer units) and 0.5, respectively. The AFM images were taken for poly-**b** (**A**), and for the complexes after 0 (**B**), and 4 h (**C**). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

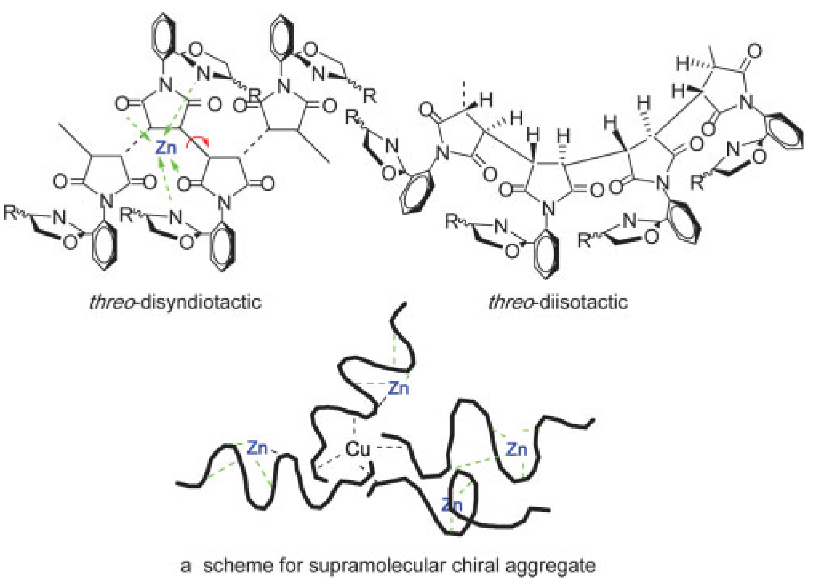


Fig. 6. The *threo*-diisotactic and *threo*-disyndiotactic structures of poly(OPMI)s and schematic drawing of supramolecular aggregates formed by the interchain coordination of Cu(II) to oxazoline pendants of poly(OPMI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nating to Zn(II) in a quasi-tetrahedron fashion as presented in Figure 6, which probably brings the segments to take a predominantly one-handed helical geometry. However, for the *threo*-diisotactic poly(OPMI)s there seems no similar coordination environments to Zn(II) ions leading to a helical conformation. On addition of Cu(II) salts, these polymers with a partial helical segment, as a chiral block, further composed chiral supramolecular aggregates by the interchain coordination of metal ions to oxazoline groups.**

CONCLUSIONS

In summary, a novel type of chiral *N*-phenylmaleimide derivatives bearing an oxazoline pendant (OPMI) was polymerized with Et_2Zn to optically active polymers. These polymers exhibited quite large specific rotation and a unique split-type CD in the UV–vis region. AFM measurements together with CD and UV/Vis spectral analysis demonstrated the formation of the chiral supramolecular aggregate of poly(OPMI)–Cu(II) complexes, which arised from the interchain coordination of oxazoline residues to metal ions. Although its exact structure is not clear at present, the supramolecular chirality of the polymeric complexes could be modulated to some extent by adjusting the Cu(II)/polymer ratio and adjusting the absolute configuration of the pendant oxazolines. We expect that the chiral supramolecular aggregates may be used as polymeric catalysts for asymmetric synthesis. This work is now in progress.

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The dependence of specific optical rotation ($[\alpha]_D^{25}$) on the concentration has been examined for the Cu(II)/poly-a** complexing system with a 1/5 mole ratio (i.e., 1:5 complexation) by means of the continuous-variation in concentrations (see: Support Information). We found that this complexing system showed the largest $[\alpha]_D^{25}$ value (−180°) at [poly-**a**] of around 1.5 mg ml^{-1}. Higher or lower concentrations resulted in an evident drop (near −140°) in specific rotations although the magnitude of $[\alpha]_D^{25}$ were larger than that of poly-**a** over the concentration range studied (0.5–3.0 mg ml^{-1}), suggesting that there was an optimal concentration range for the formation of chiral supramolecular aggregates. Because the observed concentration effect is rather distinct, we hypothesize that the chiral aggregates mainly originated from the intermolecular coordination of Cu(II) ions.

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