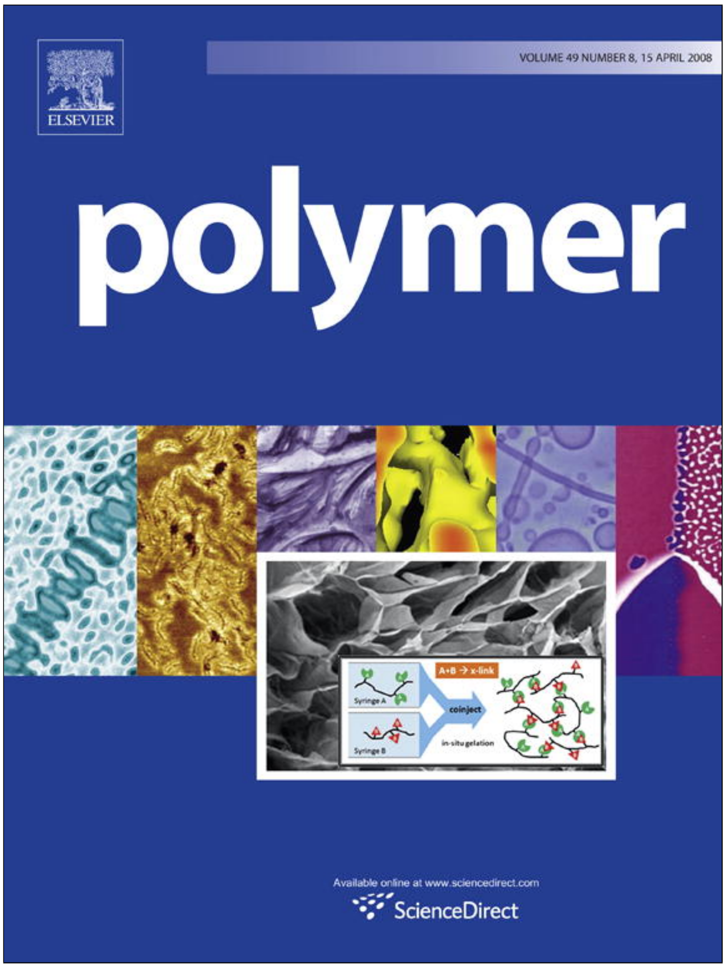

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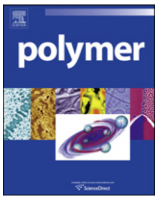

Poly(*N*-phenylmaleimides) bearing chiral oxazolinyl pendant: Supramolecular aggregation and enantioselectivity in fluorescence response

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ABSTRACT

N-Phenylmaleimide derivatives bearing a chiral oxazoline substituent at the benzene ring (*N*-[*o*-(4,5-dihydro-1,3-oxazol-2-yl)phenyl]maleimides, OPMIs) were polymerized using a binary initiating system composed of Et_2Zn and *n*-BuLi to in situ produce the zinc complexes of optically active poly(OPMI)s. The significant changes in chiroptical and fluorescent properties were observed for these polymers upon complexation with metal ions due to the formation of supramolecular structure, evidenced by circular dichroism, fluorescence spectrum and atomic force microscopy. The fluorescence spectra of poly(OPMI)/Zn^{II} complexes in the presence of (*R*)/(*S*)-1,1′-bi-2-naphthol (BINOL) and (*R*)/(*S*)-2-amino-1-propanol were studied in THF media. It was found that the fluorescence intensity of the complexes responded differently to both enantiomers of BINOL and the amino alcohol in a quenching and enhancement fashion, respectively. Furthermore, the enantioselective fluorescence response was strongly dependent on the amount of incorporated zinc in polymer matrices.

1. Introduction

Chemical sensing by use of supramolecular chemistry in combination with optical and photophysical properties has attracted considerable research attention [1]. Enantioselectivity is one of the most important goals for sensing of organic substances, since biological activity is strictly correlated with stereochemistry in most of the cases [2]. In recent years, some enantioselective sensors based on enzymes [3], on piezoelectric effects [4], or on colorimetric methods [5] have been proposed. Especially, the fluorescence-based enantioselective sensors are of great interest due to their high sensitivity and potential real-time detection for chiral compounds [6,10a]. Pu et al. synthesized a series of 1,1′-binaphthyl-based derivatives including the dendrimers containing a (*S*)-BINOL core [6a,7]. They found that the fluorescence of the chiral dendrimers is much stronger than that of BINOL; meanwhile, the fluorescence was quenched enantioselectively by the chiral amino alcohols such as 2-amino-3-methyl-1-butanol, 2-amino-4-pentanol, and 2-amino-3-phenyl-1-propanol. Owing to the unique host–guest chemistry characteristics, cyclodextrin-derived molecules were extensively studied aiming at the development of enantioselective sensors [8,9]. Corradini et al. found that modification with groups containing metal binding moieties allows the use of metal complexes of cyclodextrins as binding sites for organic molecules with donor groups. For example, enantiomeric recognition of unmodified amino acids was performed with the copper complex of a histamine-modified β-cyclodextrin and related molecules [9]. In addition, it was reported that the calixarene derivatives containing chiral fluorophores have potential applications as a fluorescent chemisensor for some chiral analytes [10,11]. Comparatively, very few examples of the optically active polymer-based fluorescent sensors with an efficient enantioselectivity are available in the literatures besides polymeric binaphthyls [12].

We lately described the synthesis and chiroptical property of maleimide-based polymers in which the side-chain chiral oxazolinyl chromophore was connected to the backbone through a benzene ring [poly(OPMI)s, see Scheme 1] [13]. These optically active polymers designed should have potential uses as chiral macromolecular ligands for asymmetric catalysis, since some metal complexes with chiral bis-oxazolines have proved to be highly enantioselective catalysts [14]. It has demonstrated that the polymerization of OPMIs initiated with Et_2Zn in situ yields polymeric complexes. Furthermore, the Zn-bound polymers occurred a supramolecular aggregation upon addition of copper salts in THF solution [13d]. Interestingly, fluorescence phenomenon was incidentally found for the poly(OPMI)s in the course of above studies, and the fluorescence property displayed a close relationship with the amount of incorporated Zn(II) ions. These findings along with our

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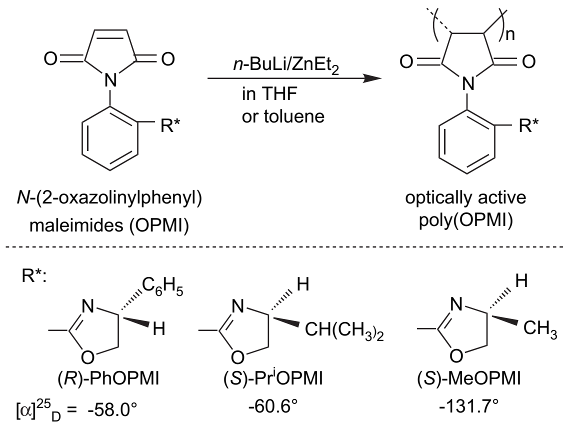

Scheme 1. Structure of chiral monomers for polymerization.

preliminary investigations on the chiral resolution by high performance liquid chromatography encouraged us to test the possibility of the poly(OPMI)/Zn^{II} complexes for chiral discrimination of optically active substrates.

This article reports the synthesis and supramolecular aggregation of optically active poly(OPMI)s as well as the investigation of their chiroptical behaviors. The fluorescent spectral properties were studied for these polymers in the metal-bound state. Also, the enantioselective recognition was briefly examined as a function of the analytes including 1,1′-bi-2-naphthol and 2-amino-1-propanol and of the polymer structure.

2. Experimental

2.1. Materials

Commercially available Et$_2$Zn and *n*-BuLi in an *n*-hexane solution (Acros) were used without further purification. Enantiopure 2-amino-1-propanol (purity = 98%) and 1,1′-bi-2-naphthol (BINOL, purity ≥ 99.0%) were purchased from Aldrich. Analytical grade solvents (tetrahydrofuran and toluene) were dried over benzophenone/Na complex and distilled in an atmosphere of dry nitrogen. Copper(II) trifluoromethanesulfonate (Cu(OTf)$_2$) was prepared according to the reported methods [15]. The chiral monomers (OPMIs) shown in Scheme 1 were synthesized by the previous work [13].

2.2. Polymerization

The polymerization was performed by Schlenk technique under dry N$_2$ atmosphere. A stock solution of initiator was prepared by mixing *n*-BuLi with Et$_2$Zn and then aging for a certain time at room temperature. After passage of the desired time, the polymerization mixture was poured into a large amount of *n*-hexane to precipitate the product. The obtained polymer was purified by reprecipitation from the THF solution to excess *n*-hexane. The polymer samples were dried in vacuum at 40 °C for two days before measurements.

2.3. Preparation of aggregates

Typical experimental process: a stock solution of polymer (for poly(PhOPMI) 1.2 mg/ml, 3.8 mM monomer units) in THF was prepared in ambient atmosphere. To this solution was added an appropriate amount of Cu(OTf)$_2$ with stirring resulting in the polymeric complexes. The polymer/Cu(II) solution suffered directly the measurement of specific optical rotation and then was diluted to 0.4 mg/ml for CD and UV–vis spectral detection. For AFM measurements, the complex solutions with various Cu(II) contents were cast on freshly cleaved mica substrates. After evaporating the solvent in a stream of nitrogen, the AFM images were recorded.

2.4. Measurements

NMR spectra were recorded on a Bruker Avance AMX-400 NMR spectrometer relative to tetramethylsilane as internal standard in CDCl$_3$. Circular dichroism (CD) and simultaneous ultraviolet–visible (UV–vis) spectra were recorded using a JASCO J-810 spectropolarimeter in 1.0 cm quartz cell. D-line specific optical rotations ($[\alpha]_D^{25}$) were measured in THF at 25 °C using a Wzz-2s automatic digital polarimeter (Shanghai Pudong Optics Apparatus Co.). Gel permeation chromatography (GPC) measurements of the polymers were conducted on a Waters 2414 GPC apparatus equipped with a differential refractometer at ambient temperature (with THF eluent, flow rate 1.0 ml/min). A set of Styragel® columns (HT-1, HT-3, and HT-4) were connected in series, and the molecular weight was calibrated with polystyrene standards. 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 contents of remained zinc in polymer samples were estimated by an IRIS Intrepid II XSP type full spectrum plasma emission spectrometer (America Thermoelectricity Co.). The photoluminescence spectra (PL) were recorded on a Perkin–Elmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics).

3. Results and discussion

3.1. Polymerization characteristics

In our previous investigations, the polymerization of OPMIs was carried out using *n*-BuLi and Et$_2$Zn as an initiator [13c,d]. The poly(OPMI)s obtained in *n*-BuLi system showed relatively low specific optical rotations, while the Et$_2$Zn-initiated polymerization gave polymeric complexes displaying very large optical rotations and intense Cotton effects in the CD spectra that is attributable to the π–π^* transition. However, Et$_2$Zn seemed to be a less efficient initiator for the polymerization in respect that the process gave polymers of low molecular weight in poor yields. In the present work, a binary anionic initiator composed of Et$_2$Zn and *n*-BuLi was employed to induce the polymerization, which is based on the assumption that the initiating system could combine advantages of both metal alkyls and then provide a variety of samples for gaining some insight into the structure–property relationship.

The polymerization of three oxazolinyl-substituted *N*-phenylmaleimide derivatives (i.e., (*R*)-PhOPMI, (*S*)-Pr^{i}OPMI, and (*S*)-MeOPMI) was performed using the binary initiator with different Li to Zn ratios in THF, as summarized in Table 1. As we expected, the polymerization with a satisfied yield has been achieved and resulted polymers possess higher molecular weights compared to those prepared using Et$_2$Zn as a single initiator. Noteworthy is a better control of the optically active polymers was achieved with this initiating system. That is, as the Li/Zn molar ratio of the initiator increases, the specific rotation of polymers decreases sharply and then rises in a reverse direction in all cases. Actually, this change in optical activity is nearly correlated with the amount of Zn(II) incorporated in polymer matrices. For example, $[\alpha]_D^{25}$ values of poly(PhOPMI)s containing 12.7 and 9.9 mol% of Zn showed −30.0° and +11.5°, respectively, although they have almost same molecular weights (runs 2 and 5 in Table 1). However, similar trends are not observed when the polymerization was carried out in toluene instead of THF (see: Supporting information).

Table 1
Anionic polymerization of OPMI with Et_2Zn/*n*-BuLi binary initiator in THF[a]

Run	Monomer	Zn/Li[b]	Yield[d] (%)	Zn cont.[e] (mol%)	M_n[f] (10^3)	M_w/M_n[f]	$[\alpha]_D^{25}$[g] (°)
1	(*R*)-PhOPMI	10/0	21.3	30.6	0.9	1.7	−171.4
2	(*R*)-PhOPMI	10/1	61.9	12.1	4.3	1.6	−30.0
3	(*R*)-PhOPMI	10/1.25	82.9	10.7	4.6	1.6	−22.1
4	(*R*)-PhOPMI	10/1.25[c]	85.2	9.9	4.9	1.6	−21.4
5	(*R*)-PhOPMI	10/2	88.4	9.9	4.9	1.5	+11.5
6	(*R*)-PhOPMI	10/4	100.0	9.0	3.8	1.5	+21.2
7	(*S*)-Pr^iOPMI	10/0	13.2	31.2	1.6	1.9	+57.8
8	(*S*)-Pr^iOPMI	10/1	47.2	15.0	2.2	1.6	−33.0
9	(*S*)-Pr^iOPMI	10/1.25	81.7	9.2	3.6	2.1	−65.4
10	(*S*)-Pr^iOPMI	10/2	89.7	8.0	3.2	2.1	−97.1
11	(*S*)-MeOPMI	10/0	26.2	24.7	0.9	1.7	+58.0
12	(*S*)-MeOPMI	10/1	26.9	24.0	1.4	1.5	+24.3
13	(*S*)-MeOPMI	10/1.25	58.8	11.4	1.5	1.5	−12.2
14	(*S*)-MeOPMI	10/2	90.9	10.2	1.8	1.6	−29.9

[a] Conditions: $[M]_0 = 0.5$ mol/L, 35 °C, 72 h.
[b] Initial molar ratio of monomer to Et_2Zn was 10/1. Initiator was obtained by mixing the metal-alkyl compounds and then aging for 10 min at room temperature.
[c] Aging time was 30 min in this case.
[d] Insoluble part in *n*-hexane/THF (2/1, v/v).
[e] Mole percent of Zn remaining in the polymer samples relative to monomer units by the emission spectral analysis, error: 0.5%.
[f] Estimated by GPC (vs polystyrene standard).
[g] $c = 0.5$ g/dL, THF, $l = 10$ cm.

Poly(OPMI)s obtained with the binary initiator exhibit an unimodal curve of GPC (Fig. 1a, b) and a narrower molecular weight distribution (PDI = 1.5–2.1), by which only one active species for initiating polymerization was deduced. The active species is most likely a bi-metal alkylide derived from the alkyl-exchange reaction between Et_2Zn and *n*-BuLi [16]. For comparison, the polymerization was initiated by adding both the metal alkyls successively with an interval of around 30 s. The polymer thus prepared shows a GPC curve with a shoulder, as shown in Fig. 1c.

3.2. Chiroptical and fluorescent spectral property

Comparison of ^{13}C NMR spectra of both poly(OPMI)s in the present studies and those previously obtained with *n*-BuLi indicates that there was no evident difference in the signals assigned to the main chain. The intensity of the peak at 41 ppm was larger than that at 43 ppm, which means that the polymers are rich in *threo-diisotactic* structure according to Oishi et al. [17]. As an illustrative example, Fig. 2 depicts the ^{13}C NMR for poly(PhOPMI) prepared with the bi-metal initiator (see run 3 in Table 1). However, these Zn-bound polymers exhibit unique chiroptical behaviors and fluorescent property different from the homologs obtained in *n*-BuLi-initiating polymerization, especially, these properties are sensitive to the contents of metal as well.

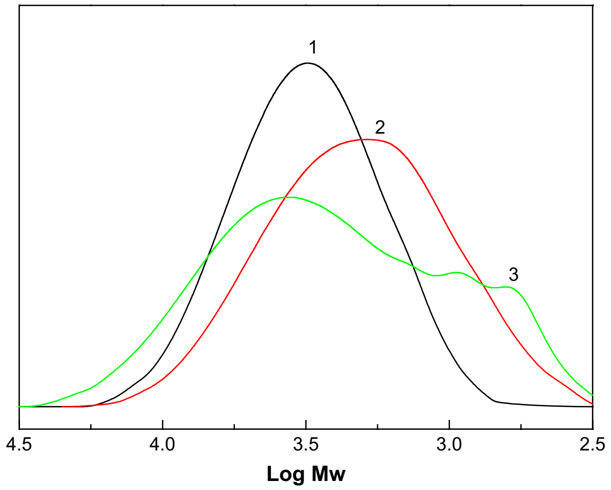

Fig. 1. GPC curves for poly(PhOPMI) obtained with Et_2Zn/*n*-BuLi binary system (Zn/Li = 10/1) in THF (run 2, Table 1) (1ine 1), in toluene (run 1, Table S1) (line 2), and for the sample (line 3) from a comparison experiment in which (*R*)-PhOPMI was polymerized via adding Et_2Zn and *n*-BuLi successively with an interval of around 30 s.

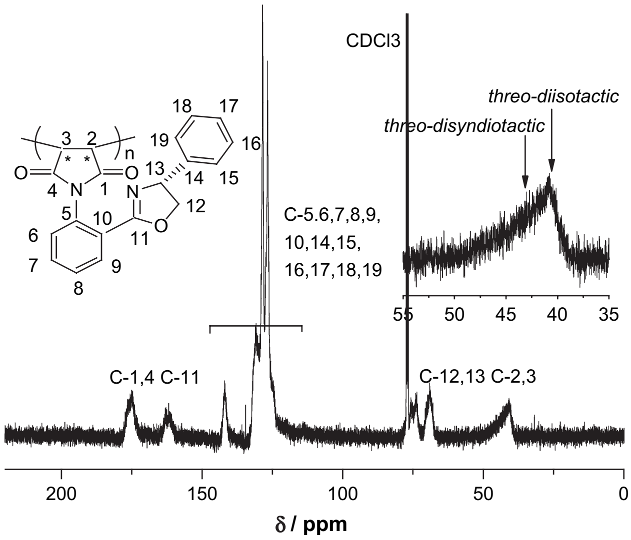

Fig. 2. ^{13}C NMR spectrum of poly(PhOPMI) (run 3 in Table 1, $[\alpha]_D^{25} = -22.1°$) in $CDCl_3$.

Fig. 3 presents the CD spectra of poly(PhOPMI)s with different contents of zinc, all of which display bisignate curves with large amplitudes, in contrast to what was observed for the sample prepared by *n*-BuLi-initiating process. In addition, the negative Cotton effect around 315 nm is remarkably dependent on the contents of zinc. In other words, the larger content in bound-metal for polymers gives the stronger CD signal accompanied by a slight red shift of λ_{max}.

From these observations, it clears that the complexing of oxazoline residues with metal ions had a significant influence on the chiroptical property, whereas the role of the main chain was minor. The change in both CD spectra and the optical rotation indicates that the polymer may possess different chiral structure at a supramolecular level due to the intra- and/or inter-chain complexation. It should be pointed out that such a polymeric aggregate was only in situ formed in the Et_2Zn or Et_2Zn/BuLi-initiating polymerization; whereas the post-synthetic treatment of pure poly(OPMI)s obtained by *n*-BuLi-initiating process with zinc salts does not bring

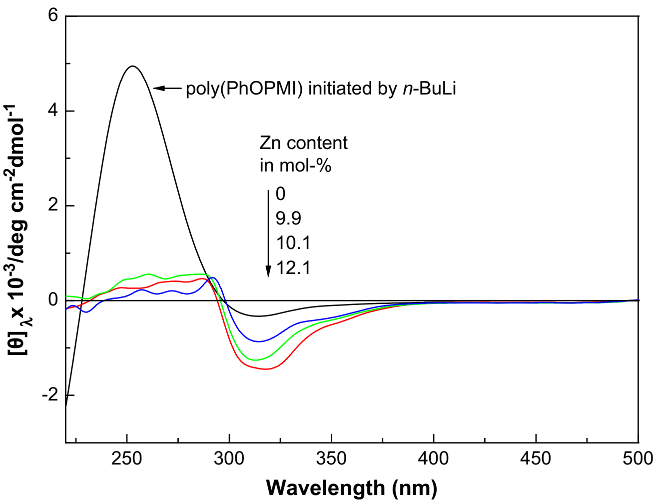

Fig. 3. CD spectral changes of poly(PhOPMI) (runs 2, 3, and 5 in Table 1).

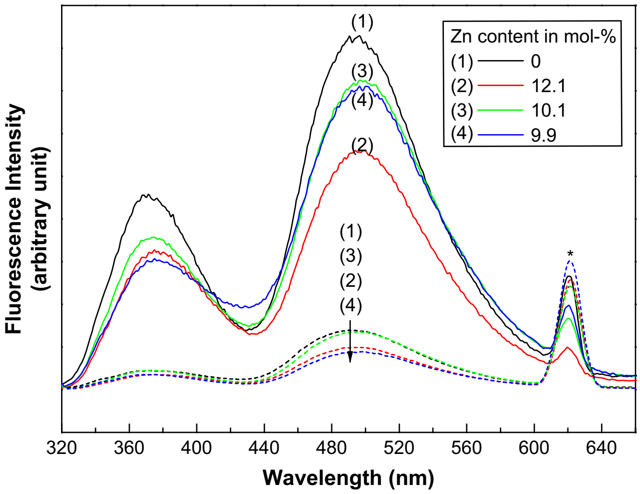

Fig. 4. The room temperature PL spectra of poly(PhOPMI)/Zn^{II} complexes (solid line) and corresponding changes in the presence of Cu(OTf)$_3$ (dashed line) obtained in THF solution. [Cu^{II}]/[monomer units of poly(PhOPMI)] = 0.1, excitation wavelength = 310 nm, normalized to the same relative intensity.

any changes to their chiroptical property. However, we do not elucidate the structure exactly at present, although a schematic formula was suggested previously [13d].

Interestingly, the corresponding variation in fluorescence was also observed for these polymeric complexes. Fig. 4 shows the room temperature PL spectra of the polymer samples identical with those for CD detection obtained in THF solution (normalized to the same relative intensity) under the excitation wavelength of 310 nm. These polymers gave two emission maximums around 370 and 500 nm. Apparently, the fluorescence intensity of poly(PhOPMI)/Zn^{II} complexes was weaker relative to the parent polymer, and the decreasing amplitude was roughly proportional to the amounts of complexed Zn ions. Especially, when adding Cu(OTf)$_2$ into the polymeric complex ([Cu^{II}]/[monomer units of poly(PhOPMI)] = 0.1), the fluorescence intensity was dramatically decreased and their emission shifted to a shorter wavelength in all cases (Fig. 4). In fact, for most of the Cu(II) fluorescent sensors reported, the bonding of the metal ion generally causes a quenching of the fluorescence emission [18], due to its paramagnetic nature [19].

On the other hand, on addition of Cu(OTf)$_2$ to the solution of poly(OPMI)s, dramatic changes in the UV–vis and CD patterns as well as in specific optical rotations were observed, as we previously reported [13d]. Similar phenomena have been also reported by Yashima et al. for the poly(phenylacetylenes) with oxazolinyl groups [20]. As a representative, Fig. 5 shows CD spectral changes of poly(MeOPMI) in the presence of increasing amounts of Cu(OTf)$_2$ ([Cu(II)]/[monomer units of polymer] = 0–0.25) in THF. The more experimental data including AFM measurements are provided as Supporting information.

3.3. Enantioselective recognition

To examine the chiral recognition ability of the poly(OPMI)s and their zinc complexes, we firstly monitored the changes in the fluorescence spectra in the presence of (*R*)- or (*S*)-1,1′-bi-2-naphthol (BINOL) under the same conditions. Choosing BINOL as a probe molecule is based on our recent NMR study, in which the hydroxyl peak of BINOL was split into two peaks due to the (*R*)- and (*S*)-enantiomer through the interaction between polyacrylamide-type analogs and the racemate [21].

As shown in Fig. 6A, addition of (*R*)- and (*S*)-enantiomer of BINOL, respectively, induced different decreases of fluorescence intensity of polymeric complexes at the emission wavelength of 498 nm, and the enantioselective quenching was sensitive to the Zn content of polymeric sensors. For example, the polymeric complex containing 9.9 mol% of Zn (5×10^{-4} M in THF) showed the highest enantioselectivity, and the emission at 498 nm was suppressed to 74.9% of the original value by (*S*)-enantiomer (5×10^{-5} M), while to 87.2% by (*R*)-enantiomer (5×10^{-5} M). The net fluorescence intensity decrease of the poly(OPMI)/Zn^{II} complex by (*S*)-BINOL was 1.97 times of (*R*)-BINOL, i.e., ef = 1.97 [ef: enantiomeric fluorescence difference ratio = $(I_S - I_0)/(I_R - I_0)$], indicating a moderate chiral discrimination. For pure poly(PhOPMI) or the polymeric complexes with a Zn content more than 9.9 mol%, poor enantioselective response was detected in fluorescence quenching (see: Table 2).

When 2-amino-1-propanol was used as an analyte instead, the fluorescence enhancement was observed with small blue shifts for the complexes under conditions similar to the use of BINOL. Because the amino alcohol does not have a fluorescence chromophore, an emission wavelength at 376 nm was used to measure the change in fluorescence intensity. Thus, changes in this wavelength can be attributed to the interaction of the guest chiral 2-amino-1-propanol with the optically active polymeric complexes due to host–guest complexation. It was found that a higher content of zinc seems to favor the enantioselective fluorescence

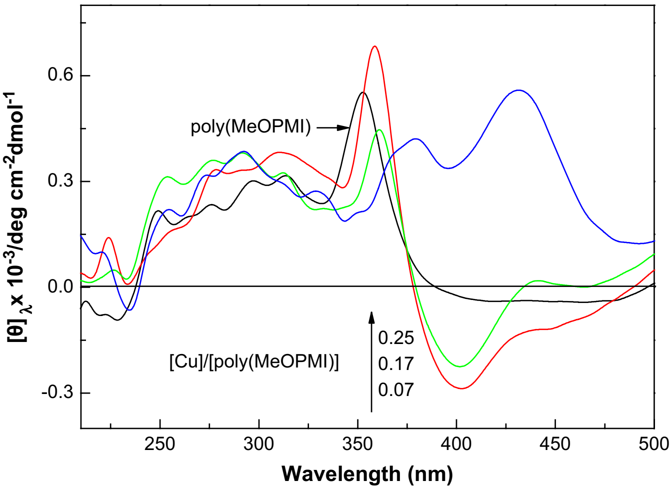

Fig. 5. CD spectral changes of poly(MeOPMI) (run 12 in Table 1, $[\alpha]_D^{25} = +24.3°$) in the presence of Cu(OTf)$_2$ in THF at ambient temperature with a polymer concentration of 1.0 mg mL^{-1}.

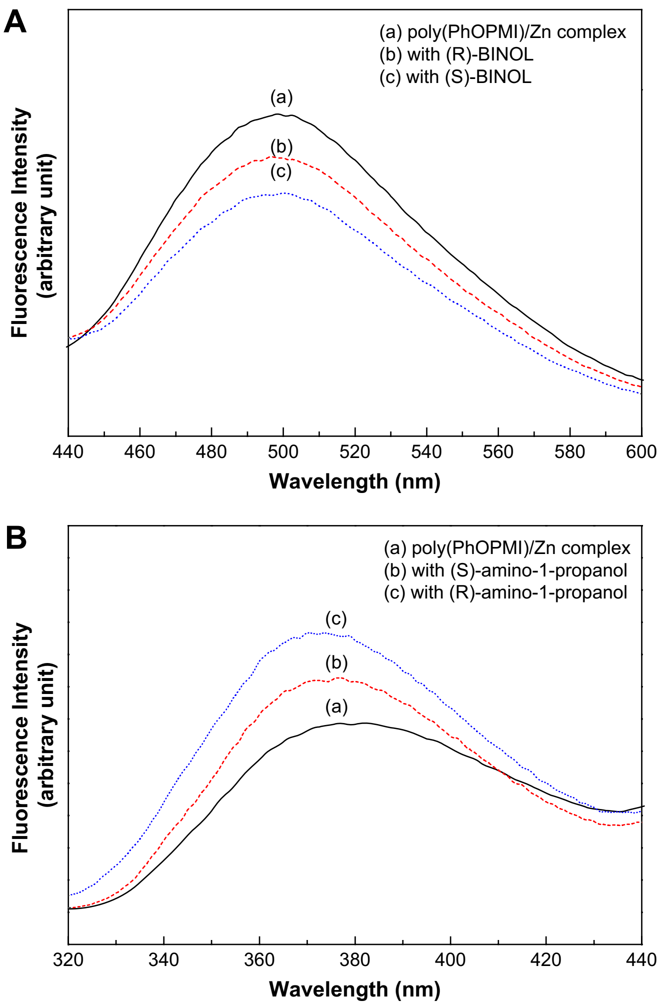

Fig. 6. Fluorescence emission spectra. (A) poly(PhOPMI)/Zn^{II} complex (run 5 in Table 1) without and with BINOL. (B) poly(PhOPMI)/Zn^{II} complex (run 2 in Table 1) without and with 2-amino-1-propanol. In both cases, the concentrations of polymer and analyte were 0.15 mg mL^{-1} (i.e., 5×10^{-4} M monomer units) and 5×10^{-5} M, respectively. $\lambda_{ex} = 310$ nm, in THF.

enhancement of the sensor. Among these samples, (*R*)-enantiomer of the amino alcohol enhanced the fluorescence of the complex containing 12.1 mol% of Zn more efficiently than the (*S*)-enantiomer, the enantiomeric fluorescence difference ratio (ef) reached 2.0. This magnitude of enantioselectivity is comparable to the reported values in related cases, where a helical diol and chiral molecular square with metallo-corners were used as a fluorescence sensor for chiral amino alcohols [22]. For other polymeric complexes, however, the enantioselectivity in the fluorescence enhancement was quite low for other complexes with ef in the range of 1.09–1.31 (Table 2 and Fig. 6B).

Table 2
Results on the enantioselective fluorescent responses of poly(PhOPMI)/Zn^{II} complexes towards BINOL and 2-amino-1-propanol in THF

Poly(PhOPMI)/Zn^{II} complex of various Zn content in mol%	Enantiomeric fluorescence difference ratio (ef)	
	BINOL[a]	2-Amino-1-propanol[b]
0	1.53	1.31
9.9	1.97	1.09
10.7	1.31	1.21
12.1	1.22	2.0

[a] $ef = (I_S - I_0)/(I_R - I_0)$, an emission wavelength (λ_{em}) at 498 nm was used to measure the change in fluorescence intensity.

[b] $ef = (I_R - I_0)/(I_S - I_0)$, $\lambda_{em} = 376$ nm. In both cases, the concentrations of polymer and analyte were 0.15 mg mL^{-1} (i.e., 5×10^{-4} M monomer units) and 5×10^{-5} M, respectively.

Poly(OPMI)s possess an imide group and an oxazoline moiety as binding sites, which are significant for the host–guest interaction. The enantio discrimination could stem from the chiral oxazoline unit and the chiral supramolecular architecture of Zn-bound complexes. The larger degree of enantioselective recognition of BINOL found with the poly(PhOPMI)/Zn^{II} complexes may be related to the π–π stacking between the oxazoline pendants and naphthalene moiety of the target molecule. In a set of comparable experiments, we found that the zinc complexes of both poly(Pr^{i}OPMI) and poly(MeOPMI) show essentially no enantioselectivity in fluorescence response towards BINOL (see: Supporting information), which seemed to support the above-mentioned supposition. Note also that no enantioselectivity in fluorescence response was observed for both OPMI monomer and its polymers of M_n less than 10^3 although there are pronounced changes in chiroptical property upon complexing with metal ions. However, further investigation is necessary to understand the chiral recognition mechanism for the present system, and related work is in progress.

4. Conclusion

In summary, we have shown that *N*-phenylmaleimide-based optically active polymers combine the chiral recognition features with the favorable spectroscopic properties of oxazolinyl chromophore. The polymers can form the metal complexes with supramolecular structure companied by significant changes in chiroptical and fluorescence properties. The Zn-bound polymers exhibited moderately high enantioselectivity in their fluorescent responses towards both the axially chiral 1,1′-bi-2-naphthol and 2-amino-1-propanol with a chiral center. In the case of BINOL as analyte, the enantio discrimination is probably due to an important contribution from the π–π stacking interaction between the substrate and the polymeric complexes. When interacting with the amino alcohol, the polymeric complex containing zinc of 12.1 mol% was found to be a more efficient fluorescent sensor than the analogs with lower metal contents. The advantage in structural adjustment might make the optically active poly(OPMI)s a good platform to understand the fundamentals of chiral recognition and even a potential fluorescent chemosensor for enantiomeric recognition, a field gaining more and more interest for practical applications.

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Appendix. Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2008.03.013.

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