Optically Active Polyacrylamides Bearing an Oxazoline Pendant: Influence of Stereoregularity on Both Chiroptical Properties and Chiral Recognition

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ABSTRACT: Enantiopure acrylamide derivatives, *N*-[*o*-(4-methyl-4,5-dihydro-1,3-oxazol-2-yl) phenyl]acrylamide (MeOPAM), *N*-[*o*-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]acrylamide (Pr^{i}OPAM), and *N*-[*o*-(4-phenyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]acrylamide (PhOPAM), were synthesized and radically polymerized in the presence of rare earth metal trifluoromethanesulfonates (Ln(OTf)$_3$, Ln = La, Nd, Sm, and Y) to yield corresponding optically active polymers. Among these Lewis acids, Y(OTf)$_3$ was found to be most effective for increasing the isotactic specificity during the radical polymerizations when using *n*-butanol as solvent. Also, the effect of the Lewis acids was significantly influenced by the ratio of Ln(OTf)$_3$ to monomer. The relationship of both chiroptical property and the chiral recognition with the stereoregularity was then examined for the resulting polymers having various tacticity by spectroscopic techniques such as NMR, fluorescence, and circular dichroism. The results indicated that the polymers rich in isotacticity exhibited a favorable enantioselective discrimination ability toward 1,1′-bi-2-naphthol as evidenced by ^{1}H NMR study, where the characteristic hydroxyl proton signal was split into two peaks that ascribed respectively to the levo- and dextro-isomer; furthermore, the splitting magnitude was linearly correlated with the diad isotacticity of the polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5411–5418, 2010

KEYWORDS: chiral; enantioselective recognition; radical polymerization; rare-earth trifluoromethanesulfonates; stereospecific polymers

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INTRODUCTION Stereochemistry is one of the main factors that determine the physical and mechanical properties of a polymeric material as well as its functions.[1,2] Polymers that have stereocenters in the repeat unit can exhibit two structures of maximum order, isotactic and syndiotactic. The stereoregular polymers are typically crystalline and have found use in many applications. Metal-based catalysts or initiators have proven to be one of the most promising methodologies for the synthesis of stereoregular polymers,[3] in which the stereospecific polymerization is usually attained via an ionic or coordination mechanism. In contrast to these controlled ionic and coordinative polymerizations, the stereocontrol in radical polymerization is very difficult because of the lack of efficient methods for providing an asymmetric coordination environment around the propagating radical species.[4] Nevertheless, this decade also witnessed great progress in terms of stereocontrol during radical polymerization. For example, Okamoto et al. first reported a general method applicable to some polar monomers, such as (meth)acrylamides, α-(alkoxymethyl)acrylates, and methacrylates where the added lanthanide trifluoromethanesulfonates (Ln(OTf)$_3$) catalytically affect the polymerization stereochemistry to isotactic-selective manner because of their strong coordination ability to the polar group.[5–8] More recently, the Lewis acids were used in conjunction with controlled/living radical polymerization techniques for the simultaneous control of the molecular weight and the tacticity of polyacrylamide derivatives.[9,10] The efficient dual control was ascribed to the effective interaction of the Lewis acid with the amide moieties around the polymer terminal and/or the incoming monomer.

For several years, we have been interested in the synthesis of polymeric derivatives bearing side-chain optically active oxazoline moieties, because the presence of these chromophores is expected to establish the dissymmetric chain conformations with a prevailing handedness and the formation of polymeric complexes. We found that maleimide- and methacrylamide-based optically active polymers bearing the oxazoline pendant show a moderate enantioselectivity toward some substrates.[11] As a part of our continuing research to understand the fundamentals of chiral recognition, we herein report an efficient Ln(OTf)$_3$-mediated radical polymerization procedure for synthesizing optically active polyacrylamide derivatives with various tacticity (Scheme 1). In addition to the polymerization features and the investigation of chiroptical and fluorescent properties of the optically active polymers, the morphology on solid substrates and the enantioselective interaction with 1,1′-bi-2-naphthol (BINOL) were examined with atomic force microscopy (AFM) and ^{1}H

Additional Supporting Information may be found in the online version of this article. Correspondence to: L. Jiang (E-mail: cejlm@zju.edu.cn)

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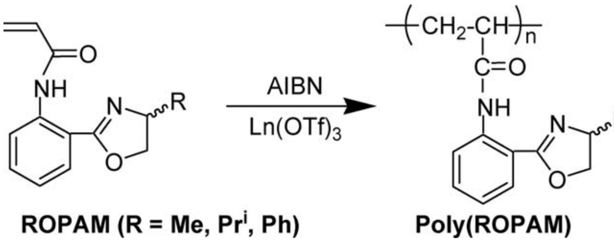

SCHEME 1 Synthesis of poly(ROPAM)s.

NMR spectroscopy, respectively. To the best our knowledge, although many poly[(meth)acrylamide]s bearing optically active side chains have been synthesized by a radical process and used as chiral stationary phases for high-performance liquid chromatography,[12] there were relatively few reports on the relationship of the stereoregularity with both chiroptical properties and chiral discrimination with respect to these optically active polymers.[5(a),8]

EXPERIMENTAL

Materials

α,α'-Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Co., China) was purified by recrystallization from methanol. Solvents for the polymerizations were treated over a benzophenone- sodium complex for three days and distilled before use. 1,1′-Bi-2-naphthol (BINOL, Aldrich) and other chemicals were used as received. Rare earth metal trifluoromethanesulfonates (Ln(OTf)$_3$, Ln = La, Nd, Sm, and Y) were prepared according to a reported method and used after drying *in vacuo*.[13]

Monomer Synthesis

The chiral monomers (ROPAM, R = Me, Pr^i, and Ph) were synthesized by the reaction of enantiopure *ortho*-oxazolinyl-substituted anilines and acryloyl chloride in the presence of triethylamine in tetrahydrofuran (THF) according to our previously described method.[14]

(S)-MeOPAM

Yield: 66%, colorless crystal; mp: 56.5–57.5 °C, $[\alpha]_D^{25} = +6.2°$ (c = 1.00 g/dL, l = 10 cm, THF). FT-IR (KBr, pellet, cm^{-1}): 3420 (—NH—); 1682, 1544 (—CONH—); 1619, 1064, 960 (oxazoline ring); 1604, 1449 (phenyl). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 12.56 (s, 1H, NH), 8.83 (d, 1H, —C$_6$H$_5$), 7.85 (d, 1H, —C$_6$H$_5$), 7.45–7.49 (t, 1H, —C$_6$H$_5$), 7.07–7.10 (t, 1H, —C$_6$H$_5$), 6.45 (d, 1H, =CH$_2$), 6.30 (m, 1H, =CHCO), 5.75 (d, 1H, —CH$_2$), 4.48 (m, 2H, OCH$_2$), 3.91 (m, 1H, =NCH), 1.37 (d, 3H, —CH$_3$). Anal. calcd. for $C_{13}H_{14}N_2O_2$: C, 68.11; H, 5.72; N, 12.22. Found: C, 68.44; H, 5.99; N, 12.01. The (R)-isomer was also synthesized by the same procedure for comparison.

(S)-Pr^{i}OPAM

Yield: 65%, colorless crystal; mp 28.0–28.5 °C, $[\alpha]_D^{25} = +28.4°$ (c = 1.00 g/dL, l = 10 cm, THF). FT-IR (KBr, pellet, cm^{-1}): 3412 cm^{-1} (—NH—); 1688, 1540 (—CONH—); 1635, 1065, 973 (oxazoline ring); 1587, 1449 (phenyl). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 12.58 (s, 1H, NH), 8.86 (d, 1H, —C$_6$H$_5$), 7.86–7.89 (d, 1H, —C$_6$H$_5$), 7.48–7.53 (t, 1H, —C$_6$H$_5$), 7.10–7.13 (t, 1H, —C$_6$H$_5$), 6.44–6.49 (d, 1H, =CH$_2$), 6.29–6.35 (m, 1H, =CHCO), 5.77–5.80 (d, 1H, —CH$_2$), 4.41–4.46 (t, 1H, OCH$_2$), 3.17–4.20 (m, 1H, =NCH), 4.07–4.11 (t, 1H, OCH$_2$), 1.83 (m, 1H, —CH(CH$_3$)$_2$), 1.00–1.09 (d, 6H, —CH(CH$_3$)$_2$). Anal. calcd. for $C_{15}H_{18}N_2O_2$: C, 69.40; H, 7.48; N, 10.79. Found: C, 69.47; H, 7.69; N, 10.61.

(R)-PhOPAM

Yield: 85%, colorless crystal; mp 127.5–128.0 °C, $[\alpha]_D^{25} = +223.0°$ (c = 1.00 g/dL, l = 10 cm, THF). FT-IR (KBr, pellet, cm^{-1}): 3408 (—NH—); 1687, 1539 (—CONH—); 1635, 1065, 957 (oxazoline ring); 1589, 1493 (phenyl). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 12.56 (s, 1H, NH), 8.87 (d, 1H, —C$_6$H$_5$), 7.94 (d, 1H, —C$_6$H$_5$), 7.50–7.54 (t, 1H, —C$_6$H$_5$), 7.25–7.41 (m, 5H, —C$_6$H$_5$), 7.11–7.15 (t, 1H, —C$_6$H$_5$), 6.31–6.35 (d, 1H, =CH), 6.17–6.23 (m, 1H, =CHCO), 5.63–5.66 (d, 2H, =CH$_2$), 5.50–5.55 (t, 1H, OCH$_2$), 4.75–4.80 (t, 1H, =NCH), 4.18–4.22 (t, 1H, OCH$_2$). Anal. calcd. for $C_{18}H_{16}N_2O_2$: C, 74.21; H, 5.21; N, 9.62. Found: C, 74.31; H, 5.47; N, 9.64.

Polymerization and Fractionation Experiment

The radical polymerization was carried out under dry nitrogen using Schlenk techniques with AIBN at 60 °C. After 24 h, the reaction mixture was poured into a large amount of mixed CH$_3$OH/H$_2$O (3:1, v/v) to precipitate the product. The collected polymer was purified by reprecipitation from a THF-CH$_3$OH system in three cycles and dried under reduced pressure at 40 °C for 2 days. For AFM measurements, the polymer samples with a narrow molecular weight distribution (MWD) ($M_w/M_n \leq 1.2$) were prepared by a successive fractionation from THF solution with n-hexane as the nonsolvent according to a reported procedure.[15]

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AMX-400 NMR instrument in CDCl$_3$. *D*-Line specific optical rotations ($[\alpha]_D^{25}$) were measured in THF at 25 °C using a Perkin Elmer polarimeter (model 341). Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 analyzer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PL-GPC 220 apparatus equipped with a PLgel 3 μm (300 mm × 7.5 mm) MIXED-B columns and a refractive index detector (eluent, THF; a flow rate, 1.0 mL/min). The GPC chromatogram was calibrated against standard polystyrenes. Circular dichroism (CD) spectra were obtained in THF at 25 °C using a quartz cell of 1 cm with a JASCO J-820 spectropolarimeter. UV spectra were recorded on a JASCO V-530 spectrophotometer. AFM measurements were carried out on a SPI3800N AFM in the tapping mode. Height and phase images were simultaneously measured at the resonance frequency of the silicon tips with cantilevers 20 μm in length. Steady-state fluorescence spectra were recorded on a PerkinElmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics). The excited wavelength for the measurement was set at 310 nm.

TABLE 1 Radical Polymerization of (*S*)-MeOPAM in the Presence of $Ln(OTf)_3$ at 60 °C[a]

Entry	Ln (mol/L)	Solvent	Yield (%)[b]	M_n (10^3)[c]	M_w/M_n[c]	Tacticity (m/r)[d]	$[\alpha]_D^{25}$ (deg)[e]
1	None	*n*-BuOH	67.9	14.5	1.75	36/64	+10.0
2	La(0.05)	*n*-BuOH	69.2	13.1	2.07	69/31	−9.3
3	Nd(0.05)	*n*-BuOH	57.2	18.2	1.84	70/30	−9.8
4	Sm(0.05)	*n*-BuOH	67.1	12.5	1.98	52/48	+3.3
5	Y(0.05)	*n*-BuOH	59.2	11.0	1.88	71/29	−16.7
6	Y(0.15)	*n*-BuOH	53.1	10.0	1.85	85/15	−19.6
7	Y(0.25)	*n*-BuOH	50.4	8.3	1.96	91/9	−28.5
8	Y(0.5)	*n*-BuOH	53.8	8.1	1.83	95/5	−33.4
9	None	MeOH	70.0	34.8	1.63	15/85	+11.4
10	Y(0.05)	MeOH	57.6	15.0	1.76	43/57	+7.4
11	Y(0.25)	MeOH	52.8	12.2	1.60	48/52	+1.7
12	None	EtOH	61.8	10.1	2.05	35/65	+10.1
13	Y(0.05)	EtOH	52.0	13.6	1.64	52/48	0
14	None	EGBE[f]	75.6	11.2	1.65	40/60	+7.7
15	Y(0.05)	EGBE[f]	38.9	10.0	1.41	50/50	+4.7
16	None	THF	67.1	2.87	1.82	45/55	+6.0
17	Y(0.05)	THF	37.8	4.46	1.75	45/55	+6.5

[a] $[\text{Monomer}]_0 = 0.5$ mol/L, $[\text{AIBN}]_0 = 0.01$mol/L, time = 24 h.

[b] Methanol-insoluble part.

[c] Determined by GPC in THF (calibrated against standard polystyrene samples).

[d] Determined by ^1H NMR measurement in $CDCl_3$.

[e] $c = 0.1$ g/dL, THF, $l = 10$ cm.

[f] EGBE, ethylene glycol butyl ether.

RESULTS AND DISCUSSION

Polymerization Characteristics

Table 1 summarizes the experimental conditions and results on the radical polymerization of (*S*)-MeOPAM in the presence of a catalytic amount of lanthanide trifluoromethanesulfonates ($Ln(OTf)_3$) in *n*-butanol, methanol, ethanol, ethylene glycol butyl ether, and THF. The tacticity of the resultant polymers could be estimated by ^{13}C NMR spectroscopy on the basis of the splitting of methine signals,[16] and a representative example is shown in Figure 1. The data from Table 1 indicate that the isotactic-rich polymers (meso diad m = 52–95%) were obtained in the $Ln(OTf)_3$-mediated radical polymerizations, whereas the conventional process without Lewis acid produced polymers rich in syndiotacticity. Among the Lewis acids, $Y(OTf)_3$ was found to be most effective with respect to the stereocontrol during the radical polymerization. When the polymerization carried out in *n*-butanol, the isotacticity of polymers increased with an increase in the amount of added $Y(OTf)_3$ and reached a maximum (meso diad m = 95%) at the ratio of $[Y(OTf)_3]/[(S)\text{-MeOPAM}] = 1.0$. Further addition of $Y(OTf)_3$ did not enhance the isotactic selectivity but resulting in the decrease of polymer yield and molecular weights.

As presented in Table 1, solvents significantly influenced the effect of Lewis acids on the radical polymerization stereochemistry. In the present systems, *n*-butanol seemed to be more favorable for the isotactic-specific polymerization of (*S*)-MeOPAM. For example, the polymerization in *n*-butanol with 10 mol % of $Y(OTf)_3$ afforded the isotactic-rich polymer

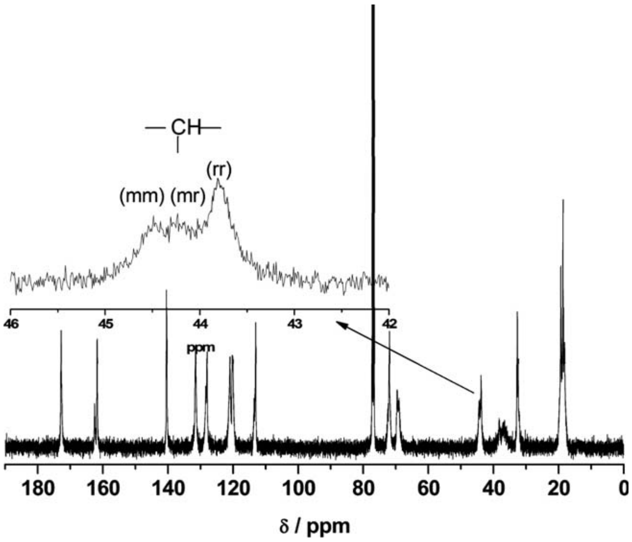

FIGURE 1 ^{13}C NMR spectrum of poly[(*S*)-MeOPAM] prepared by the radical polymerization with $Y(OTf)_3$ in *n*-butanol (entry 5 in Table 1).

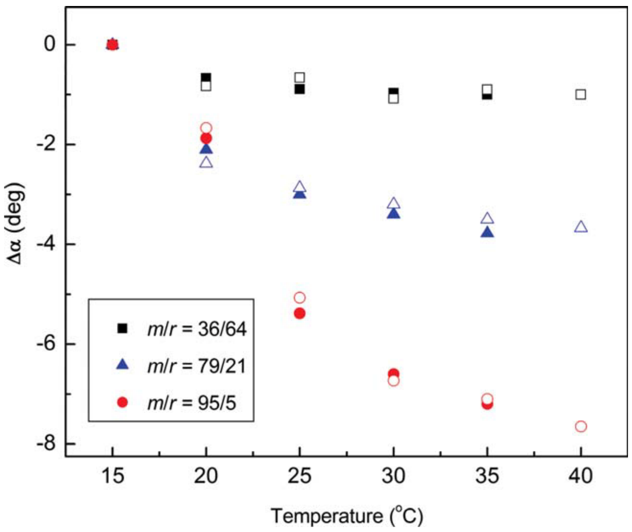

FIGURE 2 Relationship between the specific rotation and the measurement temperature in THF for poly[(*S*)-MeOPAM]s with various tacticities: (■) $m/r = 36/64$ (entry 1), (▲) $m/r = 79/21$ (entry 5), (●) $m/r = 95/5$ (entry 8). $\Delta\alpha = [\alpha]_D^{15} - [\alpha]_D^{T}$. (■, ▲ and ●: heating; □, △ and ○: cooling). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

($m/r = 79/21$, entry 5 in Table 1); but, poor stereocontrol was observed in other solvents such as methanol, ethanol, ethylene glycol butyl ether, and THF under the same conditions ($m = 43$–54%, see: entries 10, 13, 15, and 17). In fact, such a solvent dependence has been reported by Okamoto et al., in that case methanol was found to be the most suitable solvent for the stereocontrolled polymerizations of (meth)acrylamide.[5(a),6] Apparently, this phenomenon may be ascribed to the fact that the nature of solvents should affect the coordination ability of the Lewis acid thus changing its interaction with the propagating radicals and hence the stereochemistry during the polymerization.

In addition, the radical polymerization of (*S*)-Pr^{i}OPAM with Lewis acids also exhibited a similar tendency as observed in the (*S*)-MeOPAM polymerization. That is, a moderate stereocontrol was achieved in the presence of $Y(OTf)_3$ using *n*-butanol as solvent to give isotactic-rich polymers with *m* values ranging from 0.54 to 0.86. However, for the alcohol-insoluble monomer PhOPAM, we only obtained atactic polymers in THF or toluene medium. Representative data including NMR spectra can be found in the Table S1 and Figure S1 in the Supporting Information.

Chiroptical and Fluorescent Properties

As can be seen from Table 1, the optical activity of poly[(*S*)-MeOPAM]s correlated clearly with their tacticity. The syndiotactic polymers, prepared by the polymerization with or without Lewis acids, showed a specific rotation having the same sign as the corresponding monomer (*S*)-MeOPAM ($[\alpha]_D^{25} = +6.2°$). In contrast, the polymers with an isotactic-rich structure were all levorotary, and the magnitude of specific rotations increased in the negative direction with an increase in the isotacticity (entries 1, 2, and 5–8). Interestingly, the *m* content of 52% seemed to be a critical point, at which a specific rotation of $[\alpha]_D^{25} = 0$ was observed (entry 13), indicating that this polymer sample was optically inactive. Considering the tendency for the isotactic polymer chains to form a helical conformation,[17] we assume that the Lewis acid-mediated polymerization likely afforded the helical polymers with a prevailing handedness; furthermore, the higher ordered structure would exert an opposite effect on the optical activity with respect to the chiral pendant groups. In this hypothesis, the variation in optical rotation for the polymers can be interpreted as being attributed to the result of combining the configurational effect from lateral groups with the helical conformational effect of the main chain.

Figure 2 depicts the change in specific optical rotation ($[\alpha]_D$) of poly[(*S*)-MeOPAM]s with different tacticity upon the measurement temperature in THF. Clearly, the specific rotations of all the polymers decreased with increasing temperatures and this variation was strongly dependent on their stereoregularity. In the cases of syndiotactic-rich polymer ($m/r = 36/64$) and isotactic-rich polymer ($m/r = 79/21$), the values

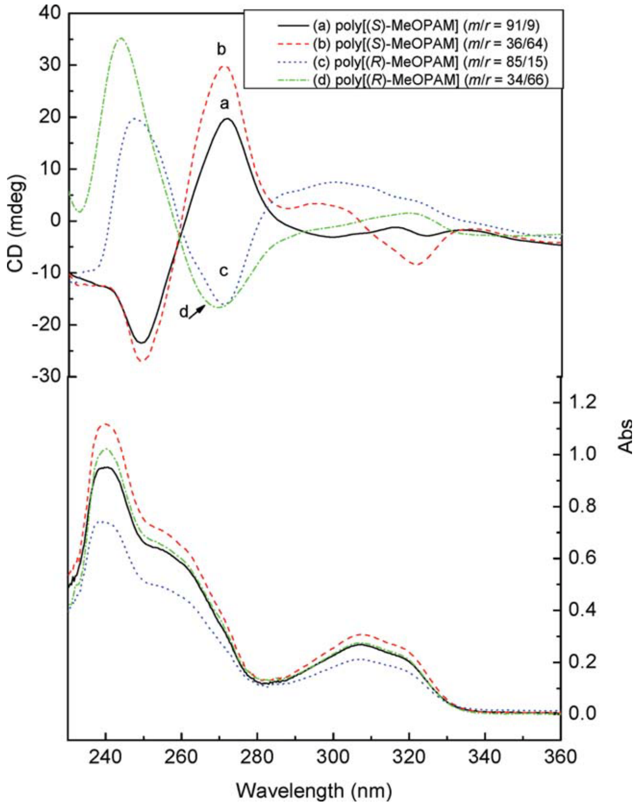

FIGURE 3 CD and UV spectra of (a) poly[(*S*)-MeOPAM] ($m/r = 91/9$, $[\alpha]_D^{25} = -28.5°$, entry 7), (b) poly[(*S*)-MeOPAM] ($m/r = 36/64$, $[\alpha]_D^{25} = +10.0°$, entry 1), (c) poly[(*R*)-MeOPAM] ($m/r = 85/15$, $[\alpha]_D^{25} = +24.4°$), and (d) poly[(*R*)-MeOPAM] ($m/r = 34/66$, $[\alpha]_D^{25} = -7.8°$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

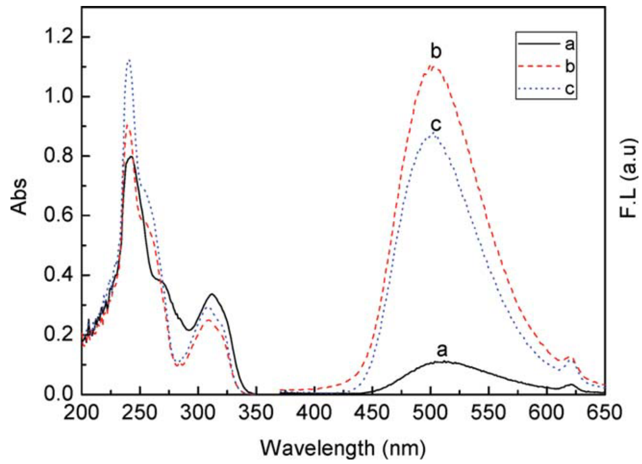

FIGURE 4 Absorption and fluorescence spectra: (a) (*S*)-MeOPAM, (b) poly[(*S*)-MeOPAM] ($m/r = 95/5$, entry 8 in Table 1), and (c) poly[(*S*)-MeOPAM] ($m/r = 36/64$, entry 1 in Table 1). $c = 5 \times 10^{-5}$ mol/L (monomeric unit); Excitation wavelength = 310 nm, in THF, 25 °C.

of temperature coefficient ($\Delta[\alpha]_D/\Delta T$) were -0.05 and -0.19, respectively. The highest value of -0.36 was observed for the polymer sample with $m/r = 95/5$ (entry 8 in Table 1). The noticeable temperature dependence indicated that the isotactic polymers might contain a conformational chirality in addition to a configurational one. However, the contribution of conformational chirality to the optical activity seems to be slight compared with one-handed helical polymethacrylates bearing a bulky pendant,[17(c),18] because the change of specific optical rotation is reversible and the temperature coefficient is rather small.

The chiroptical properties of the optically active polymers were investigated with UV–vis and CD spectroscopies. Figure 3 shows the representative spectra of poly(MeOPAM)s with different tacticities in THF solution. Poly[(*S*)-MeOPAM] and its (*R*)-analogue displayed split-type CDs of mirror images in the π–π^* transition region. In the case of poly[(*S*)-MeOPAM]s (Curves a and b), the CD peak intensity at the first and second Cotton effects for the isotactic polymer ($m/r = 91/9$, $[\alpha]_D^{25} = -28.5°$) was all smaller than that of the corresponding syndiotactic-rich sample ($m/r = 36/64$, $[\alpha]_D^{25} = +10.0°$). In other words, the CD peak intensity decreased with the increasing isotacticity of the polymers. Furthermore, this CD intensity difference at the first Cotton effect was larger than that at the second Cotton effect. On the other hand, the second Cotton effect of poly[(*R*)-MeOPAM] with $m/r = 85/15$ ($[\alpha]_D^{25} = +24.4°$) was much weak compared with the syndiotactic polymer ($m/r = 34/66$, $[\alpha]_D^{25} = -7.8°$) accompanying a minor red-shift, whereas the difference in the first Cotton effect was negligible (Curves c and d). These results suggested that a small conformational difference based on the stereoregularity may exist among these polymers.

As well as the aforementioned poly(MeOPAM)s, poly[(*S*)-Pr^{i}OPAM] also showed a similar CD spectral pattern in the π–π^* transition region with a negative first Cotton effect around 270 nm and a positive second Cotton effect around 235 nm (Supporting Information Fig. S2). In contrast to what observed in the case of poly(MeOPAM)s, the CD peak intensity seemed to be directly proportional to the *m* content of the polymers. That is, the higher *m* content of the polymers and more intensive the CD peak was observed at the both Cotton effects. As for atactic poly[(*R*)-PhOPAM]s synthesized by either the Lewis acid-mediated radical polymerization or a conventional process, split-type CD peaks with same sign were observed at 250 and 320 nm, and the pattern is different from that for poly[(*R*)-MeOPAM] and poly[(*S*)-Pr^{i}OPAM]. In addition, the CD intensity of poly[(*R*)-PhOPAM]s were almost same each other although they had different values of specific rotation. These facts indicate that the structure of substituents connecting to the lateral chiral center had a significant influence on the chiropical property of the polymers.

Because the presence of a chiral lateral chromophore connecting to the polymer backbone, by the fluorescence

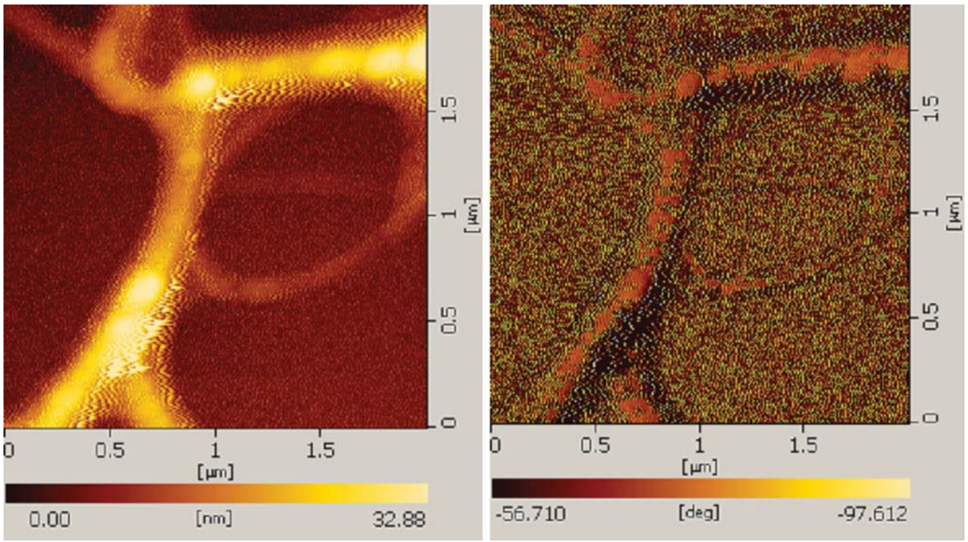

FIGURE 5 Typical tapping-mode AFM (left) height and (right) phase images of the fractionated poly[(*S*)-MeOPAM] sample ($M_n = 1.3 \times 10^4$, MWD = 1.19, $m/r = 95/5$, entry 8 in Table 1) on mica. The sample concentration was 0.5 wt % in THF.

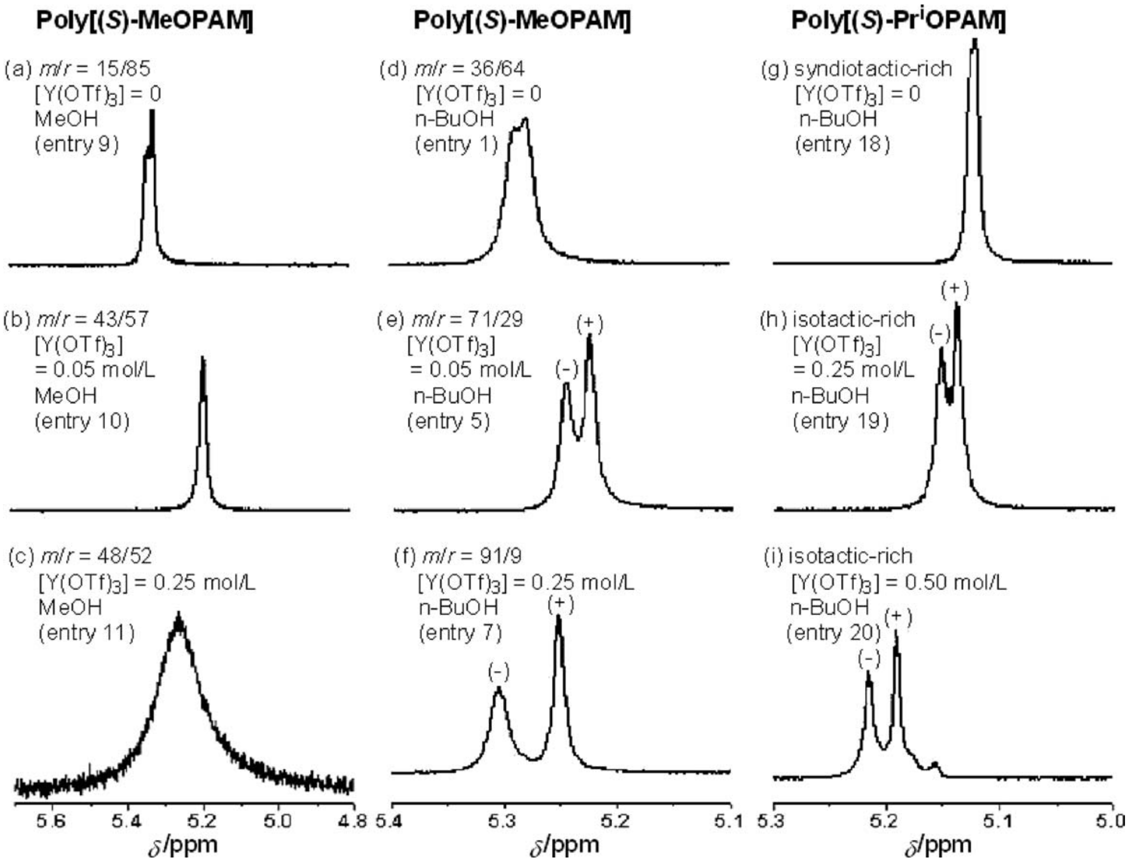

FIGURE 6 The hydroxyl region in ^{1}H NMR spectra of racemic BINOL (5 mmol/L) in the presence of poly(ROPAM)s (R = Me and Pr^i) prepared by the radical polymerization under various conditions; the polymer concentration = ~5 mmol/L (monomeric unit), $CDCl_3$, r.t.

measurement we were able to gain some additional insight into the stereoregularity and its specific effects. As shown in Figure 4, the polymers emitted excimer-based fluorescence at 510 nm with more than eight times larger intensity than the monomer did, which means the chromophore groups of poly[(*S*)-MeOPAM]s took a position that was favorable to form the excimer.[19(a)] Moreover, the isotactic-rich polymer (m/r = 95/5) exhibited a more intensive fluorescence compared with the syndiotactic-rich one (m/r = 36/64), their fluorescence quantum yield (Φ_f) were 10.8% and 8.9%, respectively. It has been reported that the emission spectra of polymers associate largely with the secondary ordered structure, and the helical structure is believed to be favorable to the formation of the excimer.[19(b,c)] Accordingly, the fact that the poly[(*S*)-MeOPAM] rich in isotacticity had a stronger fluorescence intensity may be another proof for the existence of the prevailing one-handed helical chain sections.

AFM Observations of Isotactic-Rich Poly[(*S*)-MeOAM]

To some extent, the prevailing one-handed helical conformation was responsible for the observed difference in chiroptical and fluorescent properties among the optically active polymers having various stereoregularity. This excited us to explore the possibility of whether the isotactic-rich polymers could form aggregates with spiral structure through a self-assembly process.

AFM may be one of the most powerful tools to investigate the aggregative structure of the polymers in nanometer scale. When adsorbed polymers were long enough, their helical conformations might be clearly visible in the high-resolution AFM images.[8(b),20–22] In this study, we first fractionated the original sample poly[(*S*)-MeOPAM] having the m content of 0.95 (entry 8 in Table 1) by the usual method,[15] and then chose the fifth fraction (M_n = 1.3 × 10^4, MWD = 1.19) for AFM measurements. Figure 5 shows the typical AFM images of this polymer sample deposited onto the surface of freshly cleaved mica at room temperature. In the AFM images, there seemed to be some helical aggregates with an average height of near 30 nm, although the visualization and discrimination of the right- and left-handed helical structures were not achieved. These helical shape images observed with AFM possibly reflect the macromolecular helical conformation of the polymer in solution.

NMR Study on the Interaction of Poly(ROPAM)s with BINOL

The chiral recognition ability of the obtained optically active polymers was examined by NMR technique using BINOL as a probe molecule. Because of the restricted rotation of the two naphthyl rings around its 1,1-bond, BINOL exists in the atropisomeric form; however, the racemic compound only give single hydroxyl proton signal in an achiral NMR environment.

For comparison, Figure 6 shows the hydroxyl region in the ^{1}H NMR spectra of racemic BINOL in the presence of poly(ROPAM)s (R = Me and Pr^i) with a variety of tacticity. In all cases, the hydroxyl proton signal of BINOL at δ 5.05 was shifted downfield on interaction with the polymers. With the exception of the syndiotactic-rich poly[(*S*)-MeOPAM]s synthesized by the radical polymerization in methanol (a–c), the polymers having an isotactic-rich structure made the hydroxyl signal split into two peaks that are ascribed respectively to the levo- and dextro-isomer. The assignment of the two split peaks was determined by NMR measurements with a separate enantiomer under the same measurement conditions. It is noteworthy that the magnitude of this signal split was closely dependent on the stereoregularity of the polymers that were obtained in the polymerization system using *n*-butanol as solvent, as shown in Figure 6(d–f and g–i). It is similar to that previously observed in the case of polymethacrylamide analogs.[11(b)] These results indicate that the stereoregularity of the obtained optically active poly(ROPAM)s significantly affected the chiral recognition of the polymers, as seen in other systems.[23]

CONCLUSIONS

The radical polymerization of the acrylamide derivatives bearing a chiral oxazoline chromophore was carried out in the presence of rare earth metal trifluoromethanesulfonates ($Ln(OTf)_3$, Ln = La, Nd, Sm, and Y). It was found that $Y(OTf)_3$ could effectively increase the isotactic specificity during the radical polymerizations when using *n*-butanol as solvent. The chiroptical and fluorescence properties of the optically active polymers were significantly dependent on their stereoregularity. On the basis of the temperature dependence of the specific rotation together with the preliminary AFM observations, the polymers rich in isotacticity might contain the prevailing one-handed helical chain sections in solution. Furthermore, the enantioselective interaction of the isotactic-rich polymers with BINOL predicts they have some potential uses in the area of chiral separation.

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