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Optically active copolymers of *N*-(oxazolinyl)phenylmaleimides with methyl methacrylate: Synthesis and chiral recognition ability

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ABSTRACT

The free radical copolymerization of three *N*-phenylmaleimides bearing a chiral oxazoline residue at *ortho*-position of the phenyl group (OPMI) with methyl methacrylate (MMA) was carried out in tetrahydrofuran by varying the molar ratio of the comonomers. The monomer reactivity ratios and Alfrey–Price *Q*–*e* values were determined. The data revealed that the monomer OPMI has a distinct tendency to cross-propagate and MMA is inclined to block formation. Meanwhile, the MMA co-units affected significantly the chiroptical property of resulted copolymers besides endowing them with a moderate film-forming ability. Poly(OPMI-*co*-MMA)s coated on macroporous silica were used as a high-performance liquid chromatography chiral selector, and the optical resolution performance was briefly evaluated toward some racemic compounds including amino- and hydroxy-acids as well as 1,1′-bi-2-naphthol. The observation indicated that the column combining MeOPMI/MMA copolymers with higher chiral component exhibits an extent of enantioselectivity in both normal and reversed-phase modes.

1. Introduction

There is a continued interest in both synthetic and naturally occurring optically active polymers because they can be applied to chiral recognition, asymmetric catalysis in organic transformations, and enantioseparation for racemates as well [1–6]. One of the most practical applications of optically active polymers is the use as chiral stationary phase (CSP) for the optical resolution of racemic compounds in high-performance liquid chromatography (HPLC). Many CSPs based on naturally occurring polymers such as polysaccharides have been commercialized and become indispensable materials for separation in the fields of synthetic and medicinal chemistry [7].

On the other hand, research on the synthesis and applications of various chiral polymers, especially polymethacryates [8] and poly[(meth)acrylamide]s [9], is also rapidly evolving. Some packed columns of the synthetic polymers bound to silica gel have been on the market. Attractive features of the synthetic polymers are the large chemical and structural variabilities that can be exploited in the preparation of the chiral selectors. In general, the optical resolution performance of CSPs is significantly dependent on the chiral recognition ability of the pendant group used and/or the stable higher-ordered structures of the polymers. For example, Miyano et al. reported an optically active polymethacrylate bearing binaphthol moiety in the side chain obtained by radical polymerization of the corresponding monomer. They found that the chiral recognition ability of the polymer to several racemic 3,5-dinitrophenylcarbamate derivatives is not based on its helical conformation but mainly on the interaction between the individual 1,1′-binaphthalene units and the racemates [10]. However, for poly(methacrylamide)-based CSPs the prominent recognition ability was ascribed to the conformation controlled by hydrogen bonds between amide groups [9g,h].

In our previous study, we synthesized a new type of optically active polymers based on *N*-phenylmaleimide derivatives (OPMI) in which the side-chain chiral oxazolinyl chromophore is connected to the backbone through a benzene ring [11]. It was demonstrated that the optical activity of the polymers has a close relationship with not only the configurational chirality of the lateral group but also the secondary helical structure of main chains, in some cases reversion in the direction of optical rotation was observed with increasing molecular weights. More interestingly, these polymers exhibited moderate enantioselectivity in fluorescent responses toward both the axially chiral 1,1′-bi-2-naphthol and 2-amino-1-propanol, making them a potential chemosensor for enantiomeric recognition [11f]. However, the polymers showed unsatisfactory

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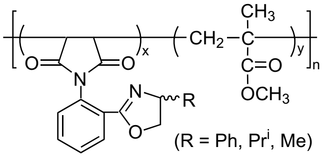

Scheme 1. General structure of poly(OPMI-*co*-MMA)s.

film-forming ability and relatively poor resistance to organic solvents, which would limit their potential applications in the materials of chiral separation film or chiral adsorbing column.

In this work, we synthesized the optically active copolymers incorporating both chiral OPMI and flexible methyl methacrylate units in the main chain, as shown in Scheme 1. Particular attention was paid on the polymerization features, structural characterization, and the chiroptical behavior of the resultant copolymers in comparison with our previous observation. The monomer reactivity ratios and *Q*–*e* values have been determined. Also, the copolymers as a chiral selector were coated on silica gel to prepare chiral stationary phases and the optical resolution performance was briefly examined by HPLC toward some racemic compounds.

2. Experimental

2.1. Materials

Chiral oxazoline-substituted *N*-phenylmaleimides, (*R*)-PhOPMI, (*S*)-Pr^{i}OPMI, and (*S*)-MeOPMI, were synthesized according to the previously reported method [11b], using (*R*)-2-phenylglycinol, (*S*)-2-amino-3-methyl-1-butanol, and (*S*)-2-amino-1-propanol as a chiral source, respectively. Methyl methacrylate (MMA; Shanghai Chemical Reagent Co., China) was washed with dilute sodium hydroxide to remove the inhibitor, followed by repeated washings with distilled water until neutral. It was dried over anhydrous sodium sulfate overnight and distilled under reduced pressure. Solvents for the polymerization were dried over a benzophenone–sodium complex for two days and then distilled prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Reagent grade *n*-hexane, 2-propanol, and analytes tested in HPLC were used as-received.

2.2. General polymerization procedure

Polymerization was performed on the Schlenk line under nitrogen atmosphere. The OPMI was copolymerized with MMA at different feed mole ratios in THF or toluene at 60 °C, while maintaining constant both the total monomer ($1.6\ \mathrm{mol\ L^{-1}}$) and initiator concentrations ($2.5 \times 10^{-2}\ \mathrm{mol\ L^{-1}}$). After the polymerization was completed, the reaction mixture was poured into ethanol to precipitate the product. The crude products were purified by reprecipitation from THF/ethanol system in three cycles and dried in vacuum at 40 °C for two days before measurements. For comparison, the homopolymer samples, i.e., poly(PhOPMI), poly(Pr^{i}OPMI) and poly(MeOPMI), were prepared under the same polymerization conditions for the corresponding copolymer just in the absence of MMA, when using *n*-hexane as precipitating agent and THF/*n*-hexane system for the sample purification.

2.3. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AMX-400 NMR spectrometer with TMS as internal standard. FT-IR spectra were recorded using a Bruker Vector 22. Absorption and CD spectra were measured on a Jasco V-570 spectrophotometer and a Jasco J-810 spectropolarimeter, respectively, in a 1.0 cm quartz cell. 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 Co.). The molecular weight of polymers was determined by gel permeation chromatography (GPC) using a Waters 2414 GPC apparatus equipped with a set of Styragel® columns (HT-1, HT-3, and HT-4) and a differential refractometer (eluent, THF; a flow rate of 0.5 mL/min). The GPC chromatogram was calibrated against standard polystyrene samples. The composition of copolymers was determined by elemental analysis data from the nitrogen content (ThermoFinnigan Flash EA 1112 analyzer; error: ±1 mol%). Thermal stability studies were performed using a Mettler Toledo Star System thermogravimetric analyzer at a heating rate of $10\ ^{\circ}\mathrm{C\ min^{-1}}$ under nitrogen atmosphere.

2.4. Preparation of CSPs and HPLC evaluations

Macroporous silica gel as a support was purchased from Lanzhou Institute of Chemistry and Physics (Chinese Academy of Sciences) with the mean particle size 5 μm, average pore diameter 5.2 nm, and specific surface area $220\ \mathrm{M^2\ g^{-1}}$. CSPs for HPLC were prepared as follows. To a stirred solution of the copolymer (0.5 g) in anhydrous THF (30 mL) was added silica gel (10 g) and allowed the suspension to stir for 2 h at room temperature. After evaporating the solvent, the silica was dried at 60 °C for 8 h to afford desired CSPs. The column packing materials thus obtained were packed into a stainless-steel tube (250 × 4.6 mm ID) by conventional high-pressure slurry packing technique using a VFD-M packer pump (Dalian Kerui Instrument Co., China). The chromatographic measurements were carried out on a DIONEX P-680 HPLC apparatus with an UV detector at ambient temperature.

3. Results and discussion

3.1. Synthesis and characterization

Table 1 summarizes the experimental polymerization conditions and results. The general structure of desired copolymers, poly(OPMI-*co*-MMA), is illustrated in Scheme 1. It can be seen that the monomer feed composition has a strong influence on the yield as well as on the copolymer composition. With increasing OPMI

Table 1
Experimental conditions and results on the radical polymerization of OPMI with AIBN in THF at 60 °C for 12 h[a].

Copolymer	f_1	F_1	Yield[b]/%	M_n[c]/10^3	M_w/M_n	$[\alpha]_D^{25}$[d]/°
PhOPMI/MMA-1	1.3	0.73	40.4	27.0	1.4	−7.8
PhOPMI/MMA-2	5.6	2.6	48.8	15.0	1.4	−18.7
PhOPMI/MMA-3	14.2	5.9	45.6	9.0	1.4	−31.6
PhOPMI/MMA-4	41.0	13.5	25.9	5.3	1.3	−35.8
PhOPMI/MMA-5	65.3	15.9	15.1	4.4	1.3	−33.2
Poly(PhOPMI)	100	0	16.2	1.4	1.2	−35.1
Pr^{i}OPMI/MMA-6	1.7	0.78	40.7	21.0	1.4	−13.6
Pr^{i}OPMI/MMA-7	6.9	3.4	49.9	15.0	1.5	−16.8
Pr^{i}OPMI/MMA-8	27.1	12.4	22.1	7.8	1.3	−19.1
Pr^{i}OPMI/MMA-9	46.4	16.4	12.4	7.5	1.3	−23.4
Pr^{i}OPMI/MMA-10	70.2	24.2	11.8	5.0	1.2	−28.4
Poly(Pr^{i}OPMI)	100	0	19.2	1.7	1.3	−11.3
MeOPMI/MMA-11	2.1	0.71	42.0	24.0	1.4	−8.4
MeOPMI/MMA-12	8.4	3.6	51.5	15.0	1.6	−17.3
MeOPMI/MMA-13	31.3	16.3	53.4	5.5	1.7	−30.7
MeOPMI/MMA-14	51.6	20.7	26.3	3.6	1.4	−36.6
MeOPMI/MMA-15	74.3	28.1	25.5	2.6	1.7	−34.8
Poly(MeOPMI)	100	0	36.2	1.7	1.2	−39.3

[a] M_1: (*R*)-PhOPMI (1–5) or (*S*)-Pr^{i}OPMI (6–10) or (*S*)-MeOPMI (11–15), M_2: MMA; f_1: feed monomer composition (mol%), *F*: copolymer molar fraction (m_1) mol%; $[\mathrm{AIBN}] = 2.5 \times 10^{-2}\ \mathrm{mol\ L^{-1}}$, $[\mathrm{M}]_{\mathrm{total}} = 1.6\ \mathrm{mol\ L^{-1}}$.

[b] Insoluble part in ethanol.

[c] By GPC.

[d] $c = 0.5\ \mathrm{g\ dL^{-1}}$, THF, $l = 10$ cm.

feed content, the yield decreases dramatically whereas the molar percentage of incorporated chiral monomeric units increases. For the monomer feed having a (*S*)-MeOPMI fraction of 74.3 mol%, the copolymer with a maximum chiral component ($F = 28.1$ mol%) was produced. In all cases the copolymers containing chiral units less than 16 mol% show relatively higher molecular weights ($M_n = 5000$–27,000) and a narrower molecular weight distribution. These polymeric materials are soluble in common organic solvents including chloroform, acetone, and THF, and show moderate film-forming ability that would be of great important for some applications such as membrane separation. For the homopolymerization, all poly(OPMI)s were obtained in low yields and the molecular weights are much lower compared to their analogs synthesized by the anionic polymerization with *n*-BuLi as an initiator [11b].

As an example, Fig. 1 depicts the comparison of FT-IR spectra between the copolymer Pr^{i}OPMI/MMA-8 (See: Table 1) and poly-(Pr^{i}OPMI). For the copolymer, the carbonyl absorption of Pr^{i}OPMI unit at 1710 cm^{-1} merged with that of MMA to form a single peak at around 1723 cm^{-1}. A shoulder peak at 1782 cm^{-1} is from the symmetric stretching of imide carbonyl group only. The characteristic absorption peaks at 1645 cm^{-1} and 1153 cm^{-1} are ascribed to oxazoline residue (C=N stretching) and the ester group of MMA, respectively.

The copolymer PhOPMI/MMA-4 presented ^{1}H NMR signals due to aromatic groups at 8.39–6.79 ppm and those due to the methine proton of oxazoline residue around 4.68 ppm (Fig. 2a). Also observed were the absorptions of methoxyl and methyl groups around 3.6 and 1.0 ppm, respectively, which are assigned to the MMA units. The multi-peak of methyl groups indicates the complicated stereoregularity of MMA segments in the main chain. The presence of the characteristic signals of OPMI in both IR and NMR spectra suggests that the chiral monomer has been incorporated into the polymer chain, and the copolymerization of this system has been achieved. This is also confirmed by the GPC traces with unimodal fashion (See: Fig. S1 in Supporting Information).

To obtain more structural information, ^{13}C NMR spectra of the copolymers have been measured and compared with those of the corresponding chiral homopolymer obtained under the same conditions. The results showed that both polymers have an evidently different spectral fashion in the range 40–50 ppm indicative of the stereoregularity of OPMI segment. The homopolymers revealed broad bands with a relatively intense peak around 43 ppm (see: Fig.S2 in Supporting Information), suggesting that the OPMI units connected mainly in *threo*-disyndiotactic mode according to Oishi et al. [9d,12]. However, two isolated peaks were observed at 48 ppm and 44 ppm as shown in Fig. 2b for the copolymer PhOPMI/MMA-4, which may be attributed to the methine carbons of PhOPMI sequence with and without connecting MMA units, respectively. This fact means that very short chiral segments are present in the main chain, which is in good agreement with their poor polymerizability.

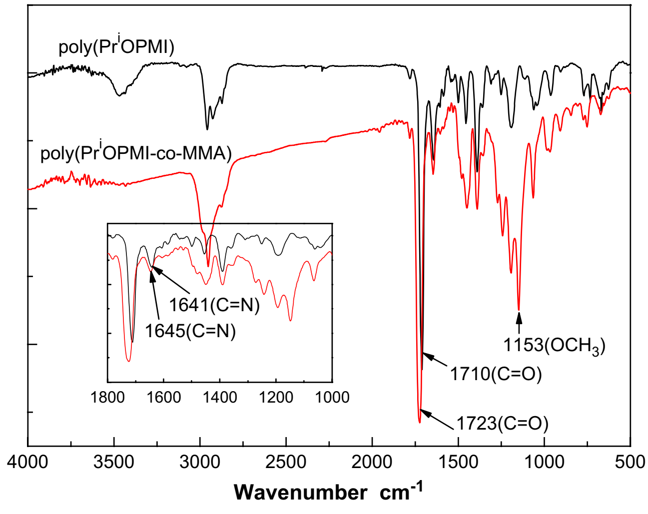

Fig. 1. IR spectra of poly(Pr^{i}OPMI) and the copolymer Pr^{i}OPMI/MMA-8 (see: Table 1).

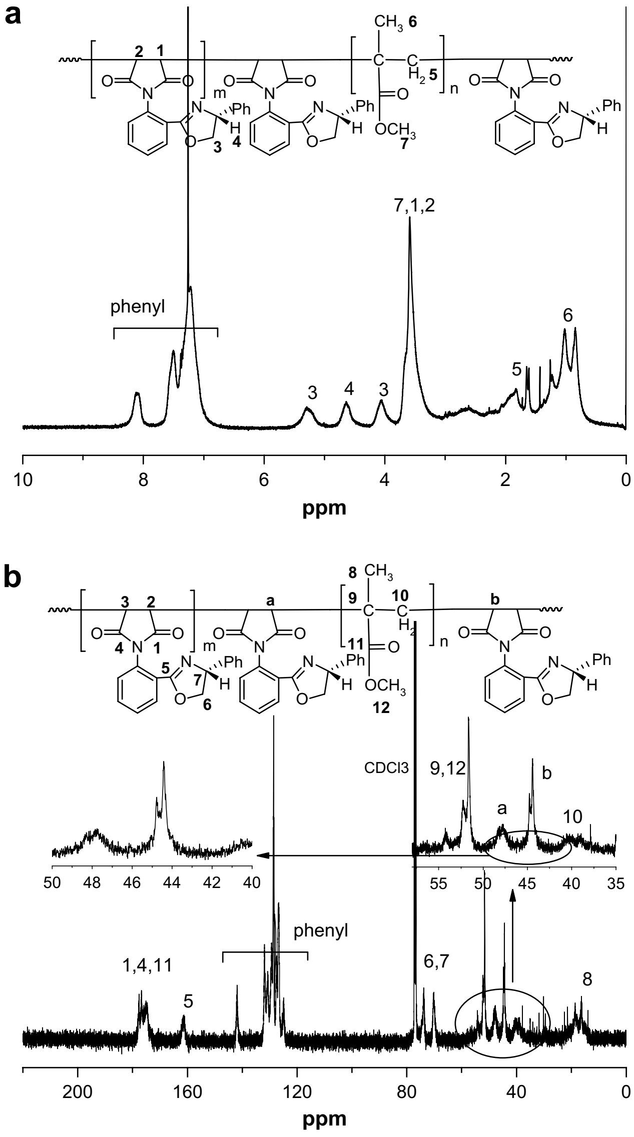

Fig. 2. (a) ^{1}H and (b) ^{13}C NMR spectra of the copolymer PhOPMI/MMA-4 (see: Table 1).

Table 2 shows the monomer reactivity ratios (MRRs) and Alfery–Price *Q*–*e* values for OPMIs [13]; the former was calculated from the monomer feed and the copolymer composition obtained at relatively high conversions by Kelen–Tüdös (K–T) method [14]. For the copolymerization system, the MRRs are r_1 (OPMI) = 0.11–0.30 and r_2 (MMA) = 2.52–2.66, respectively. These data indicate a tendency of OPMI toward cross-propagation and a clear trend toward MMA

Table 2
Monomer reactivity ratios and Alfrey–Price *Q*–*e* values.

M_1	M_2	r_1	r_2	Q_1	e_1
(*R*)-PhOPMI	MMA	0.19	2.52	0.33	1.14
(*S*)-Pr^{i}OPMI	MMA	0.11	2.54	0.45	1.53
(*S*)-MeOPMI	MMA	0.30	2.66	0.34	0.88

block formation, suggesting that the homopropagation of chiral monomers may be hindered due to steric considerations. Because of the less steric hindrance, MeOPMI has a larger value of r_1 and thus it would be expected to form a longer sequence length in its copolymer chain in comparison with the other two monomers. In addition, both resonance and polar effects seem to be subtle to discern, and it appears that the Q–e values have a limited meaning for correlating structure with reactivity.

3.2. Chiroptical property of copolymers

As shown in Fig. 3, both PhOPMI/MMA copolymer and poly(PhOPMI) exhibit a large positive CD peak at 250 nm attributed to the π–π^* electron transition of oxazolinyl-substituted aryl groups. It should be pointed out that the positive Cotton effect for either poly(PhOPMI) or the copolymer was much smaller than that of poly(PhOPMI) obtained by anionic polymerization [11b]. In the previous work, it was demonstrated that the main chain of poly(PhOPMI)s with high *threo*-diisotactic contents may result in the formation of partial helical conformation. However, for analogous homopolymers produced from the radical polymerization there seems to be no possibility of generating helical segments in the main chain due to their *threo*-disyndiotactic-rich structure and low molecular weights [12]. Also, it can be seen from Fig. 3 that the Cotton effect intensity increased with an increase of the PhOPMI content in the copolymer chain, and eventually exceeded that of the homopolymer as a comparative sample at about 5.9 mol% of incorporated PhOPMI. These results suggest that the optical activity for copolymers generated not only from chiral oxazoline pendants, but also from the conformational asymmetry of main chains induced by chiral units. Similar trends were also observed in Pr^{i}OPMI/MMA and MeOPMI/MMA copolymer systems (see: Fig. S3 in Supporting Information).

On the other hand, both PhOPMI/MMA and Pr^{i}OPMI/MMA copolymers exhibited a flat negative CD band in the range from 325 to 450 nm, but no signals were observed for the corresponding homopolymers in the same region (see: Fig. 3 and Fig. S3A). Taking into account the observations together with the very weak UV absorption appeared in 325–450 nm, the negative Cotton effect for the copolymers might be ascribed to the n–π^* electron transition of MMA segments suffered from an asymmetric induction of chiral units. That is, the CD signal in the region probably reflects to some extent the conformational asymmetry of main chains composed of MMA units, although its exact nature is not yet clear at present. In this opinion, there seemed to be chiral fractions in the main chain for the homopolymer of MeOPMI and its copolymer because both of them have the same CD fashion in the 325–450 nm range as shown in Fig. S3B.

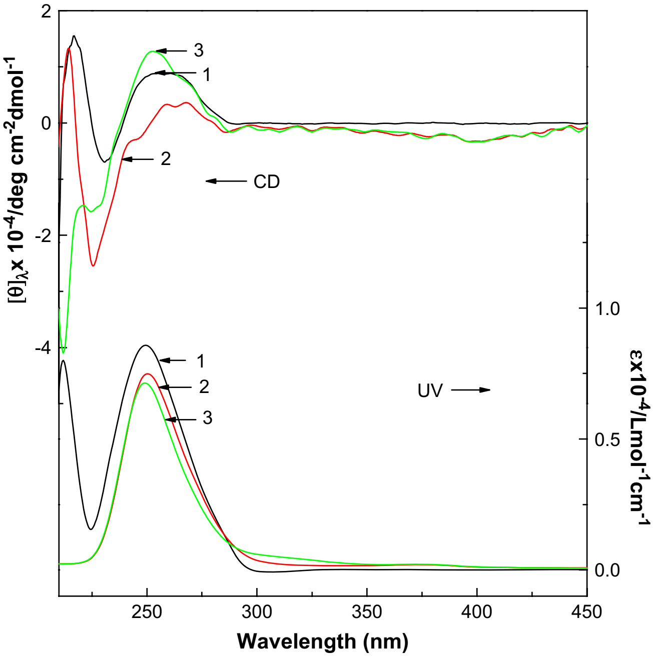

Fig. 3. CD and UV spectra in THF: (1) poly(PhOPMI), (2) PhOPMI/MMA-1, and (3) PhOPMI/MMA-3 (See: Table 1).

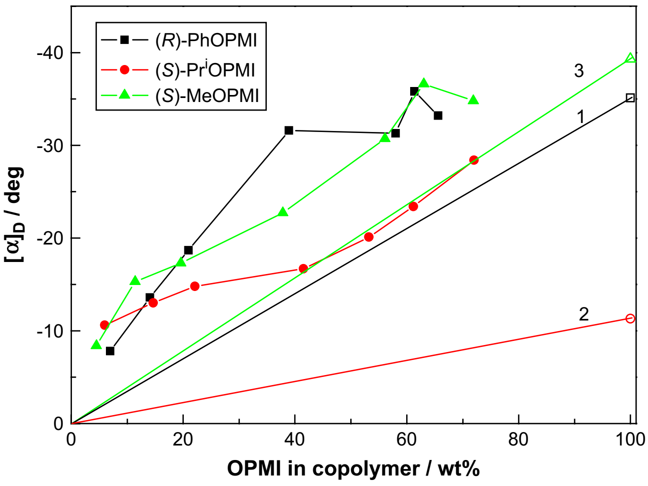

Fig. 4. Relationships between specific rotation and OPMI contents (wt%) in copolymer: (■) PhOPMI/MMA, (●) Pr^{i}OPMI/MMA, and (▲) MeOPMI/MMA; Lines 1–3 depict a corresponding relationship for the mixture of PMMA with (□) poly(PhOPMI), (○) poly(Pr^{i}OPMI), and (△) poly(MeOPMI), respectively (see: Table 1).

Fig. 4 shows the relationships between specific optical rotations ($[\alpha]_D^{25}$) and the content of the chiral units in wt% for the copolymers. As a reference, the lines 1–3 connecting 0° with $[\alpha]_D^{25}$ of poly(OPMI) depict relationships between the specific rotation and the contents (wt%) of chiral units in a mixture composed of poly(OPMI) and PMMA. It can be seen that the specific optical rotations of poly(OPMI-*co*-MMA)s showed a visible deviation from these straight lines in all cases, indicating that co-unit MMA has a significant effect on the chiroptical property of the copolymers. The phenomenon is similar to that of chiral copolymers reported by Lee et al. [15].

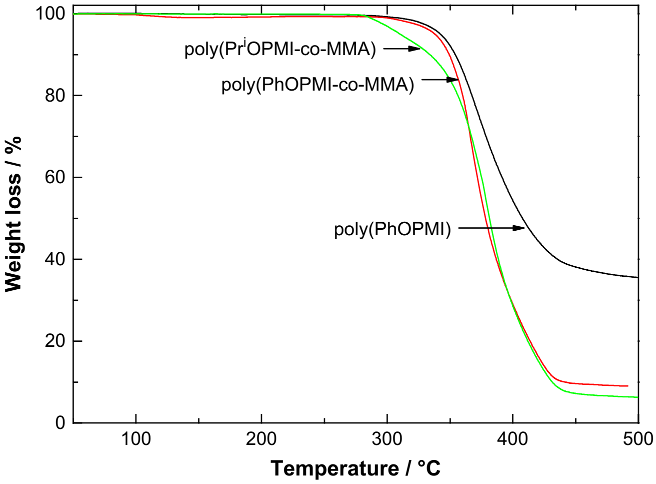

Fig. 5. TGA curves of PhOPMI/MMA-2 and Pr^{i}OPMI/MMA-7 as well as poly(PhOPMI) for comparison (see: Table 1).

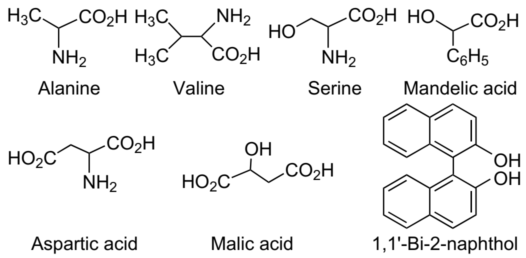

Fig. 6. Structure of analytes studied.

3.3. *Thermal stability and solvent resistance*

The copolymers showed good thermal stability due to the presence of the polar five-member imide structure [16]. As shown in Fig. 5, the copolymers present single-step degradation and an enhanced heat-resistance although the OPMI content was rather low. In the case of PhOPMI/MMA-2, the initial decomposition temperature (IDT) was very close to that of poly(PhOPMI) (296 °C), whereas Pr^iOPMI/MMA exhibited a lower IDT. In addition, no weight loss was observed for the polymer-coated CSPs after soaking for 48 h in some common organic solvents such as *n*-hexane, *n*-heptane, methanol, and isopropanol, indicating a good tolerance to the organic media, which is beneficial for chromatographic separation in normal phase mode.

3.4. *HPLC evaluations*

The chiral recognition performance of poly(OPMI-*co*-MMA)-coated CSPs was examined with HPLC toward the test compounds including 4 amino acids, 2 hydroxyl-containing carboxylic acids, and 1,1′-bi-2-naphthol as shown in Fig. 6. The chromatographic measurements were carried out respectively in normal phase (*n*-hexane/2-propanol) and reversed-phase (water or 0.1 mmol L^{-1} aqueous solution of cupper acetate) with a 1.0 mL min^{-1} flow rate. Among packing materials, the CSP coated with the copolymer MeOPMI/MMA-13 (see: Table 1) was found to be the best one in view of its chiral resolution ability and the experimental reproducibility. As shown in Table 3 and Fig. 7, the column packed with this CSP exhibits an extent of enantioselectivity in the optical resolution of aspartic acid, valine, and malic acid under reverse phase conditions. However the baseline separation was not achieved in all cases. When a hexane/2-propanol (9:1, v/v) mixture was used as an eluent, the column showed a partial resolution of 1,1′-bi-2-naphthol (BINOL) with an enantioselectivity value (α) of 1.312, while no chiral separation was observed for mandelic acid under the same conditions.

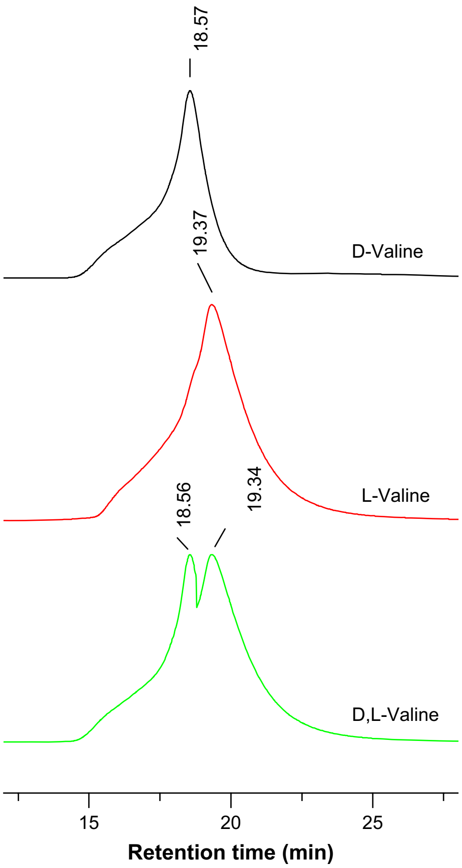

Fig. 7. HPLC chromatograms of valine and its enantiomers in water as a mobile phase with the copolymer MeOPMI/MMA-13 coated chiral stationary phase. Flow = 1.0 mL min^{-1}; column size: 250 mm × 4.6 mm; UV detection, 225 nm.

Table 3
Chromatographic resolutions of some racemates on poly(OPMI-*co*-MMA)-coated CSPs[a].

Run	Racemate	Mobile phase [b]	k_1'[c]	k_2'[c]	α[d]
1	Alanine	Water	20.442	20.442	1
2	Serine	Water	21.327	21.327	1
3	Aspartic acid	Water	20.371	21.532	1.057
4	Valine	Water	18.56	19.34	1.042
5	Malic acid	Water	18.329	21.738	1.186
6	Malic acid	$Cu(OAc)_2$ (aq.)	17.493	21.254	1.215
7	Mandelic acid	H/P = 90/10	9.591	9.591	1
8	1,1′-Bi-2-naphthol	H/P = 90/10	15.011	19.71	1.313

[a] Copolymer MeOPMI/MMA-13 (see: Table 1) was used as a chiral selector and its content in the CSP was 4.2 wt%. The flow rate = 1.0 mL min^{-1}, column size: 250 mm × 4.6 mm ID, $t_0 = 1.396$ min, column temperature: 25 °C; detection: UV at 225 nm.

[b] The concentration of $Cu(OAc)_2$ (aq.) = 0.1 mmol L^{-1}; H/P = *n*-hexane/2-propanol in volume/volume, the UV detection wavelength was 250 nm in the case of normal phase.

[c] Capacity factor of enantiomer eluting first (k_1') and second (k_2').

[d] Separation factor = k_2'/k_1'.

It should be pointed out that a rather difference in overall retention was observed for BINOL and mandelic acid: the former has a larger affinity for the stationary phase as evident from k_1' and k_2' in Table 3. This may be attributed to the additional aromatic π–π interactions between the analyte and the lateral group of the polymeric selector in a retention mechanism [17].

Noteworthy is also the chiral unit content of the copolymers is a crucial factor for the enantioseparation. When using poly(MeOPMI-*co*-MMA) containing a less chiral component as a selector, the CSPs only have a very small separation factor (see: Table S1 in Supporting Information for relative chromatographic data). As for PhOPMI/MMA and Pr^iOPMI/MMA copolymers, their poor resolution power may be attributed to the fact that the chiral segment in the main chains is too short to form an effective asymmetric microenviroment for the chiral recognition. On the basis of the preliminary observation, it appears that the chiral discrimination of the copolymers may be based on the interaction between chiral segments with an enough length and the racemates and/or the higher-ordered main chain structures.

4. Conclusion

Radical copolymerization of *N*-phenylmaleimides bearing an oxazoline pendant (OPMI) with methyl methacrylate (MMA) yielded the corresponding copolymers. On the basis of monomer reactivity ratios and Alfrey–Price *Q*–*e* values as well as structural analyses, the copolymerization showed a tendency of OPMI toward cross-propagation and a clear trend toward MMA block formation, suggesting that the homopropagation of chiral monomers may be hindered due to the steric bulk of the N-substituents. The comonomeric units have a remarkable influence on the chiroptical property of the copolymers. On the CSPs coated with poly-(MeOPMI-*co*-MMA) containing enough chiral units, a partial resolution has been achieved toward valine, aspartic acid, and malic acid under reversed-phase HPLC conditions, while for 1,1′-bi-2-naphthol in normal phase mode. These preliminary chromatographic results show that the maleimide-based polymers will find some applications as a potential chiral selector in enantiomeric separation of racemic compounds.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.11.044.

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