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Chiral polyamino alcohols and polyamino thiols for asymmetric heterogeneous catalysis

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Abstract—A series of macroporous copolymer beads were synthesized by THE free radical suspension copolymerization of (*S*)-glycidylmethacrylate (GMA), (*S*)-thiiranylmethylmethacrylate (TMA), or (*R*,*R*)-phenylglycidylmethacrylate (Ph-GMA) with ethyleneglycol dimethacrylate (EDMA) or divinylbenzene (DVB). This allowed for the evaluation of their chemical and physical properties (polymer matrix nature or the structure of the heterocyclopropane) and their influence on the catalytic efficiency. These chiral polymers were subsequently transformed into polyamino alcohol or polyamino thiol derivatives by the facile ring opening of the oxirane or thiirane group with benzylamine and methylamine. Complexed with $[RuCl_2(p\text{-cymene})]_2$, these derivatives were shown to be effective in the asymmetric hydrogen transfer reduction of acetophenone. The best results (conversion: 94%, ee: 71%) were obtained with benzylamine grafted onto poly(GMA-co-EDMA) (30/70 % wt/wt).

1. Introduction

The preparation of optically active polymers presents an interesting challenge since it involves either asymmetric polymerization[1] or polymerization of an enantiopure monomer.[2] Over the last 30 years, Svec[3] and Jovanovic[4] have reported a series of articles relating to macroporous copolymer beads based on glycidylmethacrylate (GMA) and ethyleneglycoldimethacrylate (EDMA). These polymer beads provide a wide range of applications due to the presence of the epoxy groups, which react readily with various reagents. Thus epoxide derivatives have been used in ion exchange chromatography,[5–7] as ion exchange resins,[8–10] as gas chromatography stationary phases,[11] as gas sorbents,[12,13] protecting groups,[14] and enzyme immobilization agents.[15] More recently, Kuroda and Osawa[16] prepared poly(glycidylmethacrylate-co-divinylbenzene) as macroporous beads for highly adsorptive activity.

We have previously reported the synthesis of enantiopure poly((*S*)-GMA-co-EDMA) and its subsequent transformation into polyamino alcohols by means of straightforward modification of the enantiopure epoxy groups with chiral and homochiral amines.[17] Ruthenium complexes of these polyamino alcohols were used to catalyze the asymmetric hydrogen transfer reduction of acetophenone.[18,19] The best results, in terms of activity and enantioselectivity, were obtained with polyamino alcohols derived from benzylamine and methylamine. We have recently described the synthesis of aminoethanethiol trityl ether ligands for ruthenium-catalyzed asymmetric transfer hydrogenation obtaining enantioselectivities up to 85%.[20] Herein, we report the synthesis of (*S*)-GMA, (*S*)-TMA, and (*R*,*R*)-Ph-GMA monomers, as well as the copolymerization of (*S*)-GMA with EDMA or DVB and that of (*S*)-TMA or (*R*,*R*)-Ph-GMA with EDMA. The straightforward modification of the enantiopure heterocyclopropane groups with either benzylamine or methylamine was performed, in order to obtain polyamino alcohols or polyamino thiols, which were used as ruthenium ligands for asymmetric heterogeneous catalytic hydrogen transfer of acetophenone. The catalyst selectivity has been studied as a function of the specific surface area, the structure of the heterocyclopropane and the nature of the cross-linking agent of the supported ligands.

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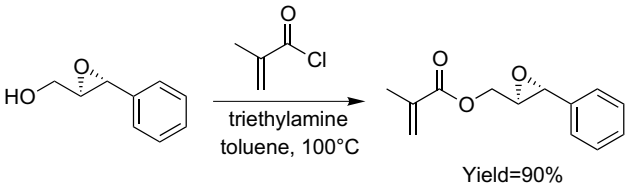
2. Results and discussion

2.1. Preparation of enantiopure monomers

In order to obtain enantiopure glycidylmethacrylate, the hydrolytic kinetic resolution of saturated terminal epoxides was attempted by using chiral cobalt-based salen as a catalyst.[21] In the presence of 0.5 mol % of [Co^{III}\{(*R*,*R*)-salen\}(OAc)] complex, the (*S*)-GMA enantiomer was obtained with an excellent enantioselectivity (greater than 99.5%) and 45% yield (selectivity factor, $S = 56$) (Scheme 1).

The synthesis of (2*R*,3*R*)-3-phenylglycidylmethacrylate (Ph-GMA) was then carried out in 90% yield by esterification of the commercially available (2*R*,3*R*)-phenylglycidol with methacryloyl chloride (Scheme 2).[22]



Scheme 2. Synthesis of enantiopure Ph-GMA.

Following Varela's methodology,[23] the enantiopure thiiranylmethylmethacrylate (TMA) was prepared from the (*S*)-GMA in a quantitative yield (Scheme 3).

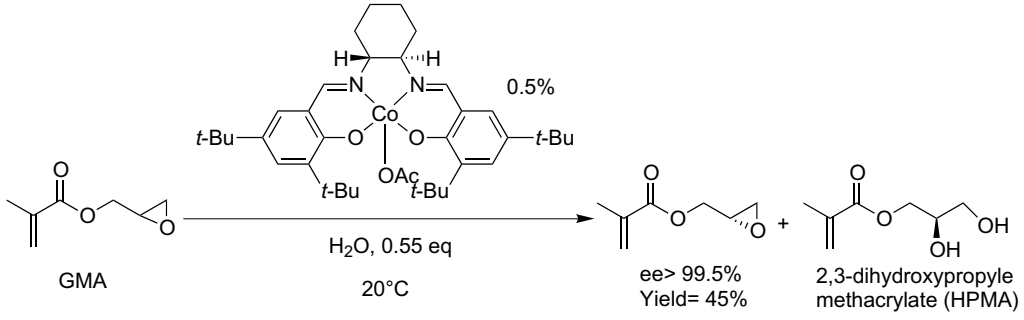
2.2. Polymerization

The copolymerization of (*S*)-GMA with EDMA or DVB, (*R*,*R*)-(Ph-GMA), and (*S*)-TMA with EDMA, were performed using radical suspension copolymerization with AIBN initiator. In order to optimize the ability of these copolymers as polymer supported catalysts, we focused our attention on the specific surface area, the nature of the cross-linking agent and the steric hindrance. As reported by Svec,[24] the specific surface area could be controlled during polymerization by changing the concentration of the cross-linking agent.

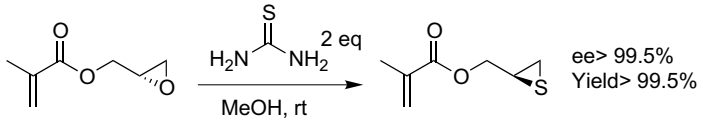
The copolymerizations were carried out in a 500 mL glass reactor equipped with a stirring anchor. The copolymerization of (*S*)-GMA, (*S*)-TMA, or (*R*,*R*)-Ph-GMA with EDMA were performed according to the procedures of Svec[3] and Jovanovic[4] (inert phase: cyclohexanol and/or dodecanol, initiator: AIBN, stabilizer: polyvinyl pyrrolidone) (Scheme 4). Poly(GMA-co-DVB) **4** was prepared following Osawa's conditions[16] using polyvinyl alcohol as a stabilizer (Scheme 4). The preparation of poly(Ph-GMA-co-EDMA) **3** was performed with 40/60 % wt/wt Ph-GMA/EDMA. These proportions correspond to a molar ratio of GMA/EDMA 30/70 % wt/wt. The copolymerization of (*S*)-TMA was carried out using only cyclohexanol as the inert phase to increase the homogeneity of the organic phase.

The level of copolymerization was determined by elemental analysis. As expected, polymer **2** (Table 1, entry 2), which contains less cross-linking agents, leads to 4.92 mmol/g of epoxy groups. For the same concentration of cross-linking agent, polymers **1** and **4** (Table 1, entries 1 and 4), show identical proportions in oxirane function (2.11 mmol/g). With poly(Ph-GMA-co-EDMA) **3** (Table 1, entry 3), the concentration of the epoxy groups was found to be 1.83 mmol/g. The poly(TMA-co-EDMA) **5** (Table 1, entry 5) contains 1.72 mmol/g of thiirane group.

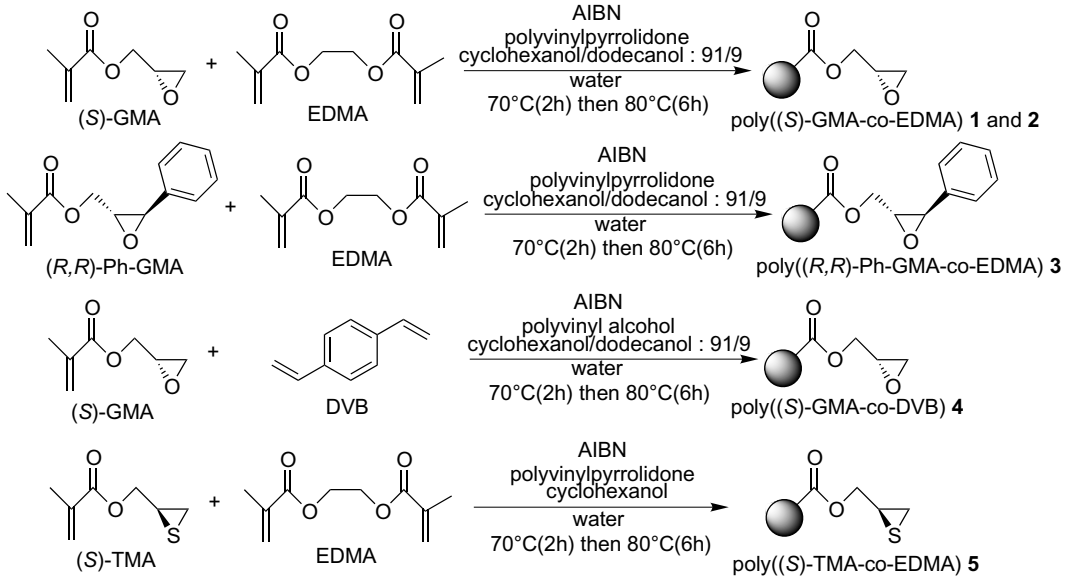
The specific surface area of these chiral copolymers was measured by B.E.T.[25] analysis (Table 1). As the cross-linked copolymers were stable at high temperatures (Kofler bench analysis), the measurements were realized after heating them at 240 °C for 3 h in vacuo without observing any noticeable deterioration. Porosity or specific surface area analyses were already realized on poly(GMA/EDMA)[16,24] and, as mentioned by Jovanovic,[4] the specific surface area depends on the ratio of GMA to EDMA. A decrease in the



Scheme 1. Hydrolytic kinetic resolution of GMA.



Scheme 3. Synthesis of enantiopure TMA.



Scheme 4. Free radical copolymerization.

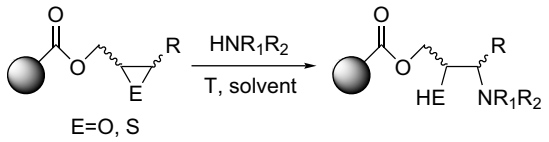
Table 1. Copolymers containing heterocyclopropane functions

Entry	Monomers (wt %)		Final polymer	f (mmol/g)	B.E.T. surface (m^2/g)
1	(S) (30)	(70)	Poly((*S*)-GMA-co-EDMA) **1**	2.11	100
2	(S) (70)	(30)	Poly((*S*)-GMA-co-EDMA) **2**	4.92	50
3	(R) (R) (40)	(60)	Poly((*R*,*R*)-Ph-GMA-co-EDMA) **3**	1.83	35
4	(S) (30)	(70)	Poly((*S*)-GMA-co-DVB) **4**	2.11	275
5	(S) (30)	(70)	Poly((*S*)-TMA-co-EDMA) **5**	1.72	92

specific surface area was observed when the concentration of EDMA decreased (Table 1, entries 1 and 2). The amount of cross-linking agent affords to the rigidity of the copolymer network and increases its specific surface area. Although polymers **4** and **5** possess the same molar ratio in cross-linking agent as polymer **1**, their specific surface areas are different. Using divinylbenzene as cross-linking agent increases the specific surface area by 2.75 (Table 1, entries 1 and 5). Compared to copolymer **1**, copolymer **5** presents a similar specific surface area showing that the nature of the heterocyclopropane has little influence on it. Compared to copolymer **1**, copolymer **3**, which contains phenyl groups presents a lower specific surface area ($35\ m^2/g$). The highest specific surface area ($275\ m^2/g$) was found for copolymer **4** using DVB as cross-linking agent (Table 1, entry 4). As these copolymers have different specific surface areas, we guess their activity would be dependent upon this factor during their modification and their use in heterogeneous catalysis (vide infra).

2.3. Grafting of amine on chiral copolymers

Polyamino alcohols **6**, **7**, **8**, **9**, **10**, and **11** and polyamino thiols **12** and **13** were prepared according to the procedure reported by Lindsay and Sherrington,[9] from oxirane-containing polymers **1**, **2**, **3**, **4**, and thiirane-containing polymer **5**, respectively, by heterocyclopropane ring opening with benzylamine or methylamine (Scheme 5).



Scheme 5. Grafting of amines onto chiral copolymers.

In the case of EDMA copolymers, we assumed that the radical polymerization was complete enough to minimize the presence of unreacted unsaturated ester groups. Therefore, we assumed the amine reacted only with the heterocyclopropane function. Moreover under these conditions, the regioselective attack at the less hindered position of the heterocyclopropane is favored.[26] Pericas[27] analyzed by ^{13}C NMR the regioselectivity of the aminolysis of the supported phenylglycidyl ether and observed selective attack at the benzyl position.

The level of functionalization of these polyamino alcohols and polyamino thiols was determined by elemental analysis of the nitrogen content (Table 6). A difference was observed between the grafting of benzylamine and that of methylamine. The levels of functionalization of benzylamine were, respectively, 85%, 49%, and 78% for polymers **1**, **3**, and **5** (Table 2, entries 1, 4, and 8), while the levels of functionalization of methylamine are, respectively, 43%, 29%, and 55% (Table 2, entries 2, 5, and 7). Benzylamine grafting onto polymer **2**, which contains more oxirane groups than polymer **1** (Table 2, entries 1 and 3), is more efficient although the specific surface area is smaller (Table 1, entry 2). Moreover, polymer **4**, having the highest specific surface area (cross-linking agent: DVB), was modified by benzylamine with a yield of 77%. Grafting the amines onto polymer **3** was less efficient than onto polymer **1**, due to the less hindered epoxide group (Table 2, entries 1, 2, 4, and 5). Polymer **5**, containing the thiirane group, attained a lower level of functionalization with benzylamine than polymer **1** (Table 2, entries 1 and 8), but was more reactive with methylamine (Table 2, entries 2 and 7).

Table 2. Functionalization ratio of epoxy polymers

Entry	Initial polymer (f_0 in mmol/g)[a]	Nucleophile	Conversion (%)[b]	Final polymer (f in mmol/g)[c]
1	**1** (2.11)	Benzylamine	85	**6** (1.46)
2	**1** (2.11)	Methylamine	43	**7** (0.85)
3	**2** (4.92)	Benzylamine	92	**8** (2.90)
4	**3** (1.83)	Benzylamine	49	**9** (0.65)
5	**3** (1.83)	Methylamine	29	**10** (0.51)
6	**4** (2.11)	Benzylamine	77	**11** (1.28)
7	**5** (1.94)	Methylamine	55	**12** (0.90)
8	**5** (1.94)	Benzylamine	78	**13** (1.11)

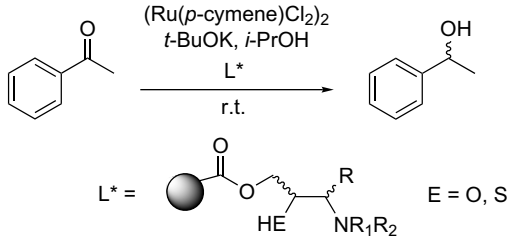
[a] f_0 = mmol of heterocyclopropane function/g of polymer.
[b] Conversion = $(\%N_{found}/\%N_{calcd}) \times 100$.
[c] $f = (f_0/(1 + f_0 M_{amine})) \times (\%N_{found}/\%N_{calcd})$.

2.4. Asymmetric hydrogen transfer reduction of acetophenone

Enantiopure amino alcohols and amino thiols, used as ligands for transition metals, are precious tools for the introduction of chirality in asymmetric catalysis of C–C, C–O, and C–H bond forming reactions.[20,28]

We chose the widely used asymmetric hydrogen transfer reduction, which is attractive because it avoids the use of pressurized hydrogen, which requires special equipment. Supported ligands are often employed and have been shown to efficiently induce enantioselectivity and can be reused.[29]

Ruthenium complexes of polyamino alcohols **6**–**11** and polyamino thiols **12**–**13** were prepared in situ using $[RuCl_2(p\text{-cymene})]_2$ as the precursor and were then involved in the hydrogen transfer reduction of acetophenone (Scheme 6). The reaction was performed under argon, with a ratio of acetophenone/Ru/ligand/*t*-BuOK of 20/1/4/5 and using isopropanol as a hydrogen donor. The results are summarized in Table 3.



Scheme 6. Hydrogen transfer reduction of acetophenone.

The ligands derived from benzylamine (Table 3, entries 1, 3, and 6) gave the best conversions and the best enantiomeric excesses (ees) compared to those modified with methylamine (Table 3, entries 2, 4, and 5). Nevertheless, ligand **7** (Table 3, entry 2) derived from methylamine was faster in converting the acetophenone. The hindrance of the phenyl group (Table 3, entries 3 and 4) decreased the activity and enantioselectivity of the ligand during the reduction. Less than 5% of the acetophenone was converted with ligand **10**. The enantioselectivity induced by both ligands **9** and **10** was lower than with the other ligands. This could be due to the presence of two asymmetric centers. The asymmetric alcohol or thiol function seemed to self-direct the enantioselectivity. The presence of the other asymmetric center unfavorably affected the enantioselectivity of the reaction. Finally, introduction of a thiol group instead of the alcohol did not give better conversions and ees (Table 3, entries 5 and 6).

Comparing the results of the benzylamine copolymer derivatives **6**, **8**, and **11**, differences in reactivity and enantioselectivity were observed (Table 4). Since copolymer **11** presents a higher specific surface area than copolymer **6**, with copolymer **11**, the conversion of acetophenone was only 58% and the ee 44%, while with copolymer **6**, the conversion was 94% and the ee 71%. A marked decrease in activity from 94% to 51% and lowered selectivity from 71% to 57% (Table 4, entries 1 and 2) were observed, respectively, for copolymers **6** and **8** when the concentration of EDMA, the cross-linking agent, was decreased (i.e., for less macroporous beads). In fact, in order to obtain highly efficient heterogeneous catalysts, it appears that, if the ligand structure is important, surface area and texture seem to be of equal importance.

Table 3. Ruthenium-catalyzed transfer hydrogenation of acetophenone: influence of the ligand

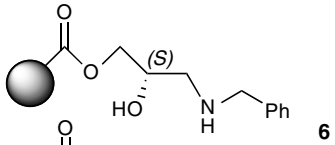
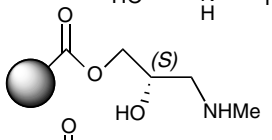
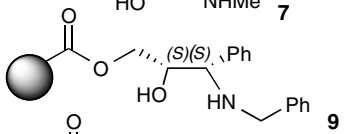
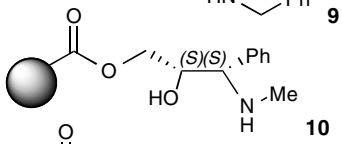
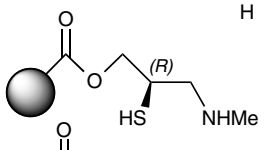
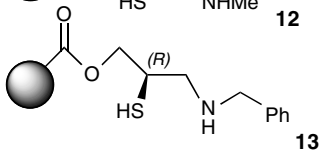
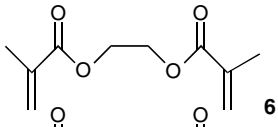
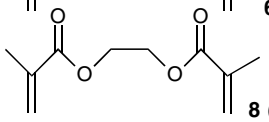
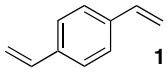
Entry	Ligand	Time (h)	Conversion (%)	ee (%) (configuration of phenylethanol)
1	 **6**	3	94	71 (*R*)
2	 **7**	1	95	65 (*R*)
3	 **9**	22	61	21 (*R*)
4	 **10**	72	<5	29 (*R*)
5	 **12**	22	50	39 (*S*)
6	 **13**	22	55	50 (*S*)

Table 4. Ruthenium-catalyzed transfer hydrogenation of acetophenone: influence of the cross-linking agent

Entry	Cross-linking agent (wt %)	Time (h)	Conversion (%)	ee (%) (configuration of phenylethanol)
1	 **6** (70%)	3	94	71 (*R*)
2	 **8** (30%)	72	51	57 (*R*)
3	 **11** (70%)	22	58	44 (*R*)

3. Conclusions

We have synthesized various chiral copolymers containing enantiopure epoxide or thiirane groups with controlled specific surface area. We have shown that these physical properties could be controlled during the copolymerization reaction by modifying the proportion and the nature of the cross-linking agent. Polyamino alcohol and polyamino thiol derivatives were obtained by the straightforward ring opening of the oxirane or thiirane with benzylamine or methylamine. They were subsequently used in ruthenium complexes for asymmetric catalytic hydrogen transfer reduction of acetophenone. We have shown that the efficiency of the catalysts depended on the specific surface area, on the nature and on the proportion of the cross-linking agent. The best results (94% activity and 71% enantioselectivity), were obtained when benzylamine was grafted onto poly(GMA-co-EDMA) 30/70 % wt/wt presenting a specific surface area of 100 m^2/g. These experiments show the significant potential of such macroporous ligands for heterogeneous asymmetric catalysis. Various substrates and metals as well as other chiral copolymers formed by means of various cross-linking agents will be investigated in order to screen the scope and limitations of these catalytic systems.

4. Experimental

4.1. General

Divinyl benzene (80%), racemic GMA (97%), EDMA (98%), (2*R*,3*R*)-phenyl glycidol (97%), methacryloyl chloride (90%), polyvinylalcohol (89%), thiourea, and dodecanol (98%) were purchased from Aldrich; (1*R*,2*R*)-1,2-diaminocyclohexane-[*N*,*N*′-bis(3,5-ditertbutylsalicydene)

cobalt(II)] from Strem; cyclohexanol, polyvinylpyrolidone 1,300,000, and AIBN (azobis isobutyronitrile) from Acros. For hydrolysis kinetic resolution of glycidyl methacrylate and hydrogen transfer reduction of acetophenone, enantiomeric excesses, and conversions were determined by GC on a Supelco β dex 225 (30 m × 0.25 mm) or Macherey-Nagel lipodex A (25 m × 0.25 mm) chiral column, using a Shimadzu GC-14A equipped with a flame ionization detector connected to a Shimadzu C-R6A integrator. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz) using TMS as the internal standard and $CDCl_3$ as solvent. Polarimetric measurements were performed on a Perkin–Elmer 241 instrument, at ambient temperature, at 589 nm concentration in grams per 100 mL solution. Elemental analyses were carried out by the CNRS (Service Central d'Analyse–Département Analyse Élémentaire), Solaize, France. B.E.T. measurements were performed on an automatic home made 'Institut de Recherches sur la Catalyse' apparatus by means of N_2 adsorption at −196 °C. Before every measurement, the support was heated to 240 °C for 3 h in vacuo. The Roberts' model was used to determine the pore size.

4.2. Preparation of enantiopure monomers

4.2.1. Preparation of enantiopure GMA monomer. Acetic acid (76 μL, 1.336 mmol) was added to a solution of (1*R*,2*R*)-1,2-diaminocyclohexane-*N*,*N*′-bis(3,5-ditertbutylsalicylidene)cobalt(II) (0.457 g, 0.668 mmol) in toluene (12 mL). After stirring for 1 h at room temperature, the solvent was removed under vacuum. Racemic glycidyl methacrylate (19 g, 133 mmol) was added to the resulting black residue, at 0 °C, followed by bidistilled water (1.2 g, 66 mmol, 0.55 equiv). The reaction mixture was stirred for 24 h at room temperature. (*S*)-Glycidyl methacrylate (6.65 g, 46.55 mmol, yield 35%) was separated from the diol by flash chromatography on silica gel (Merck 60, 40–60 mm) using dichloromethane as eluent. Ee >99.5% (determined by GC), $[\alpha]_D = +30.3$ (*c* 0.01, CH_2Cl_2).

4.2.2. Synthesis of (*R*,*R*)-phenyl glycidylmethacrylate (Ph-GMA). At 0 °C, methacryloyl chloride (8 mL, 80 mmol) and dropwise triethylamine (18.75 mL, 133 mmol) were added to a solution of (2*R*,3*R*)-phenylglycidol (10 g, 65 mmol) in toluene (100 mL). The reaction mixture was then heated at 100 °C for 3 h. At room temperature, the reaction mixture was washed with brine (3 × 50 mL), an aqueous solution of $NaHCO_3$ (3 × 50 mL), and finally dried over $MgSO_4$. After removing the solvent in vacuo, the oil obtained was purified by chromatography on aluminum oxide gel (Merck 150 type T 63-200) using heptane/ethylacetate: 9/1 as eluent. The (*R*,*R*)-phenyl glycidylmethacrylate was obtained with a yield of 90%. Ee >99.5%, $[\alpha]_D = +49.6$ (*c* 0.01, CH_2Cl_2), ^{1}H NMR (200 MHz): 1.98–2.00 (m, 1H), 3.30–3.35 (m, 1H), 3.84 (d, $J = 2$ Hz, 1H), 4.19 (dd, $J = 5.80$, 12.30 Hz, 1H), 4.57 (dd, $J = 3.3$, 12.30 Hz) 5.63–5.65 (m, 1H), 6.19–6.21 (m, 1H), 7.29–7.42 (m, 5H), ^{13}C NMR (50 MHz): 18.4, 56.5, 59.4, 64.5, 125.8, 126.4, 128.5, 128.6, 135.9, 136.3, 167.0.

4.2.3. Synthesis of (*S*)-thiiranylmethylmethacrylate (TMA). At room temperature, thiourea (10.65 g, 140 mmol) was added to a methanol solution (350 mL) of (*S*)-GMA (10 g, 70 mmol). The reaction mixture was stirred for 3 days, after which the methanol was removed under vacuum. Dichloromethane (150 mL) was added to precipitate the urea and thiourea, which were separated by filtration. After removing the solvent in vacuo, (*S*)-thiiranylmethylmethacrylate was obtained with a quantitative yield. Ee >99.5% (determined by GC), $[\alpha]_D = -37.8$ (*c* 0.01, CH_2Cl_2), ^{1}H NMR (300 MHz): 1.98 (m, 1H), 2.32 (dd, $J = 5.10$ Hz, 1.50, 1H), 2.57 (dd, $J = 6.20$ Hz, 1.50, 1H), 3.15–3.24 (m, 1H), 4.17–4.32 (m, $J = 3.3$, 12.30 Hz, 1H) 5.63–5.65 (m, 1H), 6.15–6.18 (m, 1H), ^{13}C NMR (75 MHz): 18.7, 24.2, 31.3, 68.9, 126.5, 136.4, 167.1.

4.3. Copolymerization

A solution of AIBN in a mixture of enantiopure monomer and cross-linking agent (DVB or EDMA) was added to a solution of porogen solvents (cyclohexanol and/or dodecanol). This organic mixture was added to an aqueous solution (150 mL) of stabilizer (polyvinyl pyrolidone or polyvinyl alcohol). The mixture was stirred at 600 rpm, and heated to 70 °C for 2 h and then 80 °C for a further 6 h. Two hours after allowing the mixture to cool to room temperature, the spherical particles formed were washed with acetone using a soxhlet and dried in a vacuum oven. This procedure was used for the syntheses of all the polymers using the quantities below.

4.3.1. Poly((*S*)-GMA-co-EDMA) (30/70 % wt/wt) 1. AIBN: 100 mg, (*S*)-GMA: 3 g, EDMA: 7 g, cyclohexanol: 12.06 g, dodecanol: 1.18 g, polyvinylpyrrolidone: 0.73 g. Elemental analysis: Calcd: C: 60.17, H: 7.06, O: 32.77. Found: C: 60.41, H: 7.48, O: 32.10%. Functional: 2.11 mmol/g. B.E.T. surface = 100 m^2/g.

4.3.2. Poly((*S*)-GMA-co-EDMA) (70/30 % wt/wt) 2. AIBN: 100 mg, (*S*)-GMA: 7 g, EDMA: 3 g, cyclohexanol: 12.06 g, dodecanol: 1.18 g, polyvinylpyrrolidone 0.73 g. Elemental analysis: Calcd: C: 59.50, H: 7.19, O: 33.25. Found: C: 59.86, H: 7.28, O: 32.85%. Functional: 4.92 mmol/g. B.E.T. surface = 50 m^2/g.

4.3.3. Poly((*R*,*R*)-Ph-GMA-co-EDMA) (40/60 % wt/wt) 3. AIBN: 100 mg, (*R*,*R*)-Ph-GMA: 4 g, EDMA: 6 g, cyclohexanol: 15.27 g, dodecanol: 1.56 g, polyvinylpyrrolidone: 0.63 g. Elemental analysis: Calcd: C: 65.02, H: 7.80, O: 28.18. Found: C: 62.94, H: 6.96, O: 28.88%. Functional: 1.83 mmol/g. B.E.T. surface = 35 m^2/g.

4.3.4. Poly((*S*)-GMA-co-DVB) (30/70 % wt/wt) 4. AIBN: 188 mg, (*S*)-GMA: 2.60 g, DVB: 6 g, cyclohexanol: 12.48 mL, dodecanol: 1.06 mL, polyvinylalcohol: 3 g. Elemental analysis: Calcd: C: 81.87, H: 7.75, O: 10.37. Found: C: 82.39, H: 7.98, O: 9.62%. Functional: 2.11 mmol/g. B.E.T. surface = 275 m^2/g.

4.3.5. Poly((*S*)-TMA-co-EDMA) (30/70 % wt/wt) 5. AIBN: 280 mg, (*S*)-TMA: 4 g, EDMA: 9 g, cyclohexanol: 19.2 mL, polyvinylpyrrolidone: 0.98 g. Elemental analysis: Calcd: C: 58.30, H: 6.80, O: 28.50. Found: C: 57.60, H:

Table 5. Grafting of amine onto chiral copolymers

Initial polymer (f_0 in mmol/g)[a]	Nucleophile	T (°C)	Conversion (%)[b]	Final polymer (f in mmol/g)[c]
1 (2.11)	Benzylamine (60 equiv)	100	85	**6** (1.46)
1 (2.11)	Methylamine (10 equiv, 2.0 M in THF)	50	43	**7** (0.85)
2 (4.92)	Benzylamine (60 equiv)	100	92	**8** (2.90)
3 (1.83)	Benzylamine (60 equiv)	100	49	**9** (0.65)
3 (1.83)	Methylamine 40% aq (3 equiv) with DMF	80	29	**10** (0.51)
4 (2.11)	Benzylamine (60 equiv)	100	77	**11** (1.28)
5 (1.94)	Methylamine (10 equiv, 2.0 M in THF)	50	55	**12** (0.90)
5 (1.94)	Benzylamine (60 equiv)	100	78	**13** (1.11)

[a] f_0 = mmol of heterocyclopropane function/g of polymer.
[b] Conversion = $(\%N_{found}/\%N_{calcd}) \times 100$ (Table 6).
[c] $f = (f_0/(1 + f_0 M_{amine})) \times (\%N_{found}/\%N_{calcd})$.

Table 6. Elemental analysis of grafting copolymers

Final polymer	Elemental analysis (%)	
	Calculated	Found
Poly(benzylamine-((*S*)-GMA-co-EDMA)) **6**	C: 63.54, H: 7.31, O: 26.74, N: 2.41	C: 61.12, H: 7.42, O: 29.39, N: 2.07
Poly(methylamine-((*S*)-GMA-co-EDMA)) **7**	C: 58.85, H: 7.62, O: 30.75, N: 2.78	C: 57.78, H: 7.36, O: 33.66, N: 1.20
Poly(benzylamine-((*S*)-GMA-co-EDMA)) **8**	C: 64.57, H: 7.63, O: 25.49, N: 2.30	C: 62.40, H: 7.75, O: 28.50, N: 1.35
Poly((*S*,*S*)-benzylamine-(Ph-GMA-co-EDMA)) **9**	C: 63.76, H: 7.29, O: 27.18, N: 1.76	C: 62.50, H: 7.35, O: 29.27, N: 0.86
Poly((*S*,*S*)-methylamine-(Ph-GMA-co-EDMA)) **10**	C: 63.04, H: 8.16, O: 26.40, N: 2.36	C: 62.60, H: 7.06, O: 29.64, N: 0.70
Poly(benzylamine-((*S*)-GMA-co-DVB)) **11**	C: 81.79, H: 8.05, O: 8.12, N: 2.03	C: 83.42, H: 7.44, O: 7.56, N: 1.57
Poly((*R*)-methylamine-(TMA-co-EDMA)) **12**	C: 57.40, H: 7.50, O: 27.50, N: 2.20, S: 5.30	C: 57.30, H: 7.34, O: 30.03, N: 1.22, S: 4.07
Poly((*R*)-benzylamine-(TMA-co-EDMA)) **13**	C: 61.11, H: 7.28, O: 24.99, N: 1.79, S: 4.81	C: 57.63, H: 7.26, O: 30.72, N: 1.40, S: 3.49

7.10, O: 28.60%. Functional: 1.72 mmol/g. B.E.T. surface = 92 m^2/g.

4.4. Typical polyamino alcohol or polyamino thiol synthesis

Under an argon atmosphere, the chiral copolymer was mechanically stirred (100 rpm) in the amine solution with or without solvent at the appropriate temperature for 48 h (Tables 5 and 6). The polymer was recovered by filtration and washed with water, and then for one day with acetone with a soxhlet and dried in a vacuum oven (50 °C).

4.5. Typical reduction procedure for acetophenone

Under an argon atmosphere, $[RuCl_2(p\text{-cymene})]_2$ (4 mg, 13 μmol) was introduced in a 5 mL vial with supported ligand (52 μmol) (**6**–**13**) and 2 mL of degassed isopropanol. The suspension was stirred and heated at 80 °C for 1 h, which caused the reaction mixture and polymer to turn red. The reaction was allowed to cool to room temperature and an isopropanolic solution (2 mL) of potassium *tert*-butoxide (12.8 mg, 64 μmol) and acetophenone (53 μL, 256 μmol) were added. The reaction times and ees are presented in Tables 3 and 4.

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