Chiral Ligand Controlled Helix-sense-selective Atom Transfer Radical Polymerization of 1-Phenyldibenzosuberyl Methacrylate

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The atom transfer radical polymerization (ATRP) of 1-phenyldibenzosuberyl methacrylate was carried out using (−)-sparteine (SP) as ligand. The obtained polymers showed high isotacticity, an excess of right- or left-handed helicity, and were optically active. The control of the stereochemistry might be triggered by the fact that the growing species is complexed with chiral metal complexes and thus the monomer insertion during chain propagation is controlled.

1-Phenyldibenzosuberyl methacrylate (PDBSMA) gives a nearly completely isotactic, optically active polymer with a single-handed helical conformation by asymmetric (helix-sense-selective) anionic polymerization and this polymer shows chiral recognition ability.[1] PDBSMA affords highly isotactic, helical polymer even by free-radical polymerization,[2–7] and excess helicity can be realized by using Co(II) species,[2] optically active peroxide initiator,[4,5] optically active solvent (chiral alcohols),[4,5] or chain-transfer-agent thiol compounds derived from menthol.[4,5] By using optically active chain-transfer agents,[5] a ratio of enantiomeric helices of 7/3 was achieved through the helix-sense-selective termination of a growing radical.

CuX(I)–ligand complexes are widely used as transfer agents for the ATRP of vinyl monomers and acrylate monomers.[8–12] Several chiral metal complexes were examined for possible stereochemical control.[10,13–16] However, the chiral catalysts did not significantly affect the tacticity, let alone provide helical polymer. Okamoto and Nakano achieved helical polymerization in the presence of cobalt(II)–chiral ligand complexes using AIBN as initiator.[2,17] However, the helix-sense-selective polymerization of PDBSMA by ATRP has not been reported so far.

In the present work, we performed the atom-transfer radical polymerization of PDBSMA in the presence of CuBr–chiral ligand complexes using (1-bromoethyl)benzene (beb) as initiator (Scheme 1). The polymers obtained by using the ATRP method had a high isotacticity and an excess of right- or left-handed helicity and were optically active. Furthermore a narrower

polydispersity index (PDI) (1.32–1.40) is observed compared to the simple radical polymerization.

PDBSMA was prepared according to a method reported by Okamoto.[5] Sparteine (Aldrich) was distilled under reduced pressure over calcium hydride and stored under an argon atmosphere at 0 °C in the dark. CuBr was prepared from CuBr$_2$ and further purified according to a method of Keller and Wycoff.[18] (1-Bromoethyl)benzene (beb) was purchased from Acros and used without further purification.

The results of polymerization are summarized in Table 1. The polymerization in toluene gave an almost completely isotactic polymer [triad isotactic content (mm) > 99%] (Figure 1), regardless of whether ligands used in the polymerization were achiral (Table 1, Runs 1 and 2) or chiral (Table 1, Runs 3–8), similarly to prevously reported results.[3] Compared to the simple radical polymerization of PDBSMA (Table 1, Run 11),[3] the conversion rate is lower, however the PDI is narrower (1.32–1.36) (Table 1, Runs 3–5). The polymerization

Table 1. Free-radical polymerization of PDBSMA with beb in the presence of CuBr–ligand in toluene for 24 h[a]

| Run	Ligand (mmol)	T/°C	Yield[b] /%	PDI[c]	DP[c]	THF-sol. part[i]	
						DP	$[\alpha]_{365}$/deg
1	**4** (0.17)	60	17	1.56	50	17	0
2[d]	**4** (0.17)	60	15	1.57	56	17	0
3	**1** (0.17)	60	31	1.32	58	16	+149
4	**1** (0.17)	50	19	1.36	57	16	+144
5	**1** (0.17)	40	8	1.35	55	16	+140
6	**1** (0.23)	60	29	1.36	57	16	+149
7	**1** (0.11)	60	34	1.40	59	17	+112
8	**1** (0.06)	60	32	1.35	62	15	+73
9	**2** (0.17)	60	0				
10	**3** (0.17)	60	0				
11[e]	—	60	69	2.34	179		
12[f]	**1** (0.17)	60	80	2.88	100	41	0
13[g]	**1** (0.17)	60	80	2.34	82	33	−17
14[h]	**1** (0.17)	60	60	1.70	58	20	+105

[a]Conditions: monomer, 500 mg (1.4 mmol); toluene, 4 mL; beb, 5.3 mg (0.028 mmol); CuBr, 8.2 mg (0.056 mmol). [b]MeOH-insoluble part of the products. [c]Determined by GPC of poly(MMA) derived from the poly(PDBSMA) with polystyrene standards. [d]Initiator: (+)-ethyl (2s,3s)-2-bromo-3-methylpentanoate. [e]The literature data. Initiator: AIBN. See ref. 3. [f]Polymerization with AIBN (4.6 mg, 0.028 mmol)–SP only. [g]Polymerization with AIBN (4.6 mg)–beb (5.3 mg)–SP only. [h]Polymerization with AIBN (4.6 mg)–CuBr–SP only. [i]The yield of THF-sol. part is 1–2%.
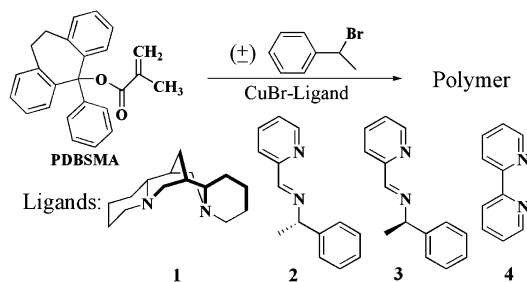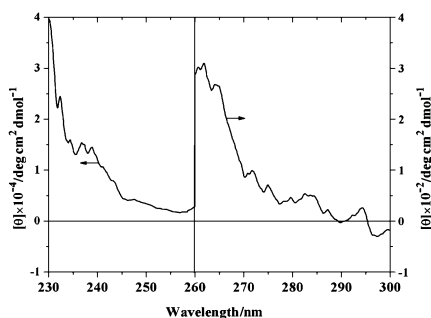

Scheme 1. ATRP of PDBSMA in the presence of CuBr(I)–ligand complex.
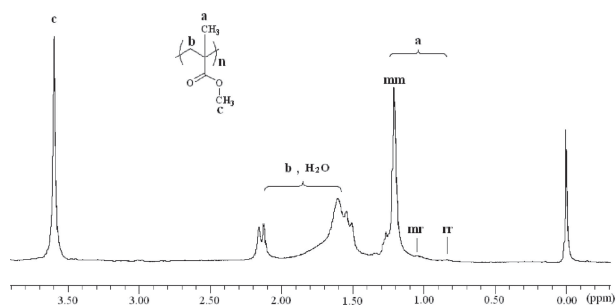
Figure 1. ^{1}H NMR spectrum of PMMA derived from poly-(PDBSMA) prepared at 60 °C in toluene (Table 1, Run 3) (CDCl$_3$, TMS).


Figure 2. CD spectrum of the THF-soluble polymer of Run 3 in Table 1.

did not occur when the ligands **2** or **3** were used (Table 1, Runs 9 and 10), perhaps this is caused by the space structure of the Cu–ligand complexes. The obtained polymers were not completely soluble in THF or chloroform and were fractionated into THF-insoluble and THF-soluble fractions having higher and lower molecular weights, respectively. In addition, the conversion of the polymerization was low, probably caused by the formation of precipitate in the system.

The THF-soluble polymers exhibited dextrorotation, which suggests that the polymers have a chiral structure. The reaction temperature has little influence on the magnitude of optical rotation, but the conversion of the polymerization increased when the temperature is increased (Table 1, Runs 3–5). With the increase of the ratio of (−)-SP/beb from 2:1 to 6:1, the magnitude of optical rotation increased (Table 1, Runs 3, 7, and 8). Yet it is essentially unchanged when the ratio of (−)-SP/beb exceeds 6:1 (Table 1, Run 6). Figure 2 shows the CD spectrum of the THF-soluble polymer obtained in Run 3. The spectral pattern was quite similar to that of the one-handed helical polymer obtained by asymmetric anionic polymerization[1] and that of the helical polymer obtained in the presence of cobalt(II)–chiral ligand complexes[2] although the CD intensity (at 240 nm) was lower. The CD characteristic of the poly-PDBSMA is in concert with its rotation: Both the rotation of poly-PDBSMA and the CD Cotton effect of it are positive. The chiroptical properties suggest that the polymer has a helical conformation with an excess of one-handed helical sense in solution.

Thus, the results obtained in this work indicate that chiral ligand can induce an excess of single-handed helical structure in the ATRP of PDBSMA. The chiral induction probably results from the chiral ligand coordinated with the active species, and
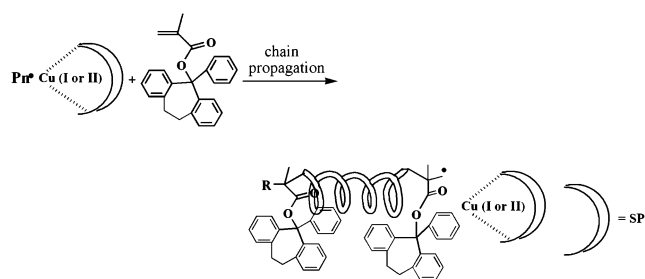
Figure 3. Chiral ligand controlled helix-sense-selective polymerization of PDBSMA.

this Cu–chiral ligand complex has a certain stereointeraction with the growing polymer radical during chain propagation (Figure 3). The chiral induction may be caused by the dormant species or the activated species.

These assumptions are supported by the following experiments: (1) Polymerization of PDBSMA using (+)-ethyl (2s,3s)-2-bromo-3-methylpentanoate as chiral initiator in the presence of achiral ligand 2,2′-bipyridine, gave nonoptical activity polymers (Table 1, Run 2). It is indicated that the chiral initiator, which has been used in this experiment cannot induce a helix-sense-selective polymerization; (2) Polymerization of PDBSMA with AIBN–SP without beb and CuBr, gave an optically inactive polymer. This means SP does not exist near the growing radical species during the initiation or propagation, and cannot induce the formation of helical polymer; (3) Even in polymerization of PDBSMA with AIBN–beb–SP without CuBr, the inductive effect is very low ($[\alpha]_{365} = -17°$); (4) Polymerization of PDBSMA with AIBN–CuBr–SP without beb, gave an optically active polymer ($[\alpha]_{365} = +105°$). It is suggested that Cu–SP complexes have a certain stereointeraction with the growing polymer radical, and induce the formation of helical polymer. Cu plays a role similar to the bridge, and it is essential for helix-sense-selective ATRP. The stereochemical effect of chiral ligand is in contrast to the fact that one usually cannot observe any influence on the tacticity of the products during the radical polymerization of vinyl monomers and acrylate monomers in the presence of chiral metal complexes.[13–15,19–21] Although the mechanism of chiral induction observed in this work is not immediately clear, it is assumed that the polymerization of PDBSMA proceeds only through the right- and left-handed helical radicals and that the two chiral radicals have different interactions or binding constants with Cu–SP. This should lead to different apparent propagation rates of the two radicals giving different molecular weights of the products derived thereof.

In conclusion, the atom-transfer radical polymerization of PDBSMA in the presence of chiral ligand (−)-SP afforded an optically active, helical polymer. In contrast to the absence of control of the stereochemistry during the radical polymerization of vinyl monomers in the presence of chiral metal complexes, the atom-transfer radical polymerization of PDBSMA by Cu(I)–SP gave not only an almost perfect isotacticity but also an excess of one-handed helical conformation. Furthermore a narrower PDI (1.32–1.40) is observed compared to simple radical polymerization. Our research indicates that the control of tacticity and the synthesis of helical polymer by ATRP are feasible by using chiral metal complexes as transfer agents.

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