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Helix-Sense-Selective Free-Radical Polymerization of 1-Phenyldibenzosuberyl Methacrylate Using a Cobalt(II) Complex

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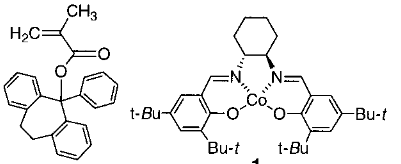
Introduction. 1-Phenyldibenzosuberyl methacrylate (PDBSMA) gives a highly isotactic, optically active polymer having a single-handed helical conformation by asymmetric (helix-sense-selective) anionic polymerization, and the polymer shows chiral recognition ability.[1] PDBSMA gives a nearly completely isotactic, helical polymer even by free-radical polymerization,[2] and excess helicity can be realized when the polymerization is carried out in the presence of optically active chain-transfer agents, including thiol compounds derived from menthol.[3] By using this method, a ratio of enantiomeric helices of $^{7}/_{3}$ was achieved through the helix-sense-selective termination of a growing radical.

In the present work, we performed the free-radical polymerization of PDBSMA in the presence of chiral (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminatocobalt(II) (**1**) and investigated the stereochemistry of the polymerization. Cobalt(II) complexes are known to interact with the growing radicals of vinyl monomers.[4−9] Several cobalt(II) complexes have been reported to act as chain-transfer agent during methacrylate polymerization giving a polymer with an ω-end vinylidene structure,[4−8] and there is an example of living radical polymerization of acrylates using a porphyrin complex.[8] However, cobalt(II) complexes have not been used for the purpose of the stereochemical control of a polymerization reaction.[9]



PDBSMA

1

Complex **1** has been known as an efficient catalyst of enantioselective ring-opening reactions of epoxies,[10a,b] and its synthesis and structure have been reported in detail.[10c,11]

Experimental Section. Materials. Complex **1** was synthesized by the reaction of $Co(OAc)_2$ with (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine[10c] by the literature method[11] with modifications. Field desorption (FD) mass = 603.3. Anal. Calcd for $C_{36}H_{52}CoN_2O_2$: C, 71.62; H, 8.68; Co, 9.67; N, 4.64; O, 5.30. Found: C, 71.68; H, 8.68; N, 4.56.

The method of PDBSMA synthesis has been reported elsewhere.[3b] Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Chloroform and pyridine were purified by distillation and stored under a nitrogen atmosphere.

Polymerization. Polymerization was carried out under a nitrogen atmosphere. PDBSMA, AIBN, and **1** were dissolved in a mixture of chloroform and pyridine, and the solution was heated to 60 °C. The products were precipitated in methanol and isolated with a centrifuge. The methanol-insoluble product was fractionated into tetrahydrofuran (THF)-insoluble and -soluble parts. The obtained poly(PDBSMA)s were converted to PMMAs by the reported method.[3b] Tacticity of the polymers was determined by ^1H NMR analysis of the PMMAs. The degree of polymerization (DP) of the polymers was determined by GPC analysis of the original polymers or by the analysis of the PMMAs using standard polystyrenes. In the GPC analysis of the original polymers, DP was estimated according to the relation between Mn and DP known for isotactic poly[1-(2-pyridyl)dibenzosubery methacrylate], i.e., $DP = 2.6 \times Mn/354$.[1]

Measurements. The ^1H NMR spectra were obtained using a Varian VXR-500 spectrometer (500 MHz for ^1H measurement). Circular dichroism (CD) spectra were obtained using a JASCO J-720L spectrometer. The GPC analysis of poly(PDBSMA) was performed with a Shodex System-21 GPC equipped with a Shodex UV-41 detector and a JASCO OR-990 polarimetric (α_{Hg}) detector using Shodex KF-803 and KF-806F GPC columns connected in series (eluent, THF; flow rate, 1.0 mL/min; temp, 40 °C). A Shodex RI-71S detector was used in place of the UV-41 for the GPC analysis of PMMA.

Results and Discussion. The conditions and results of polymerization are summarized in Table 1. The polymerization in chloroform (run 1) and that in a chloroform−pyridine mixture (run 2) gave an almost completely isotactic polymer [triad isotactic content (mm) > 99%] similarly to the reported polymerization in toluene, indicating that the stereochemistry of the free-radical polymerization of PDBSMA is not affected by the solvent. The polymerizations in the presence of **1** in a chloroform−pyridine mixture also gave almost completely isotactic polymers (runs 3−5), whereas the polymerization using **1** in pure chloroform led to no polymer (run 7). Comparison of run 1 with run 7 indicates that **1** acts as an inhibitor of the polymerization in the absence of pyridine. The obtained polymers were not completely soluble in tetrahydrofuran (THF) or chloroform and were fractionated into THF-soluble and -insoluble parts having higher and lower molecular weights, respectively. With a larger amount of **1**, the polymer yield was lower and the ratio of the THF-soluble fraction in the products was higher. In addition, the DP of the MeOH-insoluble product was smaller when **1** was used (runs 2 and 4). These result may suggest that the interaction between **1** and the growing radical reduces the rate of propagation.

The THF-soluble polymers exhibited dextrorotation, which suggests that the polymers have a chiral structure. The specific rotation values were estimated by GPC analysis (vide infra). The magnitude of optical activity depended on the reaction conditions, and the polymer obtained in run 4 exhibited the highest value. Figure 1 shows the CD spectrum of the THF-soluble polymer obtained in run 4. The spectral pattern was quite similar to that of the spectrum for the one-handed helical polymer obtained by asymmetric anionic poly-

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Table 1. Free-Radical Polymerization of PDBSMA with AIBN in the Presence of 1 in a Chloroform−Pyridine Mixture at 60 °C for 24 h[a]

				THF-soluble part			
run	[**1**]$_o$, M	[pyridine]$_o$, M	yield,[b] %	yield, %	DP[c]	Mw/Mn[c]	$[\alpha]_{365}$,[d] deg
1	0	0	74[e]	4	22	1.24	
2	0	0.51	86[f]	3	19	1.27	
3	0.011	0.54	59	2	19	1.20	+270
4	0.039	0.50	39[g]	3	19[h]	1.18	+550
5	0.057	0.54	16	4	19	1.19	+160
6	0.13	0.51	0				
7	0.039	0	0				

[a] Conditions: monomer 0.5 g, $[\text{monomer}]_o = 0.44-0.45$ M, $[\text{AIBN}]_o = 0.029-0.031$ M. [b] MeOH-insoluble part of the products. [c] Determined by GPC of poly(PDBSMA). [d] Estimated based on GPC curves obtained by UV and polarimetric detections (see text). [e] DP = 155 ($Mw/Mn = 3.72$) as determined by GPC of PMMA.[f] DP = 170 ($Mw/Mn = 2.78$) as determined by GPC of PMMA. [g] DP = 78 ($Mw/Mn = 1.60$) as determined by GPC of PMMA. [h] DP = 20 ($Mw/Mn = 1.14$) as determined by GPC of PMMA.

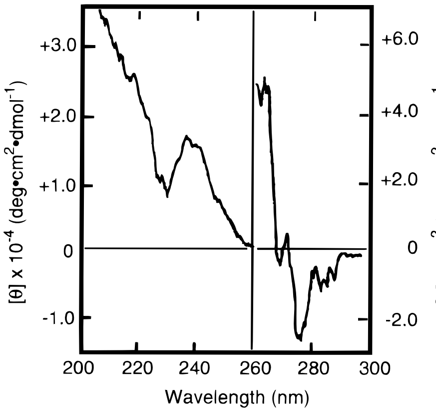

Figure 1. CD spectrum of the THF-soluble polymer of run 4 in Table 1.

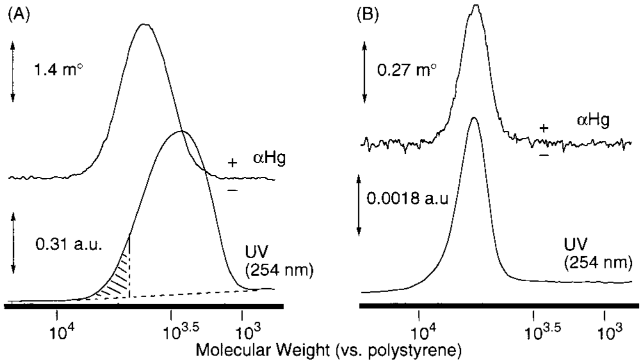

Figure 2. GPC curves obtained by polarimetric (top) and UV (bottom) detectors of (A) the THF-soluble polymer of run 4 in Table 1 and (B) the high-molecular-weight fraction separated from the THF-soluble polymer.

merization[1] although the absorption intensity (at 240 nm) was about one-quarter of that of the spectrum of the one-handed helical polymer. The chiroptical properties and the highly isotactic main-chain configuration suggest that the THF-soluble polymer has a helical conformation with excess helical sense. To obtain information about the chiral structure of the polymer, GPC analysis was performed using UV and polarimetric detectors (Figure 2A). The GPC curves indicate that the polymer does not contain levorotatory fractions and the higher-molecular-weight fractions show higher optical activity. On the basis of the intensity ratio of the polarimetric and UV chromatograms, specific rotation of the polymer was estimated to be $[\alpha]_{365}$ +550° using the one-handed helical polymer[1] ($[\alpha]_{365}$ +1778°) as a standard sample. From the CD intensity and the estimated specific rotation, the polymer is considered to have about 25−30% excess of right- or left-handed helical sense. GPC fractionation of the high-molecular-weight part (shaded area in Figure 2A) gave 8 wt % of the THF-soluble part having a DP of 43 whose GPC curves obtained by UV and polarimetric detection were in good agreement (Figure 2B). Specific rotation of this fraction was estimated to be $[\alpha]_{365}$ +1600° and this fraction showed the CD bands whose intensity was comparable to that of the spectrum of the one-handed helical polymer obtained by anionic polymerization,[1] suggesting that the polymer has an almost single-handed helical conformation. This result along with the fact that higher-molecular-weight fractions show higher optical activity in the GPC analysis of the THF-soluble part may suggest that the THF-insoluble polymer, which is the majority of the polymerization products, may have a single-handed helical structure.

Thus, the results obtained in this work indicate that **1** can induce a single-handed helical structure in the radical polymerization of PDBSMA. The chiral induction is based most probably on the interaction of the Co(II) radical with the growing polymer radical. This assumption is supported by a polymerization experiment in the presence of (*R*,*R*)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine without a metal center which led to a polymer with negligible optical activity. The stereochemical effect of **1** is in contrast to the fact that during the radical polymerization of vinyl monomers mediated by metal complexes, usually one cannot observe any influence of the metal species on the tacticity of the products.[6,8] 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 chiral **1**. This should lead to different apparent propagation rates of the two radicals giving different molecular weights of the products derived therefrom. The dependence of optical activity on DP (Figure 2A) is indicative of a mechanism that both helical senses are formed at a low DP of growing species and one of the two has stronger interaction with **1**, resulting in a lower apparent propagation rate.

On the basis of the NMR analyses of the PMMAs derived from the poly(PDBSMA)s obtained in run 3, the existence of the ω-end vinylidene structure was not clearly confirmed, suggesting that the interaction between **1** and the growing species in the present reaction systems does not involve β-hydrogen elimination and that the polymerization mechanism in the present systems involving **1** is different from the typical catalytic chain transfer known for methacrylate polymerization in the presence of Co(II) species.[4−7] Efforts are under way to clarify the mechanism and to learn the applicability of the present method to other radical polymerization systems.

Conclusion. The free-radical polymerization of PDBSMA in the presence of **1** afforded an optically active, helical polymer. The GPC separation of the optically active polymer gave the polymer whose helical structure appeared to be almost single-handed.

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