Enantioselective Cyclopolymerization of Benzaldehyde Divinyl Acetal with a Chiral 10-Camphorsulfonic Acid/Zinc Dichloride Initiating System

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Received September 17, 1992
Revised Manuscript Received January 13, 1993

A continuous effort has been made for the syntheses of optically active polymers that are investigated with the aim of obtaining chiral catalysts for asymmetric syntheses, chiral materials for enantiomer separation, and biologically active polymers.[1] Asymmetric cyclopolymerization has recently developed as one of the most important methods for synthesizing optically active polymers.[2] Waymouth et al. reported the enantioselective cyclopolymerization of 1,5-hexadiene with a chiral metallocene catalyst.[3] Recently, we reported the synthesis of optically active poly(methyl methacrylate) by the cyclopolymerization of 2,3-*O*-isopropylidene-1,4-di-*O*-methacryloyl-L-threitol with azobis(isobutyronitrile) (AIBN), in which the chirality of L-threitol units directly transferred to the methacrylate main chain.[4]

Another useful hint as to a methodology of asymmetric cyclopolymerization can be found in living polymerization. Higashimura et al. have established that suitable combinations of an electrophile and a Lewis acid lead to initiating systems for the cationic living polymerization of vinyl ethers.[5] According to the mechanism for this polymerization, the vinyl ether ($ROCH{=}CH_2$) and the electrophile (HB) form an adduct ($ROCHBCH_3$) whose C–B bond is stable and is activated by the Lewis acid. The formation of this bond may exert a strong influence on the stereochemistry of the approaching monomer. One possibility, therefore, exists that the initiating system using a chiral electrophile might act as a enantioselective catalyst for the cyclopolymerization of the achiral divinyl monomer. Here we report the cyclopolymerization of benzaldehyde divinyl acetal (**1**)[6] with a (+)- and (−)-10-camphorsulfonic acid [(+)- or (−)-**2**]/zinc dichloride ($ZnCl_2$) initiating system (Scheme I).

Divinyl acetal **1** in toluene was treated with a solution of **2** in tetrahydrofuran, and then the polymerization was initiated by adding a solution of $ZnCl_2{\cdot}OEt_2$ in dichloromethane.[7] Table I lists the results of the cyclopolymerization of **1** with the (+)- or (−)-**2**/$ZnCl_2{\cdot}OEt_2$ initiating system. Although the polymerizations proceeded heterogeneously, the resulting polymers (**3**) were soluble in chloroform and tetrahydrofuran. The polymer was purified several times by reprecipitation with chloroform/methanol until a constant specific rotation of the polymer was reached. The number-average molecular weights (M_n) of the polymers were from 2000 to 2500 which corresponded to the polymerization degrees (P_n) from 11.4 to 14.2. These P_n values were smaller than the [1]/[2] ratio of 40, and the molecular weight distributions were broad, having a M_w/M_n ratio of 1.39–2.02. The nonliving character of this cyclopolymerization should be caused by the heterogeneous polymerization system.

Figure 1 shows the ^1H and the ^{13}C NMR spectra of polymer **3** prepared with (+)-**2**. The characteristic absorptions at 6.4–6.8 ppm due to the vinyloxy groups and at 147.3 ppm due to the vinyl carbon disappeared in the ^1H and ^{13}C NMR spectra of polymer **3**, which means that

Scheme I

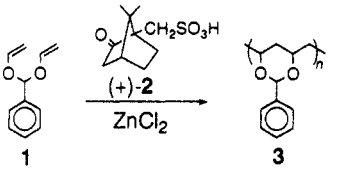

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Table I
Cyclopolymerization of Benzaldehyde Divinyl Acetal (1) with a (+)- or (−)-10-Camphorsulfonic acid [(+)- or (−)-2]/$ZnCl_2$ Initiating System[a]

2[b]	$[ZnCl_2{\cdot}OEt_2]/[2]$	yield (%)	M_n[c] × 10^{-3}	M_w/M_n[c]	$[\alpha]^{20}_{435}$[d]
+	0.5	20	2.0	1.64	−17.0
+	1.0	27	2.4	1.39	−17.1
−	0.5	27	2.4	1.50	+13.7
−	1.0	45	2.5	2.02	+11.9

[a] [1] = 0.30 M, [1]/[2] = 40; temp, 0 °C; time, 24 h. [b] The sign of the specific rotation of **2**. [c] Determined by GPC (polystyrene standard). [d] *c* 1.0, $CHCl_3$.

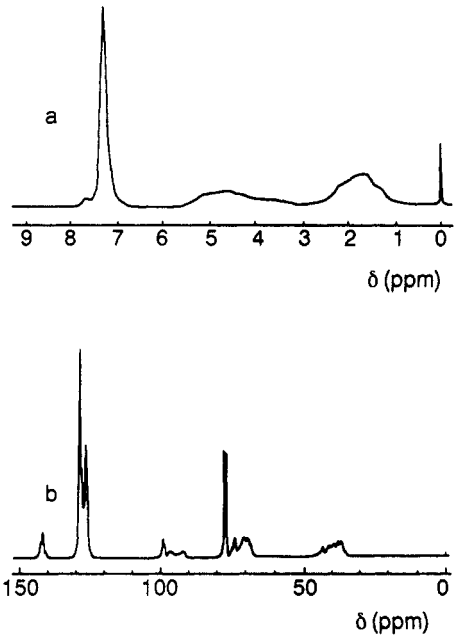

Figure 1. ^1H (a) and ^{13}C (b) NMR spectra of polymer **3**, prepared by cyclopolymerization of benzaldehyde divinyl acetal (**1**) with (+)-**2**/$ZnCl_2{\cdot}OEt_2$ (molar ratio 1.0), measured in $CDCl_3$ at 21 °C.

polymer **3** consisted of only the cyclic repeating units. Since the cyclopolymerization of divinyl ethers with a cationic initiator proceeds through a head-to-tail addition,[8,9] the constitutional units of the polymers should be essentially the cyclic structure corresponding to the 1,3-dioxane.

Polymer **3** prepared using (+)-**2** exhibited optical activity with a specific rotation ($[\alpha]^{20}_{435}$, *c* 1.0 in $CHCl_3$) of −17.0 and −17.1 [polymer (−)-**3**] and those using (−)-**2** exhibited optical activity with a specific rotation of +11.9 and +13.7 [polymer (+)-**3**]. Four possible structures **5**–**8** (Chart I) are considered for the cyclic units of polymer **3**, in which only **5** and **6** with a trans configuration are chiral. The optical activity of the polymer **3** arises from the chiral cyclic units corresponding to **5** or **6**. (4*S*,6*S*)-(−)- and (4*R*,6*R*)-(+)-4,6-dimethyl-2-phenyl-1,3-dioxane [(*S*,*S*)- and (*R*,*R*)-**4**, respectively],[10] whose configurations are identical to those of **5** and **6**, respectively, were synthesized as model compounds in order to confirm the absolute configuration of the cyclic units. A negative specific rotation ($[\alpha]^{20}_{435}$ = −31.3, *c* 1.7 in $CHCl_3$) was found for the model compound (*S*,*S*)-**4**, having the same sign as that of polymer **3** prepared

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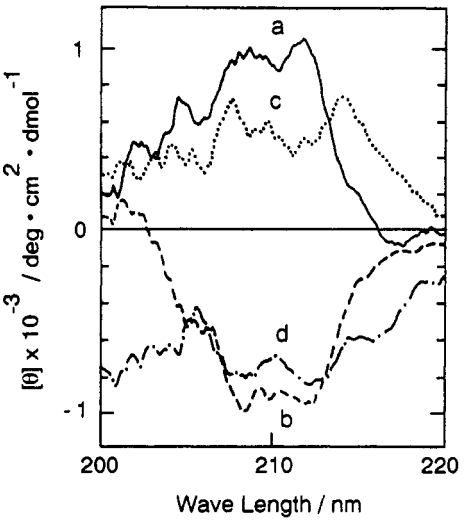
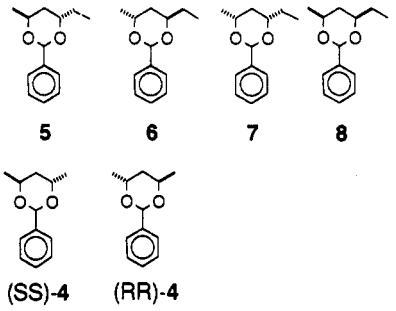


Figure 2. CD spectra of the model compounds and the chiral polymers **3**: (a) (4*S*,6*S*)-(−)-4,6-dimethyl-2-phenyl-1,3-dioxane [(*S*,*S*)-**4**]; (b) (4*R*,6*R*)-(+)-4,6-dimethyl-2-phenyl-1,3-dioxane [(*R*,*R*)-**4**]; (c) polymer (−)-**3** prepared from benzaldehyde divinyl acetal (**1**) with (+)-**2**/$ZnCl_2$·OEt (molar ratio 1.0); (d) polymer (+)-**3** prepared with (−)-**2**/$ZnCl_2$·OEt_2 (molar ratio 1.0). All spectra were measured at 21 °C in hexafluoroisopropyl alcohol, and the path length was 0.5 cm: $c = 3.4 \times 10^{-4}$ M for (a), 2.6×10^{-4} M for (b), 3.3×10^{-4} M for (c), and 3.6×10^{-4} M for (d).

Chart I



with (+)-**2**. A positive one ($[\alpha]^{20}_{435} = +31.6$, *c* 1.6 in $CHCl_3$) for (*R*,*R*)-**4** was the same sign as that of (+)-**3** prepared with (−)-**2**.

Figure 2 shows the CD spectra of polymers (−)- and (+)-**3** ($[\alpha]^{20}_{435} = -17.1$ and +13.7, respectively) and model compounds (*S*,*S*)- and (*R*,*R*)-**4**. Both (−)-**3** and (*S*,*S*)-**4** show the negative Cotton effect at 210 nm, and (+)-**3** and (*R*,*R*)-**4** show the mirror image CD curves with the positive Cotton effect at 210 nm. The absolute configuration of the major, chiral cyclic units in polymer (−)-**3** should correspond to **5**, and that in polymer (+)-**3**, to **6**.

In summary, we report the enantioselective synthesis of a main-chain chiral polymer by the cyclopolymerization of a divinyl monomer using the initiating system consisting of chiral alkylsulfonic acid and Lewis acid. More detailed studies including the mechanism of the present asymmetric cyclopolymerization are now in progress.

References and Notes

(1) Ciardelli, F. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1987; Vol. 10, p 463.
(2) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 21.
(3) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270.
(4) Kakuchi, T.; Kawai, H.; Katoh, S.; Haba, O.; Yokota, K. *Macromolecules* **1992**, *25*, 5545.
(5) Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 131.
(6) Matsoyan, S. G. *J. Polym. Sci.* **1961**, *52*, 189.
(7) The solution of $ZnCl_2$ in diethyl ether is usually used in the living polymerization of vinyl ethers (see ref 5). For the polymerization of **1** with **2**, however, 5 equiv of $ZnCl_2$ to **2** was necessary. Here, $ZnCl_2$·OEt_2 as a solution in dichloromethane, a more efficient Lewis acid, was used instead of $ZnCl_2$ as a solution in diethyl ether. A typical polymerization procedure is as follows: To a solution of **1** (0.32 g, 1.6 mmol) in toluene (6 mL) was added a 1.0 M solution (45 μL) of (+)-**2** (0.045 mmol) in tetrahydrofuran at 0 °C. After 1 h, the polymerization was initiated by adding a 2.2 M solution (20 μL) of $ZnCl_2$·OEt_2 (0.044 mmol) in CH_2Cl_2 at 0 °C. The mixture was kept at 0 °C for 15 h and then poured into ammoniacal methanol. The resulting white powder was purified by reprecipitation with chloroform–methanol.
(8) Butler, G. B.; Lien, Q. S. *Cyclopolymerization and Polymer with Chain Ring Structure*; ACS Symposium Series 195; American Chemical Society: Washington, DC, 1982; p 145.
(9) Kakuchi, T.; Haba, O.; Yokota, K. *Macromolecules* **1992**, *25*, 4854.
(10) (*S*,*S*)-**4** was prepared as follows: A solution of (2*S*,4*S*)-2,4-pentanediol (1.0 g, 9.6 mmol), benzaldehyde dimethyl acetal (1.6 g, 10 mmol), and *p*-toluenesulfonic acid (50 mg) in dry *N*,*N*-dimethylformamide (3.5 mL) was refluxed at 60 °C for 1 h under reduced pressure. After cooling to room temperature, 10% aqueous sodium carbonate (5 mL) and ether (10 mL) were added. The organic layer was washed with three 5-mL portions of brine, dried over anhydrous $MgSO_4$, and evaporated, and then the residue was distilled to give a product as a colorless liquid: bp 94–97 °C (0.5 mmHg); yield 1.2 g (65%); $[\alpha]^{20}_D$ −15.8 (*c* 1.7, $CHCl_3$). (*R*,*R*)-**4** was also obtained from (2*R*,4*R*)-2,4-pentanediol and benzaldehyde dimethyl acetal: bp 102–106 °C (0.8 mmHg); yield 1.0 g (54%); $[\alpha]^{20}_D$ +16.8 (*c* 1.9, $CHCl_3$).
(11) CD spectra were measured at 20 °C in hexafluoroisopropyl alcohol (HFIP) with 0.5-cm path length using a Jasco J-720 spectropolarimeter.