

A new chiral poly(alkyl vinyl ether): Synthesis and chiroptical properties

Emo Chiellini*, Laura Senatori, and Roberto Solaro

Department of Chemistry and Industrial Chemistry, CNR Center of Stereoordered Optically Active Macromolecules, University of Pisa, Via Risorgimento 35, I-56100 Pisa, Italy

SUMMARY

The paper reports on the synthesis and characterization of a new chiral alkyl vinyl ether derived from the head-to-tail dimer of (S)-1,2-propanediol having high optical purity. The prepared vinyl ether has been polymerized in the presence of different cationic catalysts and the polymer optical rotation has been reported and commented in respect to the structure of the starting monomer.

INTRODUCTION

The synthesis and the study of the chiroptical properties of optically active poly(alkyl vinyl ether)s with different tacticity has constituted the object of extensive investigation aimed at establishing the correlation between their optical rotation and conformation in solution (1-4).

As a part of this continuing interest, also connected at the present with the synthesis of chiral semiflexible liquid crystalline polyesters (5-7) and functional polymers for catalytic applications (8), we have been involved in the preparation of structurally and stereochemically defined propylene glycol oligomers (9). Monoalkyl derivatives of these last oligomers have been converted to the corresponding alkyl vinyl ethers whose polymerizability as well as the characterization of the corresponding polymers became matter of interest and development.

In this context the present communication reports on the synthesis of the vinyl ether of the monobenzyl derivative of the head-to-tail dimer of propylene glycol [(4S,7S)-10-phenyl-4,7-dimethyl-3,6,9-trioxa-1-decene (1)], its polymerizability with different catalysts and the characterization of the corresponding homopolymers.

EXPERIMENTAL

(2S,5S)-8-phenyl-5-methyl-4,7-dioxa-2-octanol (2)

By following the procedure reported in Scheme, optically active **2**, having b.p. 103°C/0.2 mm, $\alpha_D^{25} +15.3$ (neat) {lit. $\alpha_D^{25} +15.26$ (9)} and $[\phi]_D^{25} +24.6$ (cyclohexane) was prepared in 28% yield from commercial (-)-ethyl lactate (9).

(4S,7S)-10-phenyl-4,7-dimethyl-3,6,9-trioxa-1-decene (1)

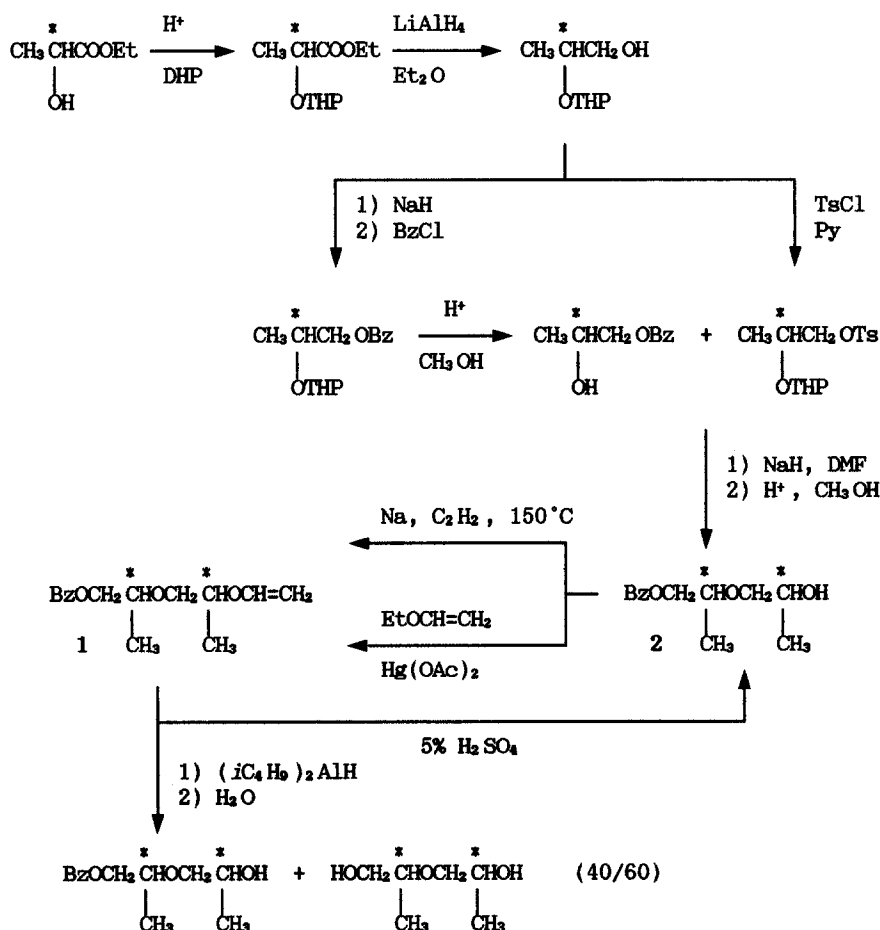
By direct vinylation (10)

In a 35 ml vial were placed under dry nitrogen atmosphere, 15.04 g (67 mmol) of **2** and 0.15 g (6.3 mmol) of Na. The

* To whom offprint requests should be sent

mixture was heated at 90°C under stirring until complete disappearance of the Na and then transferred into a 150 ml stainless steel pressure vessel. The vessel was filled with acetylene up to 10 atm and then heated at 150°C for 20 h under mechanical shaking. After cooling, the reaction mixture was diluted with diethyl ether, washed with 5% NaHCO₃, dried over K₂CO₃ and distilled under vacuum. The distillation product, after addition of 0.075 g (0.38 mmol) of triisobutylaluminum, was stirred under dry nitrogen for 3 h and then distilled under vacuum to give 12.8 g (76% yield) of 1 having b.p. 87°C/0.4 mm and $[\Phi]_D^{25} -17.7$ (cyclohexane).
 1H-NMR (CDCl₃): $\delta = 7.2$ (s, 5H, aromatic protons), 6.3 (dd, 1H, CH=), 4.5 (s, 2H, benzylic protons), 4.3-3.3 (m, 8H, CH₂ = + CH₂O + CHO) and 1.2 ppm (m, 6H, CH₃).
 IR (liquid film): $\bar{\nu} = 3120-3000$ (ν CH olefinic), 2940-2870

SCHEME. Synthesis of (4S,7S)-10-phenyl-4,7-dimethyl-3,6,9-trioxo-1-decene.



(ν CH aliphatic), 1630 (ν C=C olefinic), 1450 (δ CH₂ and δ_{as} CH₃), 1370 (δ_s CH₃), 1195 (ν C-O-C=), 1100 (ν C-O-C), 730 and 690 cm⁻¹ (δ CH aromatic).
 MS: m/e (I%) = 224 (1.0), 206 (13.6), 201 (1.6), 163 (20), 107 (10.4), 91 (100), 71 (9), 59 (26.4) and 41 (12.8).
 By transvinylation (11)

A mixture of 13.9 g (62 mmol) of 2, 100 g (1.39 mol) of ethyl vinyl ether and 13.9 g (43 mmol) of mercuric acetate was heated at reflux for two hours under dry nitrogen atmosphere and then left under stirring overnight. The reaction was interrupted by addition of 10 g of Na₂CO₃ and after 30 min stirring the precipitate was filtered off. The solution was washed with 5% NaHCO₃, dried over K₂CO₃ and then, after removal of the volatile products, distilled under vacuum to give 14.9 g of crude product having b.p. 85-100°C/0.1mm and constituted by a 64/36 1/2 mixture, as determined by ¹H-NMR and glc. This product, after stirring over Na/K alloy, completely decomposed giving rise mainly to a mixture of 2, debenzylated 2 and traces of unidentified by-products. On the contrary distillation of the crude mixture in the presence of triisobutylaluminum gave rise to 61% yield of alkyl vinyl ether having the same optical rotation as 1 obtained by direct vinylation.

Determination of the optical purity of 1

Hydrogenolysis with (*i*-C₄H₉)₂AlH (12)

To 2.26 g (15.9 mmol) of (*i*-C₄H₉)₂AlH placed in a 20 ml flask under dry nitrogen atmosphere 1.0 g (4.0 mmol) of 1 were slowly added under stirring. The solution was stirred for 3 h at 120°C then, after cooling to room temperature, 40 ml of wet diethyl ether and 1.5 ml of water were added in that order. The ether solution, after removal of the solvent, was mainly constituted by 2 (40%) and its debenylation product (60%) as shown by glc and ¹H-NMR analysis.

Acid hydrolysis

While cooling at 0°C, 0.98 g (3.9 mmol) of 1 were slowly added under magnetic stirring to 2 ml of 5% sulfuric acid and the stirring was continued for 5 h at room temperature. The reaction product was salted out by saturation with NaCl, extracted with diethyl ether and the extracts, after washing with water to neutrality, were dried over sodium sulfate. After removal of the solvent the reaction product was distilled under vacuum to yield 0.47 g of product having $[\alpha]_D^{25} +24.6$ (cyclohexane) that was identified as pure 2 by glc and ¹H-NMR analysis.

Catalysts

Bis(diisobutylaluminum) sulfate and bis(diisopropoxyaluminum) sulfate were prepared as previously reported (13). Boron trifluoride etherate and triisobutylaluminum were purified by distillation. A sample of tropylium hexachloroantimonate, kindly supplied by Prof. A.Ledwith, was purified by crystallization in benzene. The two heterogeneous catalytic systems, (*i*-C₄H₉)₂Al/H₂SO₄ and (*i*-C₃H₇O)₂Al/H₂SO₄, were prepared by adding pure sulfuric acid to a twofold excess of the corresponding aluminum derivative in hydrocarbon solution at -15°C under vigorous stirring, according to the procedure reported by Vandenberg (14).

Polymerization experiments by different catalysts***Boron trifluoride etherate (Run V1)***

In a 10 ml vial were placed under dry nitrogen 0.45 g (1.8 mmol) of 1 and 1.0 ml of toluene containing 32 mg of 1,2-diphenylethane as an internal standard. After cooling at -78°C , 0.4 ml (0.07 mmol) of a 0.18 M solution of $\text{BF}_3 \cdot \text{OEt}_2$ in toluene were added. The mixture was kept under stirring at -78°C for 2 h then 10 ml of methanol were added and the resulting clear solution was analyzed by glc and GPC. After removal of the solvent a waxy solid product having $[\Phi]_D^{25} +16.8$ (cyclohexane) was obtained.

Tropylum hexachloroantimonate (Run V2)

In a 50 ml vial were placed under dry nitrogen 0.45 g (1.8 mmol) of 1 and 1.0 ml of dichloromethane containing 32 mg of 1,2-diphenylethane as an internal standard. After cooling at 0°C 2.75 ml ($6.6 \cdot 10^{-6}$ mol) of a 2.4 mM solution of $\text{C}_7\text{H}_7\text{SbCl}_6$ in dichloromethane were added under stirring. After 60 min 10 ml of methanol were added and the resulting clear solution was analyzed by glc and GPC. After removal of the solvents a viscous oily product having $[\Phi]_D^{25} +14.0$ (cyclohexane) was obtained.

Organoaluminum sulfates (Runs V3-V6)

Polymerization runs were carried out by following a common procedure, data relevant to individual runs are summarized in Table. Run V4 is described as a typical example, as follows.

In a 20 ml vial were placed, under dry nitrogen, 0.45 g (1.8 mmol) of 1, 4.0 ml of toluene, 0.5 ml (0.11 mmol) of a 0.22 M $\text{Al}(i\text{-C}_4\text{H}_9)_3$ solution in toluene and 32 mg of 1,2-diphenylethane as an internal standard. The solution was cooled at -78°C then 0.51 ml ($3.6 \cdot 10^{-5}$ mol) of a 0.07 M solution of $[(i\text{-C}_3\text{H}_7\text{O})_2\text{Al}]_2\text{SO}_4$ in toluene were added under stirring. The mixture was kept at -78°C for 30 min and two weeks at room temperature. Monomer conversion was determined by glc. The polymerization mixture was interrupted by pouring the reaction mixture into 200 ml of methanol and, after removal of the volatile products under vacuum, the residue was extracted with *n*-pentane. An oily product having $[\Phi]_D^{25} +2.8$ (cyclohexane) was finally isolated.

Characterization of high and low molar mass products

GPC analyses were performed in THF solution with a Perkin Elmer 2/2 liquid chromatograph equipped with two Shodex columns (803S and 804S) connected in series and by using poly(styrene) standards for calibration. IR spectra were recorded by a Perkin Elmer mod. 1330 spectrophotometer. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 solutions with a Varian T60 spectrometer and by using tetramethylsilane as internal standard. Optical rotatory measurements were performed at 25°C by a Perkin Elmer mod. 141 spectropolarimeter. Mass spectra were recorded by a V.G. Analytical 70-70E spectrometer.

RESULTS AND DISCUSSION

The alkyl vinyl ether 1 was obtained by starting from the commercially available (S)-ethyl lactate as optically active precursor having 100% optical purity (Scheme). The (S)-ethyl

Table. Polymerization of (4S,7S)-10-phenyl-4,7-dimethyl-3,6,9-trioxa-1-decene in the presence of different catalytic systems.

Run	Polymerization conditions ^{a)}			Conv. ^{b)} (%)	Polymer [ϕ] _D ^{25 c)}
	Catalyst type	1/Cat. (mol/mol)	Duration (h)		
V1 ^{d)}	BF ₃ ·OEt ₂	25	2	76	+16.8
V2 ^{e)}	C ₇ H ₇ SbCl ₆	270	1	87	+14.0
V3 ^{f)}	[(<i>i</i> -C ₄ H ₉) ₂ Al] ₂ SO ₄	20	336	6	- 2.0
V4 ^{f)}	[(<i>i</i> -C ₃ H ₇ O) ₂ Al] ₂ SO ₄	50	336	11	+ 2.8
V5 ^{f)}	(<i>i</i> -C ₄ H ₉) ₃ Al/H ₂ SO ₄ ^{g)}	15	336	72	+ 7.8
V6 ^{f)}	(<i>i</i> -C ₃ H ₇ O) ₃ Al/H ₂ SO ₄ ^{g)}	15	336	47	+ 5.8

^{a)} Monomer 1.80 mmol. ^{b)} By glc by using 1,2-diphenylethane as an internal standard. ^{c)} In cyclohexane (c = 1-5 g/dl, l = 1 dm). ^{d)} In toluene at -78°C. ^{e)} In dichloromethane at 0°C. ^{f)} In the presence of 0.11 mmol of Al(*i*-C₄H₉)₃ at -78°C for 30 min and hence at room temperature. ^{g)} Slurry-type catalyst, molar ratio Al/H₂SO₄=3.

lactate was converted to the monobenzyl derivative of the head-to-tail dipropylene glycol (2) as previously described (9). The conversion of 2 to the corresponding vinyl ether 1 was carried out both by direct vinylation with acetylene (10) and by transvinylation reaction (11). In both cases pure 1 was isolated with chemical yield higher than 60%. The optical yield of the different vinylation processes, as tested by devinylation reaction performed with dilute acid solution, resulted to be practically 100%. A maximum molar optical rotation [ϕ]_D²⁵ -17.7 (cyclohexane) can be therefore assigned to 1. It is worth mentioning that the devinylation reaction based on the hydrogenolysis with (*i*-C₄H₉)₂AlH is not convenient in this case because of the simultaneous occurrence of extensive debenzylation. Debenzylation is also detected in the purification of 1 over Na/K alloy and is attributed to the hydrogenolysis reaction promoted by native hydrogen generated from impurities present in crude 1.

The vinyl ether was submitted to polymerization in the presence of different cationic catalysts (Table) operating under either homogeneous (Runs V1-V4) or heterogeneous conditions (Runs V5 and V6). Monomer conversions variable between 6 and 87% were obtained in the presence of the different catalytic systems and it is rather surprising that the activity of the soluble organoaluminum sulfates results much lower than that of the corresponding heterogeneous analogs.

All the polymer samples as recovered from the polymerization mixture, exhibited positive optical rotation, with the only exception of the sample obtained with the lowest conversion. Apart from the sign, the optical rotation of the

polymer was of the same order of magnitude as that of the starting monomer. It is however worth mentioning that the observed behaviour is fairly unusual for optically active poly(alkyl vinyl ether)s derived from secondary carbinols, for which a large increase sometimes even of one order of magnitude in the optical rotation is observed in going from the monomer or the low molar mass model to the corresponding polymer (1,2). Therefore in polymers of chiral alkyl vinyl ethers the lengthening of the side chain appears to populate conformers tending to depress the overall optical rotation of the relevant monomeric unit in keeping with what previously stated (3, 13).

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