BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 21, pp. 4151-4154, 1995

0032-3861/95/$10.00+0.00

(2*S*,4*S*)-2,4-Pentanediol as the acyclic template for asymmetric induction in cyclocopolymerization

Osamu Haba, Yasushi Morimoto, Takahiro Uesaka and Kazuaki Yokota*
Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

and Toyoji Kakuchi
Division of Bioscience, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan
(Received 17 April 1995)

The copolymerizations of (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate), a monomer having a chiral acyclic template, with styrene (St) were carried out using azobisisobutyronitrile in toluene at 60°C. The copolymers obtained (**4**) essentially consisted of the cyclic repeating and St units, because characteristic absorption at 5.3 and 5.8 ppm due to the vinyl protons disappeared in the ^{1}H nuclear magnetic resonance spectra. The specific rotation ($[\alpha]_{435}^{23}$, *c* 1.0, $CHCl_3$) of **4** changed from +319.3° to +395.2°. The removal of the chiral template from **4** was carried out in aqueous MeOH using KOH, and the resulting hydrolysed copolymers were then converted into poly(methyl 4-vinylbenzoate-*co*-styrene) (**5**) by reacting with diazomethane. The specific rotation ($[\alpha]_{435}^{23}$, *c* 1.0, $CHCl_3$) of **5** was −9.4° to −46.3°. The circular dichroic (c.d.) spectrum of **5** showed a splitting Cotton effect with a negative Cotton effect at 255.2 nm and a positive one at 237.2 nm. According to the c.d. exciton chirality method, copolymer **5** had a negative chirality in which two 4-vinylbenzoyl groups twisted counterclockwise, i.e. an (*R*,*R*)-configuration of the vicinal (methyl 4-vinylbenzoate) units in the main chain.

(Keywords: cyclopolymerization; chirality; acyclic template)

Introduction

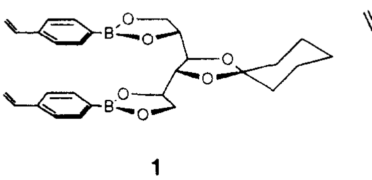
Cyclopolymerization is one of the key polymerizations for producing a well-controlled macromolecular architecture, for example, polymers with macrocyclic units[1-5] and with optical activity[6-10]. In addition, asymmetrically inductive cyclocopolymerization is one of the most important synthetic methods for an optically active polymer whose chirality is due to the configurational asymmetry of the main chain. Wulff and co-workers have been developing a theory that an optically active vinyl polymer is synthesized through the cyclocopolymerization of the divinyl monomer having a chiral template with the vinyl comonomer, followed by removal of the template[11-15]. They designed and used 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl) borate] (**1**) and analogues. Utilizing this cyclocopolymerization method, we recently reported that optically active poly(methyl 4-vinylbenzoate-*co*-styrene) was synthesized using the bis(4-vinylbenzoic acid) esters of 2,3-*O*-isopropylidene-L-threitol (**2**) and the chiral diad configuration in the polymer chain was determined using the circular dichroic (c.d.) exciton chirality method[16]. For these monomers, the structures are characterized such that two 4-vinylphenyl groups are connected to the chiral cyclic templates. The cyclic structure of the templates is considered to be necessary to fix the two vinyl groups to form enantiomeric racemo diads. The relation between the structure and asymmetric induction ability of the templates, however, has not been well studied. Therefore, it is interesting to study whether the acyclic compound having low rotational barrier potentials acts as a chiral template for the asymmetric induction during cyclocopolymerization. Here we report that the optically active polymer is obtained using (2*S*, 4*S*)-2,4-pentanediyl bis(4-vinylbenzoate) (**3**) as the monomer with the chiral acyclic template.

Results

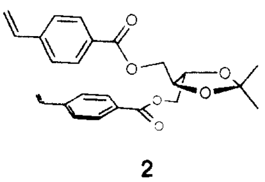
The monomer **3**, which was prepared by reacting (2*S*,4*S*)-2,4-pentanediol with 4-vinylbenzoyl chloride in pyridine, was a viscous oil. *Table 1* lists the typical results of the copolymerizations of **3** with styrene (St) using azobisisobutyronitrile (AIBN) in toluene at 60°C. The polymerizations proceeded homogeneously and the resulting copolymers (**4**) were soluble in chloroform and tetrahydrofuran. The number-averaged molecular weights (M_ns) of these polymers ranged from 5000 to 31 300. Since the characteristic absorption at 5.3 and 5.8 ppm due to the vinyl protons disappeared in the ^{1}H nuclear magnetic resonance (n.m.r.) spectrum of the poly (**3**-*co*-St) (*Figure 1a*), the extent of the cyclic repeating units that originated from **3** was 100%. The copolymerization reactivity of **3** was higher than that of St, resulting in the fact that the mole fraction of the **3** unit in **4** was higher than that in the monomer feed. The specific rotation ($[\alpha]_{435}^{23}$, *c* 1.0, $CHCl_3$) of the cyclopolymers **4** was +319.3° to +395.2°.

---

* To whom correspondence should be addressed



1



2

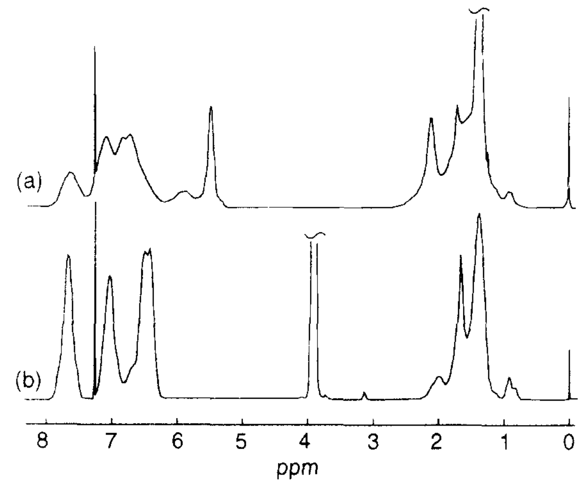


Figure 1 ^{1}H n.m.r. spectra of copolymers **4** (x/y = 0.49/0.51 in copolymer) (a) and **5** (x/y = 0.49/0.51) (b) measured in $CDCl_3$ at 23°C

Asymmetric induction in these copolymer systems can be confirmed by completely removing the chiral templates from the polymers. The removal of the chiral template from **4** was carried out in aqueous MeOH using KOH, and then the hydrolysed copolymers were converted into polymer **5** by treatment with diazomethane. The results of the preparation of **5** are summarized in *Table 1*. The removal of the chiral template in polymer **5** was complete, because the absorption at 5.3–5.4 ppm due to the methine protons of the (2*S*,4*S*)-2,4-pentanediyl units disappeared in the ^{1}H n.m.r. spectrum (*Figure 1b*). The obtained copolymer **5**, poly(methyl 4-vinylbenzoate-*co*-styrene), exhibited optical activity with a specific rotation ($[\alpha]_{435}^{23}$, *c* 1.0, $CHCl_3$) ranging from −9.4° to −46.3°. This sign of the values was opposite to that for **3** at every composition. These results indicate that the new chirality was induced in the main chain of the monomeric units from **3** by twisting of (2*S*,4*S*)-2,4-pentanediol template.

The c.d. exciton chirality method for determination of the absolute stereochemistry on the basis of a chiral exciton coupling between two chromophores[17] is effective not only for a monomeric system but also for a polymeric one. For analysing the stereochemistry of monomer **3** using the exciton chirality method, the c.d. spectrum of (2*S*,4*S*)-2,4-pentanediyl bis(4-bromobenzoate) (**6**) reported by Harada *et al.*[18] offered a helpful suggestion. The c.d. spectrum of **6** in ethanol first showed the positive and then the negative Cotton effects (λ_{ext} 252.5 nm, $\Delta\epsilon$ + 26.5 and λ_{ext} 236.0 nm, $\Delta\epsilon$ − 9.1) in the region of the $\pi \rightarrow \pi^*$ transition (λ_{max} 243.0 nm, ϵ 35 600). *Figure 2* shows the c.d. and u.v. spectra of **3** in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). The c.d. spectrum exhibits a positive Cotton effect at 282.6 nm ($\Delta\epsilon$ + 28.6) and a negative one at 259.2 nm ($\Delta\epsilon$ − 14.7) in the region of the $\pi \rightarrow \pi^*$ transition (λ_{max} 270.5 nm, ϵ 35 000). This result was similar to that of **6** except for the red shift in u.v. absorbance caused by the extension of the conjugated system due to the vinyl groups. Therefore, monomer **3** has a positive chirality and its benzoate chromophores, the two 4-vinylbenzoyl groups, twist clockwise similarly to **6**.

The c.d. spectrum of copolymer **5** (**3**/St= 0.49/0.51) in

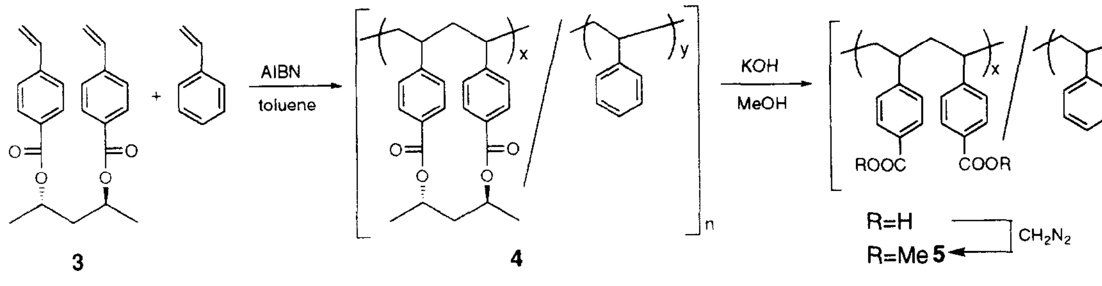


Table 1 Cyclocopolymerization of (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate) (**3**) and styrene (St) and synthesis of poly(methyl 4-vinylbenzoate-*co*-styrene)

	Polymer **4**[a]					Polymer **5**[b]		
Mole fraction of **3** in monomer feed	Time (h)	Yield (%)	Mole fraction of **3** unit in copolymer[c]	$M_n (M_w/M_n)$[d]	$[\alpha]_{435}$[e]	Yield (%)	$M_n (M_w/M_n)$[d]	$[\alpha]_{435}$[e]
0.70	1.8	23.9	0.89	31 300 (1.89)	+394.1°	41.0	21 800 (1.98)	− 9.4°
0.40	2.3	21.8	0.71	11 200 (1.76)	+395.2°	66.8	10 700 (1.71)	−31.6°
0.30	4.0	20.5	0.61	9000 (2.09)	+354.0°	63.7	6900 (2.16)	−36.4°
0.21	5.0	21.6	0.49	5000 (1.60)	+319.3°	69.5	5500 (1.47)	−46.3°

[a] Solvent, toluene; initiator, AIBN; temperature, 60°C; [**3**+St]= 0.1 mol l^{-1}; [AIBN]= 1 g l^{-1}
[b] Prepared from polymer **4** through hydrolysis using KOH in aqueous MeOH for 50 h under reflux, and then treatment with diazomethane in benzene/ether
[c] Determined by ^{1}H n.m.r spectra
[d] Determined by gel permeation chromatography using polystyrene standard
[e] Measured in $CHCl_3$ at 23°C (c = 1.0)

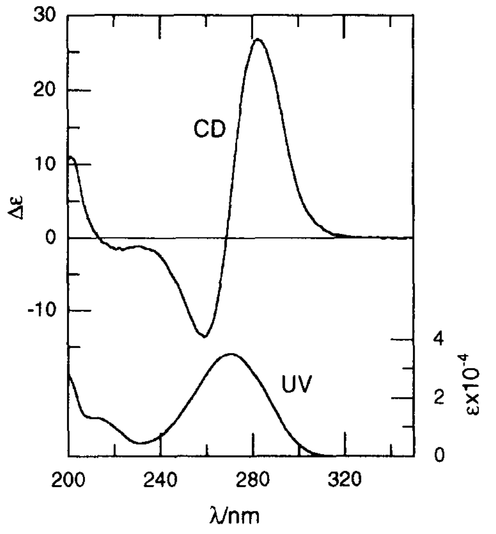


Figure 2 C.d. and u.v. spectra of monomer **3**, measured in HFP at 21°C. Sample concentration was 0.206 mg/10 ml (5.65×10^{-5} mol l^{-1}). Path length was 0.5 cm

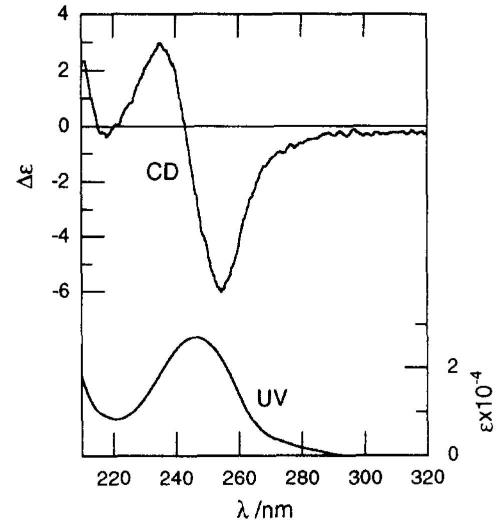


Figure 3 C.d. and u.v. spectra of polymer **5** (**3**/St = 0.49/0.51), measured in HFP at 21°C. Sample concentration was 0.277 mg/10 ml. The Δε and ε values were based on the concentration of methyl 4-vinylbenzoate units (6.40×10^{-5} mol l^{-1}) calculated using the copolymer composition of 0.49. Path length was 0.5 cm

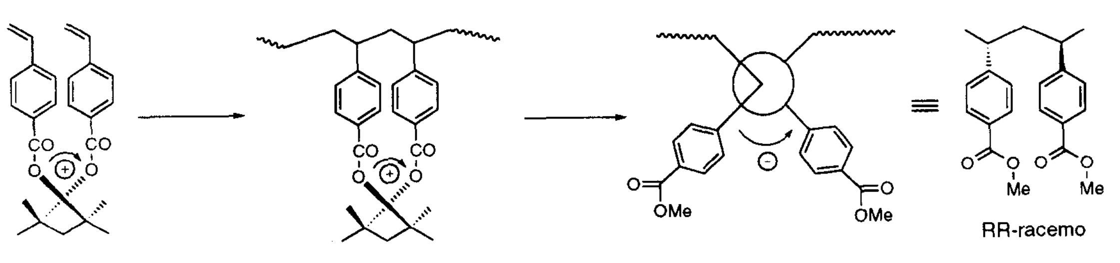
HFP showed a splitting Cotton effect with a negative Cotton effect at 254 nm and a positive one at 235 nm (*Figure 3*). This result indicates that **5** has a negative chirality in which two 4-vinylbenzoyl groups are twisted counterclockwise, i.e. the configuration of the main-chain carbon originated from the **3** units has an (*R*,*R*)-configuration. *Scheme 1* represents the configurational change in the polymerization process. The acyclic template, (2*S*,4*S*)-2,4-pentanediol, transmitted its chirality to the main chain during the intramolecular cyclization to form an enantiomeric *R*,*R*-racemo configuration in polymer **5**.

In summary, poly(methyl 4-vinylbenzoate-*co*-styrene) (**5**), which was prepared through the radical cyclocopolymerization of (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate) (**3**) with styrene (St), was optically active. The chiroptical property of **5** was opposite to that for the cyclocopolymerization system of 2,3-*O*-isopropylidene-1,4-bis-*O*-(4-vinylbenzoyl)-L-threitol (**2**) and St. The maximum value of the specific rotation ($[\alpha]_{435}^{23}$, *c* 1.0, $CHCl_3$) of **5** for the **3**/St system was −46.3°, which was significantly higher than the value of +7.0 for the **2**/St system. This fact means that an acyclic template such as (2*S*,4*S*)-2,4-pentanediol was as effective as cyclic templates such as the D-mannitol and L-threitol residues in **1** and **2**.

Experimental

For the preparation of monomer **3**, a solution of (2*S*,4*S*)-2,4-pentanediol (Tokyo Kasei Kogyo Co.) (4.2 g, 20 mmol) in dry pyridine (200 ml) was cooled to 5°C in an ice bath. To this solution, a solution of 4-vinylbenzoyl chloride[19] (14 g, 84 mmol) in benzene (150 ml) was gradually added so that the temperature of the solution did not rise above 10°C. The reaction mixture was stirred overnight at room temperature. The precipitate was filtered off, and the filtrate was successively washed with several portions of aqueous potassium bicarbonate and water, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with *n*-hexane/ether (0.85/0.15) to yield (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate) (**3**) (10.4 g, 72%). $[\alpha]_D^{23} = +216.8°$, $[\alpha]_{435}^{23} = +516.5°$ (*c* 1.0, $CHCl_3$). ^1H n.m.r. (270 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 8.4$ Hz, 4H, Ar), 7.36 (d, $J = 8.3$ Hz, 4H, Ar), 6.70 (dd, $J_{trans} = 17.6$ Hz, $J_{cis} = 10.9$ Hz, 2H, =CH–), 5.81 (d, $J_{trans} = 17.5$ Hz, 2H, $=CH_2$), 5.33 (d, $J_{cis} = 10.8$ Hz, 2H, $=CH_2$), 5.28–5.36 (m, 2H, CH), 2.08 (t, $J = 6.3$ Hz, 2H, CH_2), 1.40 (d, $J = 6.3$ Hz, 6H, CH_3), ^{13}C n.m.r. (67.8 MHz, $CDCl_3$): $\delta = 165.6$ (C=O), 141.7, 129.8, 129.6, 125.6 (arom), 136.0 (=CH–), 116.3 (CH_2=), 68.2 (CH), 42.1 (CH_2), 20.5 (CH_3). Anal. calcd for $C_{23}H_{24}O_4$ (364.4): C 75.79; H 6.64. Found: C 76.21; H 6.79.

A typical procedure for the copolymerization of **3** with styrene is as follows. A solution of **3** (0.778 g, 2.13 mmol), styrene (0.222 g, 2.13 mmol), AIBN (43 g) in dry toluene (43.0 ml) was placed in a glass ampoule. This solution



Scheme 1 Schematic conclusion of c.d. spectrum measurements for the asymmetric induction during cyclocopolymerization of **3** and St

was degassed *in vacuo* and gaseous N_2 was introduced. Polymerization was initiated by heating to 60°C in a water bath. After 2.5 h, the polymerization mixture was poured into methanol (500 ml) and the precipitate was filtered. The white powder obtained was purified by reprecipitation with chloroform/methanol and dried *in vacuo*. Yield 0.22 g (22%). The composition of **3** was 0.79/0.21 (x/y) which was estimated from the area ratio of aromatic and aliphatic regions in the ^{1}H n.m.r spectrum.

A typical procedure for hydrolysis and methylation is as follows. To a solution of **4** (0.12 g, x/y= 0.79/0.21) in THF (5 ml) in a Teflon bottle, 25% methanolic KOH (50 eq. to C=O group in **4**) was added. The reaction mixture was refluxed for 50 h while periodically adding a small portion of water. After neutralization by 2 N hydrochloric acid with cooling in an ice bath, the mixture was transferred to a cellulose tube and dialysed for 2 days with distilled water. The aqueous solution was freeze-dried to yield a white powder. This was added to a mixture of an ether solution (60 ml, $\sim$0.5 mol l^{-1}) of diazomethane[20]($\sim$30 mmol) and benzene (60 ml). The polymer was dissolved with evolution of nitrogen gas. The mixture was left alone for 14 h at room temperature and all solvents were removed under reduced pressure. The residue was dissolved in 0.5 ml of chloroform and the solution was poured into 50 ml of methanol. The white precipitate was filtered and dried *in vacuo*. Yield, 77 mg (72%).

Acknowledgement

This research was supported by a Research Grant from the Ministry of Education, Science and Culture, Japan.

References

1 Mathias, L. J. and Canterberry, J. B. in 'Cyclopolymerization and Polymers with Chain-Ring Structures' (Eds G B. Butler and J. E Kresta), American Chemical Society, Washington DC, 1982, p. 139

2 Kakuchi, T., Aoki, K., Haba, O. and Yokota, K. *Polym. Bull.* 1993, **31**, 37

3 Hashimoto, H., Kakuchi, T., Haba, O. and Yokota, K. *Macromolecules* 1992, **25**, 1828

4 Kakuchi, T., Haba, O. and Yokota, K. *Macromolecules* 1992, **25** 4854

5 Kakuchi, T., Haba, O., Harada, Y., Hashimoto, H. and Yokota, K. *Polym. Bull.* 1992, **27**, 599

6 Coates, G. W. and Waymouth, R. M. *J. Am. Chem. Soc.* 1991, **113**, 6270

7 Cavallo, L., Guerra, G., Corradini, P., Resconi, L. and Waymouth, R. M. *Macromolecules* 1993, **26**, 260

8 Coates, G. and Waymouth, R.M. *J. Am. Chem. Soc.* 1993, **115**, 91

9 Yokota, K., Kakuchi, T., Yamamoto, T., Hasegawa, T. and Haba, O. *Makromol. Chem.* 1992, **193**, 1805

10 Haba, O., Kakuchi, T. and Yokota, K. *Macromolecules* 1993, **26**, 1782

11 Dhal, P. K., Vogt, B., Steigel, A. and Wulff, G. *Macromolecules* 1992, **25**, 5601

12 Wulff, G., Kemmerer, R. and Vogt, B. *J. Am. Chem. Soc.* 1987, **109**, 7449

13 Wulff, G., Schmidt, H., Witt, H. and Zentel, R. *Angew. Chem. Int. Edn Engl.* 1994, **33**, 188

14 Wulff, G. *Angew. Chem., Int. Edn Engl.* 1989, **28**, 21

15 Wulff, G. and Krieger, S. *Macromol. Chem. Phys.* 1994, **195**, 3679

16 Kakuchi, T., Haba, O., Fukui, N. and Yokota, K. *Macromolecules* in press

17 Harada, N. and Nakanishi, K. 'Circular Dichroic Spectroscopy–Exciton Coupling in Organic Stereochemistry', Mill Valley, CA and Oxford University Press, Oxford, 1983

18 Harada, N., Saito, A., Ono, H., Gawronski, J., Gawronska, K., Sugioka, T., Uda, H. and Kuriki, T. *J. Am. Chem. Soc.* 1991, **113**, 3842

19 Hirao, A., Ishino, Y. and Nakahama, S. *Macromolecules* 1988, **21**, 561

20 Boer, T. H. and Backer, H. J. *Org. Syn Coll.* 1963, **IV**, 250