Template Monomer Control of the Chirality Induction in the Polymer Backbone during Asymmetric Vinyl Polymerization[1]

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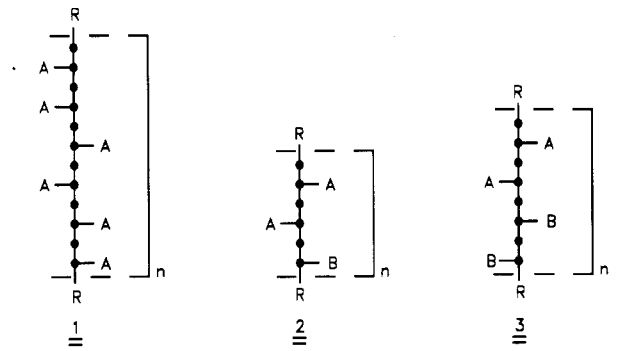
Received January 16, 1990; Revised Manuscript Received March 27, 1990

ABSTRACT: Diastereoselective cyclocopolymerization was investigated. Two monomeric units were attached to an optically active template molecule with varying of distance of the double bonds from the stereogenic centers of the template. After copolymerization the template was split off and the chiroptical properties of the resulting linear vinyl copolymers were investigated. Longer distances diminish the diastereoselective influence of the template on the asymmetric cyclocopolymerization.

Introduction

Chiral vinyl polymers showing optical activity arising from chiral configurations or conformations of the main chain are matters of long-standing interest and are fascinating in the current time from the viewpoint of molecular design of speciality polymers.[2] Despite some success achieved recently, realization of such polymers still constitutes a synthetic challenge.[3] Incorporation of bulky substituents enabled synthesis of optically active vinyl and allied polymers possessing stable single-handed helical conformations.[4] On the other hand, synthesis of optically active vinyl polymers obtained from prochiral vinyl monomers with chirality arising from main-chain configurations has caused many problems. The reason behind this fact has been ascribed to the peculiarities associated with long macromolecular chains, wherein the chiral centers generated during chain propagation in most cases become "cryptochiral" after a certain degree of polymerization.[3]

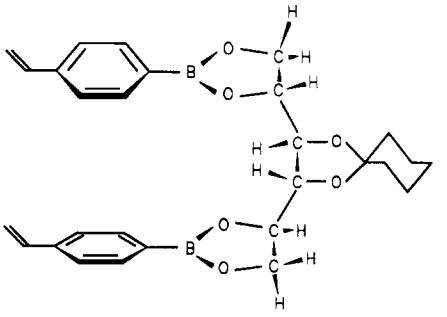
In a systematic endeavor, we have recently attempted to understand the configurational stereochemistry of macromolecular chains. Our study, based on molecular symmetry considerations, revealed the presence of certain stereochemical arrangements for the polymer backbone, which are chiral (**1–3**).[3b,5] This suggested that devising



1 **2** **3**

appropriate synthetic routes for obtaining polymer chains possessing such asymmetric arrangements in a preferred enantiomeric configuration would enable us to realize optical activity in these polymers. As the first example of obtaining such polymers possessing the structural type **2**, we devised a template-assisted asymmetric copolymerization technique.

The process involves the synthesis of appropriate vinyl monomers consisting of a chiral template bearing two units of polymerizable groups being present in an appropriate structural requirement, e.g., **4**. Copolymerization of **4** with



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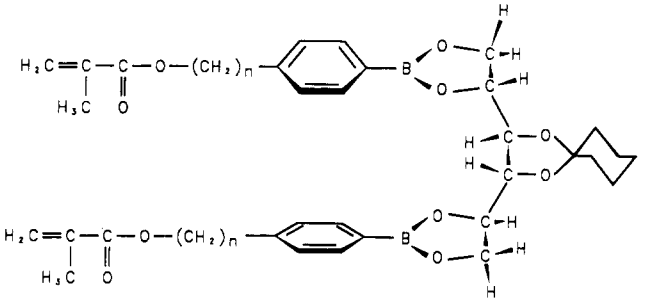
other vinyl monomers followed by removal of chiral template units offered optically active polymers of a preferred configuration determined by the chiral template.[6]

In order to synthesize optically active vinyl polymers possessing other types of asymmetric arrangements, we have looked for the synthesis of newer types of template monomers based on the same template,[7] i.e., D-mannitol derivative, which was used for the synthesis of **4**. Toward this end, we have synthesized two new template monomers **5a** and **5b**, where the structural differences are the varying



5a n = 0
5b n = 1

distances between the polymerizable double bonds and the chiral moiety. In order to determine the role of these spatial relationships between the double bonds and chiral template in inducing enantioselectivity in polymer backbone, we have copolymerized **5a** and **5b** separately with styrene. After removal of the template chiral linear polymers of type **2** are expected. The first results on this study are described in the present paper. Future work will be concerned with the copolymerization of **4** with **5a** or

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0024-9297/90/2223-4525$02.50/0

Table I
Asymmetric Copolymerization of Template Monomers (5a and 5b) with Styrene

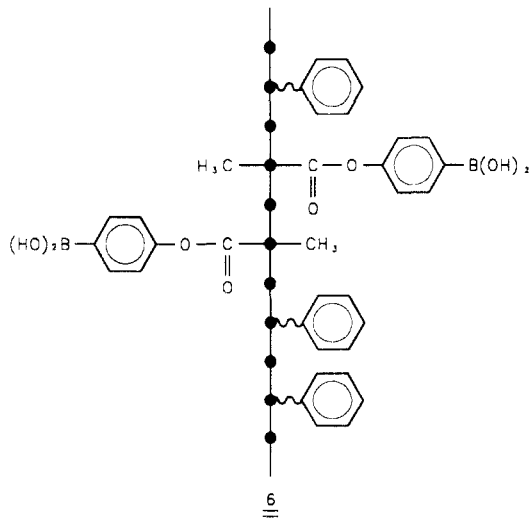
entry	mol fractn of template monomer in reaction mixt	mol fractn of template monomer in copolymer	$[\alpha]^{30}_{365}$,[a] deg
	Template Monomer **5a**		
1	0.11	0.26	+15
2	0.20	0.33	+19
3	0.26	0.41	+18
4	0.48	0.62	+11
	Template Monomer **5b**		
5	0.14	0.25	0
6	0.24	0.36	0
7	0.31	0.43	0
8	0.51	0.59	0

[a] After complete removal of the template units.

5b in order to obtain after removal of the templates chiral polymers of type **3**.

Results and Discussion

The new template monomers 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[[4-(methacryloyloxy)phenyl]-boronate] (**5a**) and 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[[4-[(methacryloyloxy)methyl]phenyl]boronate] (**5b**) were prepared by reacting 3,4-*O*-cyclohexylidene-D-mannitol[8] with 4-(dihydroxyboryl)phenyl methacrylate[9] and 4-(dihydroxyboryl)benzyl methacrylate,[9] respectively. The monomers were copolymerized with styrene in different molar ratios by using toluene as solvent under free-radical initiation. Despite the bifunctional nature of these monomers, the polymers obtained after about 10% conversion were soluble in the reaction medium, which is indicative of the operation of a cyclopolymerization process, as was observed in the earlier case with **4** as the template monomer.[6] Removal of D-mannitol templates from the copolymers offered styrene-*co*-4-(dihydroxyboryl)-phenyl methacrylate (**6**) and styrene-*co*-4-(dihydroxyboryl)-



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benzyl methacrylate copolymers. Elemental analyses, infrared, and ^{13}C NMR spectral methods enabled us to determine the chemical compositions and structures of these two sets of copolymers. The results are summarized in Table I.

Regarding the optical activity, the two sets of copolymers exhibit interesting and differing behavior. The copolymers based on **5a** are positively rotating ($[\alpha]_{365}$ +11 to +19°), and the magnitudes of their specific optical rotation values

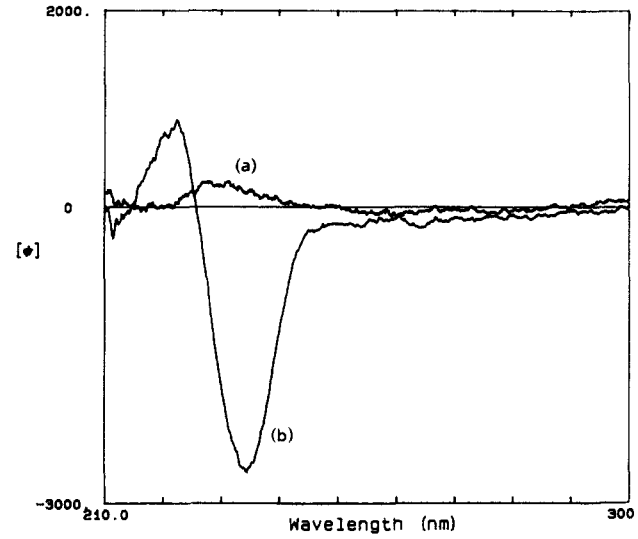


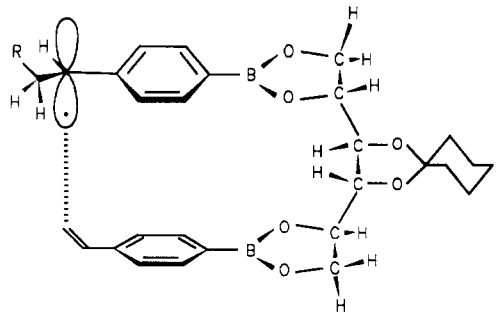
Figure 1. CD spectra of **6** (entry 3 of Table I) (a) and of a copolymer of styrene and (4-vinylphenyl)boronic acid (50:50) (b) produced by copolymerization of **4** and styrene and splitting off of the template. The ordinate shows the specific ellipticity in (deg·dm)/(g·mL). Solvent: dioxane/water 9:1.

are nonlinearly dependent on the copolymer compositions (Table I, entries 1–4). The CD spectrum of a typical sample of this system shows a small positive Cotton effect around 229 nm (Figure 1), which could correspond to an overlap of absorption bands of styrene moieties and of the 4-substituted phenylboronic acid chromophores.

It may be recalled that copolymers of styrene with **4** (after removal of the template) and with the 4-substituted phenylboronic acid directly linked to the polymer backbone showed a negative Cotton effect at around 234 nm. The absolute magnitude of the specific ellipticity of the positive Cotton effect of the present copolymer is nearly one-tenth of that based on **4** (see Figure 1).

In the case of copolymers of **4** the chiroptical properties were attributed to the presence of isolated (4-vinylphenyl)-boronic acid diads. The specific optical rotations and the CD were dependent on the relative concentrations of the diads in the chain. The specific positive optical rotation values in the case of copolymers **6** obtained from **5a** with styrene are in terms of absolute values smaller compared to those of copolymers of **4** with styrene, which showed larger negative values ($[\alpha]^{30}_{365} = -34°$).[10] On the other hand, none of the copolymers obtained with **5b** show any measurable optical activity (Table I, entries 5–8). The only difference in structure between copolymers of **5a** and **5b** is the presence of an additional methylene bridge between the double bond and the template moiety in the case of **5b**.

The difference in the chiroptical properties of copolymers of styrene with **4**, **5a**, and **5b**, respectively, might be explained as caused by two different effects. The first one is related to the difference of magnitudes of stereoselectivity of the propagation steps during the formation of the polymers and the second one to the difference in location of the chromophores with regard to the chiral polymer backbone in the resulting polymers. For the optical activity of the copolymers of **4**, the diastereoselectivity of the propagation steps was ascribed to preferential endo–endo additions of the double bonds of **4**. The reaction intermediate as shown in **7** is stabilized by resonance of the p orbital (containing the unpaired radical electron) with the aromatic ring. This results in a strong energy barrier to rotation about the benzylic bond, thus holding the p orbital in a perpendicular position with respect to the



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aromatic ring leading to the desired endo–endo addition. Although a rotation around this bond is possible, the rate of rotation for this barrier should be slower compared with the rate of the next step involving a diastereoselective ring closure (see ref 6). In the case of **5a** the distance between the double bond and the phenyl ring is longer. Nevertheless, there might still be some resonance stabilization between the p orbital generated at the methacrylic ester moiety and the phenyl ring. On the other hand, in the case of **5b**, such a resonance stabilization is impossible. Therefore, in this case any influence of the chiral template on the stereochemistry of the ring closure is not likely to occur. It is therefore to be expected that the diastereoselectivity of the propagation step in **5a** is less than that in **4** and is nonexistent in **5b**.

The lower optical activity of copolymers of **5a** compared to those of **4** might be ascribed to another additional factor. The aromatic chromophores in the final polymers of **5a** are more remotely situated from the chiral configurational centers of the main chain. Other allied investigations from our laboratory[1] have shown that this causes a substantial reduction of the magnitudes of chiroptical properties related to this chromophore. In the case of copolymers of **5a**, it cannot be quantified to what extent the two factors (i.e., lower diastereoselectivity and longer distance between polymer chain and the chromophores) have led to a reduction of the optical activity. Analysis of the microstructure of these copolymers pertaining to the stereochemical arrangements of these monomer units is in progress.

We are also investigating use of other template monomer structures with differing flexibility/rigidity in inducing enantioselectivity.[11] These results would enable us to further testify the reasons behind the observed behavior during asymmetric copolymerization.

Experimental Section

Elemental analyses were performed in the microanalytical laboratories of the Faculty of Natural Sciences of the Heinrich-Heine-Universität Düsseldorf. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter. CD spectral measurements were carried out at 25 °C in 1,4-dioxane with 10% water by using a Jasco J-600 spectropolarimeter.

Monomers. The monomers **5a** and **5b** were prepared by reacting 3,4-*O*-cyclohexylidene-D-mannitol with the corresponding boronic acid derivatives in a 1:2 mole ratio in dry methylene chloride by azeotropic distillation of the formed water. The compounds were purified by repeated recrystallization from absolute petroleum ether (40–60 °C). Both compounds gave consistent spectral data. **5a**. ^1H NMR ($CDCl_3$): 1.4–1.7 (m, 10 H), 2.05 (s, 2 H), 4.1 (m, 2 H), 4.4–4.5 (m, 4 H), 4.7 (m, 2 H), 5.7 (s, 2 H), 6.2 (s, 2 H), 7.35 (m, 4 H), 8.0 (m, 4 H). Anal. Calcd for $C_{32}H_{36}B_2O_{10}$: C, 63.82; H, 6.03. Found: C, 64.15; H, 5.93. M^+ 602; $[\alpha]^{30}_D$ +6° (*c* 2.5, THF). **5b**. ^1H NMR ($CDCl_3$): nearly identical as **5a** besides an extra peak at 5.2 (s, 4 H). Anal. Calcd for $C_{34}H_{40}B_2O_{10}$: C, 64.76; H, 6.35. Found: C, 64.51; H, 6.24. M^+ 630; $[\alpha]^{30}_D$ +10° (*c* 3.0, THF). The compounds polymerized at ~105 °C before melting.

Polymer Synthesis. The copolymerization reactions were carried out at 60 °C under N_2 atmosphere by mixing the appropriate amounts of monomers and AIBN (1.6% w/w) in toluene to make a solution of 0.5 mol/L. The conversion of monomers to polymers was always restricted to below 15%. Detailed procedures dealing with analogous polymer synthesis, isolation, removal of the template, and purification are described elsewhere.[6]

Acknowledgment. This work was performed with financial support from the Alexander von Humboldt Foundation (to P.K.D), the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and the Fonds der Chemischen Industrie.

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