

# Chirality of Polyvinyl Compounds. 5.<sup>1</sup> Optically Active Polymers with Structural Chirality in the Main Chain Prepared through an Asymmetric Cyclocopolymerization

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**Abstract:** Until recently, optical activity of polymers prepared from 1-substituted olefins due to chirality arising from stereogenic relationships in the main chain was thought to be unattainable. It has now been theoretically deduced that there are a number of structural arrangements where this phenomenon should be observed. One of such possibilities has been realized by fixing two monomeric units at an appropriate chiral template molecule and copolymerizing with a comonomer. After splitting off the template, linear copolymers showing strong optical activity were obtained. The mechanism of this asymmetric reaction has been investigated in detail in the case of the copolymerization of 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**11**) with methacrylonitrile and methyl methacrylate. The polymerization proceeds through an asymmetric cyclocopolymerization involving an unusually large 19-membered ring. The optical activity stems from the formation of chiral distyryl dyads in the main chain. They are separated from one another by the comonomer; the chirality of the polymer is independent of the configurations at these centers. The absolute configuration of the asymmetric dyad building block has been established to be (*S,S*) by synthesis of suitable well-defined oligomeric model compounds. For this purpose, *meso*- and (*S,S*)-1,5-dibromo-2,4-diphenylpentanes (**14b** and **16b**) were coupled with pure oligomers of methyl methacrylate in the form of the ester enolates, resulting in good yields of the desired model compounds (e.g., **15a** and **17a**).

Within the framework of our investigations on molecular recognition in polymers prepared by imprinting with templates,<sup>2</sup> we were interested in studying the possibility of existence of optical activity in linear vinyl polymers due to chirality arising from configurational relationships in the main chain (so-called backbone or main-chain chirality). According to the existing literature,<sup>3,4</sup> polymers prepared from 1-substituted olefins  $\text{CH}_2=\text{CHR}$  cannot be optically active due to the chirality of the main chain. This has been attributed to the peculiar type of stereochemistry associated with very long polymer chains.

For polymers prepared from 1-substituted olefins, the stereogenic centers along the chain contain four different groups, two being hydrogen and the substituent and the other two being the two chain ends of different length. To recognize whether these chains as a whole are chiral or not they are usually treated as finite chains with identical terminal groups or as infinite chains.<sup>3b,5-7</sup> Looking at the three kinds of typical arrangements of polymer chains, viz., atactic, isotactic, and syndiotactic, the last one contains stereogenic centers with regularly alternating (*R*) and (*S*) configuration. In the infinite-chain model these chains are achiral, since the main chain represents a glide-reflection axis.<sup>6</sup> Isotactic polymers in the finite chain model with identical terminal groups possess a reflection plane and in the infinite-chain model possess a translational axis with transverse symmetry planes and are therefore achiral also.

Atactic polymers have equal numbers of (*R*) and (*S*) configurations along the chain in a random sequence distribution.<sup>8</sup> This

arrangement will usually be chiral but would not be able to show optical activity. It has recently been put forward by Green and Garetz<sup>9</sup> that atactic polymers with sufficiently high molecular weight ( $P_n > 70$ ) will usually be present as the molecules of single enantiomers, since the number of possible diastereoisomers is so high that the probability of finding its optical antipode in the sample is extremely low. Nevertheless, the probability of finding optical activity is extremely low. This can be seen as arising from intramolecular racemic arrangements in single chains or as suggested by Green and Garetz for bulk samples,<sup>9</sup> by intermolecular compensation among chiral diastereomers.

This is the current status given in standard text books of macromolecular chemistry and in relevant review articles. Optical activity of vinyl polymers, on the contrary, is well documented for polymers bearing pendant chiral side groups.<sup>3,4</sup>

Some time ago<sup>7,10</sup> we were able to show by symmetry considerations that there are several possible structures both for stereoregular homo- as well as copolymers where optical activity due to chirality arising from configurational relationships in the main chain can be expected. Using the infinite-chain model, symmetry properties of stereoregular polymer chains can be best recognized by placing the repeating unit in the form of a ring structure.<sup>3b,7</sup> The ring possesses comparable symmetry properties as a hypothetical infinitely long chain. Examples for chiral homopolymers are shown in formulas **1** and **2**, for chiral copolymers in formulas **3-6**, and for chiral terpolymers in formulas **7-10**.<sup>7,11</sup> The number of possible chiral arrangements along the chain increases sharply for longer repeating units. Particularly with stereoregular co- and terpolymers, there are many further possible arrangements in the polymer chain leading to main-chain chirality.

For a copolymer, the simplest chiral arrangement in the main chain is represented by formula **3**. This stereoregular polymer chain is built up of asymmetric triads. In this case, the configuration of the dyad bearing two A substituents is decisive. They

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(5) After submission of this paper, an excellent and comprehensive review on the stereochemistry of linear macromolecules appeared: Farina, M. *Top. Stereochem.* **1987**, 17, 1-111.

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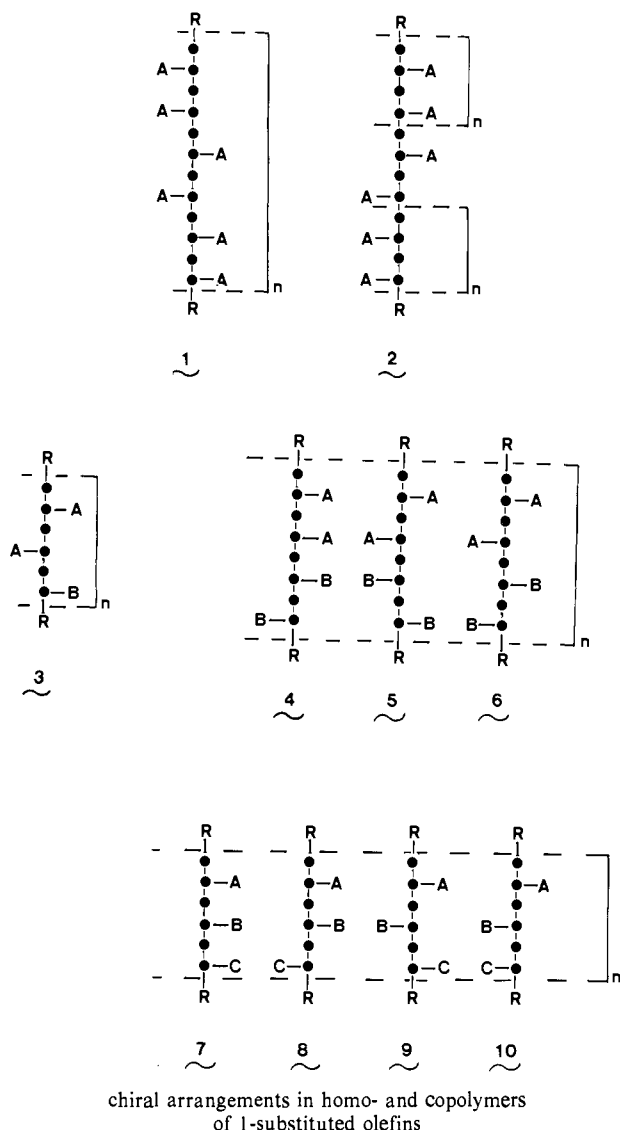
(7) An outline of main chain chirality is given: Wulff, G. *Nachr. Chem. Tech. Lab.* **1985**, 33, 956-961.

(8) IUPAC Macromolecular Division: "Stereochemical Definitions and Notations Relating to Polymers" *Pure Appl. Chem.* **1981**, 53, 733-752.

(9) Green, M. M.; Garetz, B. A. *Tetrahedron Lett.* **1984**, 25, 2831-2835.

(10) (a) Wulff, G.; Zabrocki, K.; Hohn, J. *Angew. Chem.* **1978**, 90, 567-568; *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 535-536. (b) Wulff, G.; Hohn, J. *Macromolecules* **1982**, 15, 1255-1261. (c) Wulff, G.; Kemmerer, R.; Vietmeier, J.; Poll, H.-G. *Nouv. J. Chim.* **1982**, 6, 681-687.

(11) All formulas are given in the usual, upright Fischer projection. This is in contrast to the recommendations of the IUPAC Macromolecular Division,<sup>8</sup> where horizontal Fischer projections for macromolecules are recommended. In the case of known absolute configuration of the polymer chain, with horizontal Fischer projections no unambiguous assignments are possible.



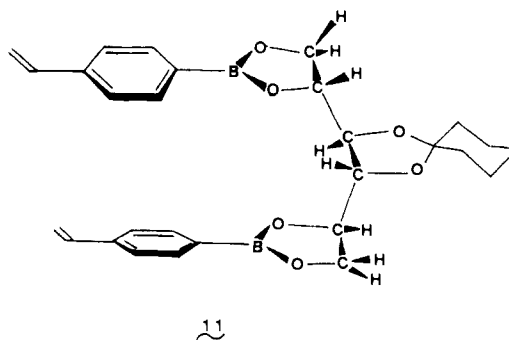
are separated from other dyads by the B unit; the chirality of the polymer is independent of the configurations at these centers.

Polymers possessing such type of monomeric arrangement were synthesized successfully by our group<sup>10</sup> by an asymmetric copolymerization of different *D*-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronates] with methyl methacrylate or styrene. After complete removal of the chiral template (3,4-substituted *D*-mannitol) from the copolymer, an optically active copolymer of (4-vinylphenyl)boronic acid and methyl methacrylate (or styrene) was obtained. This was the first example demonstrating optical activity of vinyl polymers due to the chirality arising from configurational relationships in the polymer backbone.

The present paper describes the results of our investigations for elucidating the mechanism of this asymmetric copolymerization. The mechanism of this polymerization was revealed to proceed through an asymmetric cyclopolymerization involving a 19-membered ring. The absolute configuration of the asymmetric triad building block of the polymer chain was established by synthesis of suitable model compounds.

## Results

**Preparation of the Optically Active Copolymers.** In this investigation 3,4-*O*-cyclohexylidene-*D*-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**11**) has been used as the template monomer for inducing optical activity in the polymer. In contrast to its 3,4-*O*-isopropylidene,<sup>10a</sup> 3,4-*O*-carbonate,<sup>10b</sup> and 3,4-*O*-(4-vinylphenyl)boronate<sup>10a,b</sup> counterparts in earlier studies, **11** can easily be prepared in pure form. It crystallizes readily, and it has better solubility in several organic solvents. Its synthesis involves



esterification of 3,4-*O*-cyclohexylidene-*D*-mannitol<sup>12</sup> with (4-vinylphenyl)boronic acid with azeotropic removal of the formed water.

For the preparation of the polymers, **11** was copolymerized by free-radical initiation in toluene at 60 °C with different comonomers in a molar ratio of 1:1. In order to obtain copolymers having a homogeneous composition, conversion of monomers to polymers was restricted to 10–20%. Although **11** bearing two polymerizable double bonds could allow branched structures and cross-linking, the polymers obtained were soluble in the reaction medium. This indicates no or very low cross-linking during the polymerization, although the existence of some branched structures cannot be completely ruled out.

When the polymerization was followed in a polarimeter cuvette, the optical rotation of the reaction mixture during polymerization increased to higher positive values. In most cases it was not possible to isolate soluble polymers still containing the template, since during the workup procedure cross-linking by transesterification occurred. Polymers prepared from methyl methacrylate and **11** containing 7% of **11** units could be separated from the unreacted monomers and were soluble in THF. The optical rotation value was found to be  $[\alpha]_{365}^{30} +14^\circ$ , which implies the theoretical optical rotation for the polymer containing 100% **11** would be  $+52.3^\circ$ .<sup>13</sup> Monomeric **11** shows a specific optical rotation of  $+44^\circ$ . This suggests some increase in optical rotation during polymerization.

The 3,4-*O*-cyclohexylidene-*D*-mannitol could be split off quantitatively from the polymers. The copolymers of (4-vinylphenyl)boronate with different comonomers (see Table I) could be obtained in pure form, being free from the template and from rest of the monomers. All the copolymers show a relatively broad molecular weight distribution. Molecular weight lies in the range of 40 000–120 000 (membrane osmometry). Results on optical rotations of the polymers are presented in Table I. Most of these polymers exhibit strong negative rotations. The results of this investigation suggest that a large number of comonomers are capable of undergoing such type of asymmetric copolymerization. From these data it is, however, not possible to estimate quantitatively the amount of asymmetric induction, since the specific optical rotations of the completely stereoregular polymers are not known. Even if a positive rotation was observed (Table I, with comonomers 4-nitro- and 4-cyanostyrene), it does not manifest the formation of polymer chains with opposite absolute configuration. It has been established recently<sup>14</sup> that the absolute configurations of these copolymers and of the negatively rotating ones are the same.

The polymers showing the highest negative optical rotations were obtained with methacrylonitrile or methyl methacrylate as the comonomers. Copolymerization behavior was therefore investigated systematically for these comonomers. Different molar ratios of the monomers were used during polymerization, and the compositions of the resulting copolymers were estimated. Figure

(12) Bourne, E. J.; Corbett, W. M.; Erienne, D. *J. Chem. Soc.* 1950, 786–790.

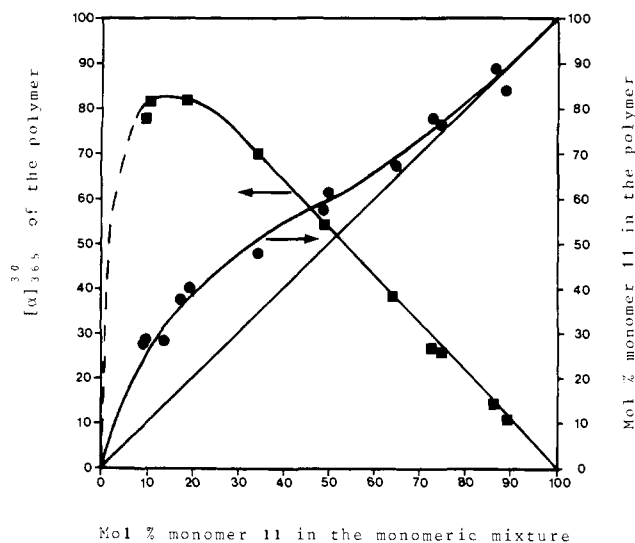
(13) For the calculation the mol ratio of 7% has to be first transformed to a weight ratio (26.8% **11** units by weight in the copolymer having a specific optical rotation of  $[\alpha] +14^\circ$ ). From these data, the specific optical rotation of a hypothetical polymer containing 100% **11** units of  $[\alpha] +52.3^\circ$  is obtained.

(14) Wulff, G.; Dhal, P. K. *Macromolecules*, in press.

**Table I.** Preparation and Optical Rotation of Copolymers of **11** with Different Comonomers<sup>a</sup>

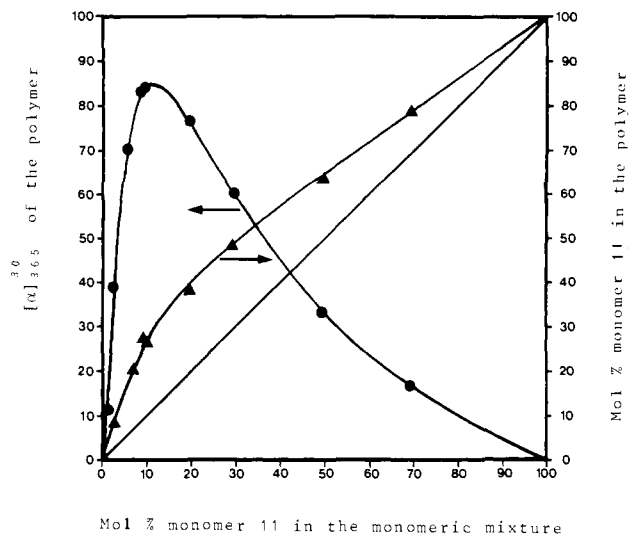
no.	comonomer	conversion, %	$[\alpha]_{365}^{20}$ , deg
1	methacrylonitrile	10	-56.0
2	methyl methacrylate	23	-33.8
3	methyl acrylate	23	-33.5
4	isobutyl methacrylate	25	-33.5
5	<i>n</i> -butyl methacrylate	19	-31.9
6	<i>n</i> -decyl methacrylate	23	-29.0
7	styrene	19	-23.0
8	3-methylstyrene	27	-18.8
9	4-methylstyrene	9	-7.7
10	4-methoxystyrene	19	-3.5
11	4-chlorostyrene	17	+1.5
12	4-nitrostyrene	12	+20.7 <sup>b</sup>
13	4-cyanostyrene	17	+22.1 <sup>b</sup>
14	4-vinylpyridine	n.d.	-13.8 <sup>b</sup>

<sup>a</sup> Copolymers prepared from **11** and a given comonomer in a 1:1 molar ratio in toluene, radical initiation with azobis(isobutyronitrile) at 60 or 70 °C. After a conversion of 9–27% (data given), the polymer was isolated and the template 3,4-*O*-cyclohexylidene-D-mannitol was split off. The optical rotation at 365 nm was measured in acetone/water (9:1) at concentrations of 10 mg/mL. <sup>b</sup> In these cases the optical rotation was measured at 436 nm.

**Figure 1.** Composition of copolymers of **11** with methacrylonitrile and their optical rotations after removal of the template. Optical rotations were measured at 365 nm in acetone/water (9:1) at concentrations of 10 mg/mL. The preparation and determination of the composition of the polymers is described in the Experimental Section.

1 shows the copolymerization behavior of **11** with methacrylonitrile and Figure 2 shows that with methyl methacrylate, depicting the correlation between the mole ratio of **11** in the initial monomeric mixtures and in the resulting copolymers. In both cases it can be seen that at a low content of **11** in the monomer mixture copolymers containing much higher amounts of **11** were obtained. Considering complete cyclopolymerization of **11** (see later section), these composition data can be used<sup>15</sup> for calculating monomer reactivity ratios by the Fineman and Ross<sup>16</sup> method. The values were found to be  $r_1 = 0.90$ ,  $r_2 = 0.25$  and  $r_1 = 1.33$ ,  $r_2 = 0.22$  with methacrylonitrile and methyl methacrylate, respectively, where  $r_1$  refers to the reactivity ratio for **11** and  $r_2$  to that for the comonomer. These data suggest that **11** has a tendency to homopolymerize more readily than the two comonomers, which prefer alternating copolymerization.

The specific rotations of the resulting copolymers are also presented in Figures 1 and 2. It is interesting to note that the

**Figure 2.** Composition of copolymers of **11** with methyl methacrylate and their optical rotations after removal of the template. Experimental conditions as with Figure 1.**Table II.** Dependence of the Optical Rotation of the Copolymers of **11** and Methacrylonitrile on the Concentration of the Comonomers during Polymerization<sup>a</sup>

mol % <b>11</b>		concn of monomers, mol/L	copolymer $[\alpha]_{365}^{30}$ , deg
monomeric mixture	copolymer		
9.7	30	0.9	-83
9.8	29	1.4	-79
10.8	29	1.8	-73
49.3	59	0.5	-56
50.2	62	0.1	-75

<sup>a</sup> The mole percent of **11** in the copolymer was determined by elemental N analysis. The concentration for the monomer given refers to the sum of both comonomers. For further details, see Table I.

**Table III.** Optical Rotation of Copolymers of Styrene and Methyl Methacrylate Obtained by Deboronation<sup>a</sup>

<b>11</b> , mol %		$[\alpha]_{365}^{30}$ , deg	
in monomeric mixture	in polymer	before deboronation	after deboronation
2	8	-39	-15
10	27	-85	-25
30	49	-60	-19

<sup>a</sup> For details, see Table I. Optical rotations measured in acetone/water (9:1, for polymers before deboronation) and in acetone (after deboronation).

optical rotation value of the copolymer reaches its maximum at 10–20 mol % **11** in the monomeric mixture and hence approximately 35 mol % **11** in the copolymer. In both cases, maximum optical rotation  $[\alpha]_{365}^{30}$  over 80° is observed. The optical rotation of the resulting polymers is also dependent on the concentration of the monomers in the polymerization mixture. Table II shows that for the same ratio of comonomers the optical rotation increases with decreasing concentration.

The structural features of the styrene–methyl methacrylate copolymers have been extensively investigated by NMR spectroscopy.<sup>17</sup> In order to elucidate the microstructures of our copolymers it was desirable to transform the copolymers of (4-vinylphenyl)boronic acid–methyl methacrylate to styrene–methyl methacrylate copolymers. The deboronation could be achieved by a method known for low molecular weight substances using silver nitrate/ $\text{NH}_3$ .<sup>18</sup> By adopting necessary modifications re-

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(16) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259–262.

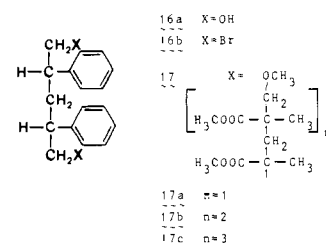
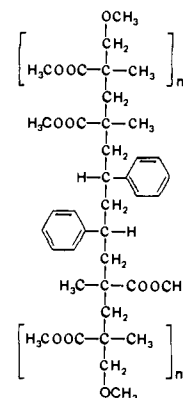
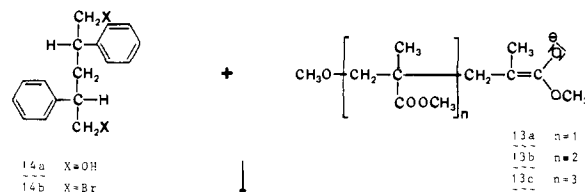
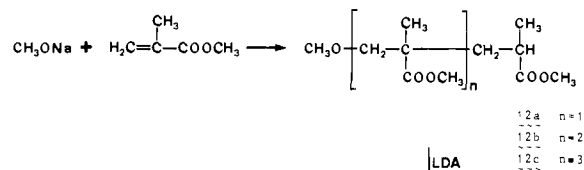
(17) Katritzky, A. R.; Smith, A.; Weiss, D. E. *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1547–1554. Hirai, H.; Tanabe, T.; Koinuma, H. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 203–222.

quired for polymers, it was possible to replace the boronic acid residues by hydrogen quantitatively. Neither side reactions involving methyl methacrylate units (controlled by NMR) nor cross-linking yielding insoluble polymers were observed. Styrene-methyl methacrylate copolymers thus obtained also exhibited negative optical rotations that were, however, lower compared with their precursors (see Table III).

Copolymers of **11** with styrene, after splitting off the mannitol residues, were deboronated in a similar manner. By this procedure, a copolymer of (4-vinylphenyl)boronic acid and styrene showing an optical rotation of  $[\alpha]_{365}^{30} -23.0^\circ$  is transformed to an optically inactive polystyrene. This clearly attests to the role of copolymeric asymmetric triads on the polymeric chirality.<sup>19</sup>

**Synthesis of Model Compounds.**<sup>20</sup> By the above-mentioned deboronation procedure, it was possible to achieve chiral styrene-methyl methacrylate copolymers showing negative optical rotations (see Table III). Even with 8 mol % styrene moieties in the chain an appreciable amount of rotation is observed. Although <sup>13</sup>C NMR investigations revealed the predominant presence of distyryl dyad units in the polymeric chain and only about 5% isolated styrene units,<sup>21</sup> it was not possible to elucidate the relative configuration of these dyads, as the documented literature does not provide any such information. Appropriate low molecular weight model compounds were therefore synthesized to supplement <sup>13</sup>C NMR assignments of the relative configuration of dyads. More importantly, with the help of the stereochemistry of these model compounds it will be possible to elucidate the absolute configuration of the chiral chain building blocks constituting the optically active copolymers. The necessary structure for these model compounds requires a dimeric styrene unit of definite stereochemistry [i.e., (*R,S*) = meso, (*R,R*), (*S,S*)] sandwiched by oligomeric methyl methacrylate chains (e.g., **15** or **17**). The synthetic strategy for obtaining a compound such as **15** involves coupling of 1,5-dibromo-2,4-diphenylpentane (**14b**) with ester enolates of oligo(methyl methacrylates).

*meso*- and (*S,S*)-1,5-dihydroxy-2,4-diphenylpentanes (**14a** and **16a**) have been synthesized following the method of Tatemitsu et al.<sup>22</sup> By use of tetrabromomethane/triphenylphosphine reagent<sup>23</sup> both the diastereomers could be converted to the desired dibromides **14b** and **16b**. Ester enolates of type **13** can be obtained by anionic polymerization of methyl methacrylate under appropriate conditions for obtaining "living polymers". Formation of oligomers with a broad molecular weight distribution is the main shortcoming of this procedure. Therefore it was preferable to isolate the pure oligomers and subsequently reactivate them to the ester enolates with lithium diisopropylamide (LDA).<sup>24</sup> The preparation of the oligomers involves anionic polymerization of methyl methacrylate with sodium methoxide/methanol.<sup>25</sup> Oligomers **12** having uniform molecular weight with  $n = 1-3$  were obtained by fractional distillation of the above product. These oligomers could be reactivated to ester enolates of type **13** by LDA at  $-78^\circ\text{C}$ . Unlike ester enolates of simple esters,<sup>26</sup> ester enolates of oligomeric esters tend to decompose at temperatures near 0



$^\circ\text{C}$ ,<sup>24b</sup> while the reactivity toward halides at low temperatures ( $-78^\circ\text{C}$ ) is too low. A compromise could be achieved by carrying out the reaction in THF/DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone)<sup>27</sup> at  $-40^\circ\text{C}$ . This solvent system facilitates alkylation of the ester enolates, and good yields of disubstituted products **15** and **17**, respectively, were obtained. The reaction was performed with  $n = 1$ ; with  $n = 2$  the yield is quite low, and with  $n = 3$  products with moderate yields are achieved.

In this manner, model compounds with (*R,R*)-distyryl units (**15a**) and *meso*-distyryl units (**17a**) could be obtained. The stereochemical course of this reaction was investigated by use of the (*R,R*) compound with  $n = 1$  (**15a**).

<sup>13</sup>C NMR spectral data<sup>21</sup> of **15a** reveal that the alkylation of the ester enolate leads to two diastereoisomers of the methyl methacrylate dyad with a *meso* to racemic dyad ratio of nearly 1:4. An asymmetric induction of the distyryl unit on the methacrylate residue was not observed. A complex mixture of diastereoisomers is thus obtained. It is quite logical to assume that (*R,R*)- or (*S,S*)-distyryl dyads in the optically active poly(styrene-*co*-methyl methacrylates) with low styrene content possess a similar structural neighborhood in the chain.

The *meso*- and the (*R,R*)-distyryl dyads in **17a** and **15a**, respectively, can be distinguished by <sup>13</sup>C NMR looking at the CH<sub>2</sub> group between the two carbons bearing the phenyl ring and the C-1 of the phenyl rings (Table IV). Stereochemical structural differences for both compounds can also be seen from the <sup>13</sup>C resonance patterns of the CH<sub>3</sub> and OCH<sub>3</sub> of the methacrylate units coupled to the distyryl dyad.<sup>21</sup>

(18) Seaman, W.; Johnson, J. R. *J. Am. Chem. Soc.* **1931**, *53*, 711-723.

(19) By this procedure, however, optically active homopolymers (though with lower optical activity) should in principle be obtained. Under the present conditions, this was not observed. The homopolymer possesses a chiral structure and is built up of (*S,S*)-distyryl units separated by atactic parts of the polystyrene chain. Wulff, G.; Dhal, P. K., unpublished results.

(20) Wulff, G.; Kemmerer, R.; Vogt, B. Presented at the Makromolekulares Kolloquium, Freiburg, March 1986; Abstract p 31.

(21) Wulff, G.; Kemmerer, R.; Vogt, B.; Dhal, P. K.; Steigel, A., unpublished results. A detailed NMR study of the newly synthesized model compounds and the optically active polymers will be published separately.

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(23) Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801. Castro, B. *R. Org. React. (N.Y.)* **1983**, *29*, 1-162.

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Table IV.  $^{13}\text{C}$  NMR Data of Model Compounds and Copolymers<sup>a</sup>

(R,R) compd <b>15a</b>	meso compd <b>17a</b>	copolymer
C-1 of Phenyl Rings		
143.64 (12.9)	144.12 (28.4)	143.9 (12.6)
143.67 (11.7)	144.52 (26.3)	144.3 (11.3)
144.00 (9.4)	145.80 (17.7)	144.6 (10.6)
145.28 (23.4)	145.84 (13.8)	145.0 (14.9)
145.33 (22.7)	146.20 (13.8)	145.4 (27.6)
145.37 (11.7)		145.9 (13.4)
145.41 (10.1)		146.3 (9.6)
CH <sub>2</sub> groups ( $\delta$ 46.6–49.5)		
46.74 (19.5)	47.75 (22.0)	46.8 (7.8)
46.83 (12.9)	48.04 (19.5)	47.3 (7.5)
47.83 (10.6)	48.38 (19.6)	47.7 (9.7)
47.89 (13.1)	48.85 (19.5)	48.0 (14.6)
47.99 (33.7)	49.11 (19.4)	48.4 (18.0)
49.08 (10.2)		49.2 (15.1)
		49.5 (15.4)

<sup>a</sup> $^{13}\text{C}$  NMR absorptions for the C-1 of the phenyl rings (ipso C) and the CH<sub>2</sub> groups between  $\delta$  46.6 and 49.5 are given. The latter represent mainly the CH<sub>2</sub> groups between the two carbons bearing the phenyl ring. Relative intensities of the peaks are given in parentheses. The copolymer consists of 8 mol % styrene and 92 mol % methyl methacrylate units, produced by copolymerization of **11** with methyl methacrylate, splitting off of the template, and deboronation. Spectra of **15a** and **17a** were measured in CDCl<sub>3</sub> at 75 MHz; the spectrum of the copolymer was measured in CDCl<sub>3</sub> at 90.52 MHz.

This new method for preparation of appropriate model compounds for copolymers with definite stereochemical arrangement of monomer units can be extended to several other copolymers. The central dyad units can be varied to different chemical structures, and the methyl methacrylate oligomers could be atactic, partially stereoregular, or even optically active.<sup>1</sup> Precisely speaking, this method furnishes a new route to synthesize a large variety of model compounds for accurate structural analysis of vinyl copolymers.

### Discussion

Copolymerization of the mannitol-based template monomer **11** with a number of comonomers followed by removal of the mannitol moiety yields linear, optically active copolymers. It has been established by using  $^{14}\text{C}$ -labeled mannitol that practically no mannitol residue is left in the polymer,<sup>10b</sup> thus affirming the origin of optical activity to the chirality arising from stereogenic relationships of the main chain. The chirality obviously arises due to chain configuration, and the possibility of conformation-based chirality such as helicity as in case of polytrityl methacrylates,<sup>28</sup> polytrichloroacetaldehyde,<sup>29</sup> or poly(isocyanides)<sup>30</sup> can be ruled out. There are no bulky groups to stabilize such single-handed conformation, and interactions like hydrogen bonding do not contribute to such supermolecular structure, as the polymer remains optically active after removal of the boronic acid moieties. No strong influence of solvent on the optical rotation is observed.

The observation that **11** yields soluble copolymers when copolymerized with different comonomers leads to the conclusion that a type of cyclopolymerization takes place. Calculations with the mathematical approximation given by Gibbs and McHenry<sup>15</sup> show nearly quantitative cyclopolymerization for **11**. This type of polymerization is well-known for nonconjugated dienes with a specific arrangement of the two double bonds.<sup>31</sup> In monomer

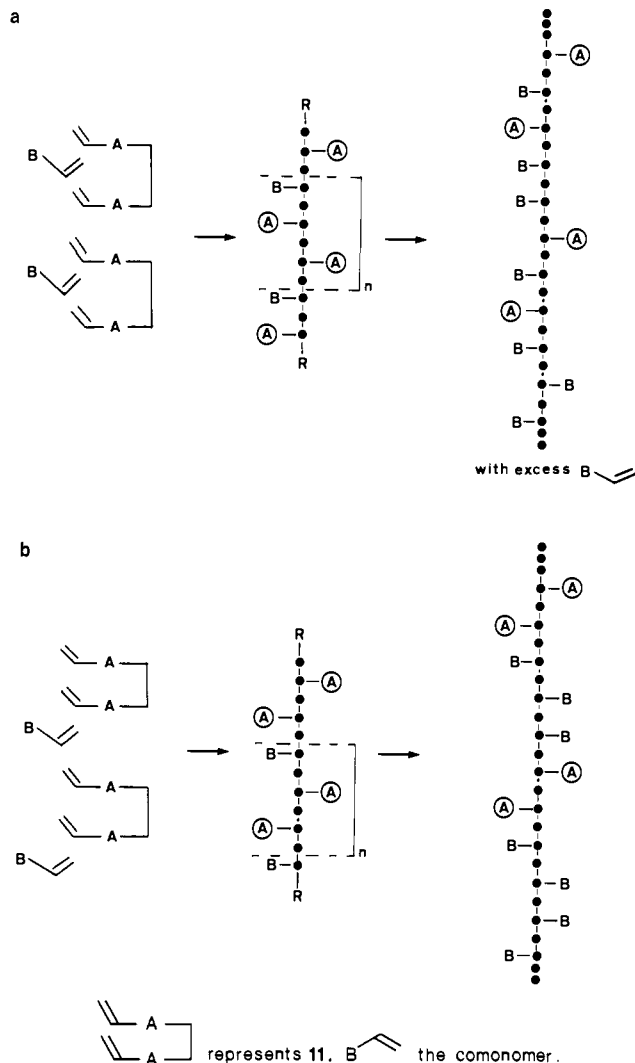


Figure 3. Schematic picture of two possible mechanisms for the formation of chiral triads. Key: (a) formation of an insertion complex with the comonomer, which undergoes a homopolymerization; (b) cyclopolymerization of **11** together with a copolymerization. The last column shows the structure of the polymer chains with an excess of the comonomer.

**11** a cyclopolymerization should be possible in the conformation given in the formula **11**. This conformation is supported by the X-ray crystallographic study of D-mannitol 1,2:3,4:5,6-tris-*O*-(phenylboronate).<sup>32</sup> Both compounds should possess a closely similar conformation, as in both cases it is fixed by a five-membered ring in the 3,4-position. 1,2:5,6-Bis[(4-vinylphenyl)boronyl]-D-mannitol derivatives with another conformational arrangement of polymerizable double bonds (e.g., the 3,4-di-*O*-benzyl derivative) do not produce optically active polymers.<sup>10b</sup>

On the basis of the aforementioned observation, the following two possible mechanisms can be put forward for this asymmetric copolymerization:

(a) **11** first forms an insertion complex with the comonomer, which afterwards undergoes a homopolymerization. A conformational analysis predicts the formation of optically active triads through this mechanism, as shown in Figure 3a.

(b) **11** undergoes a cyclopolymerization together with a copolymerization with the added comonomer. This mechanism also yields optically active triads as with mechanism a. (See Figure 3b.)

In order to ascertain the exact mechanism of this polymerization, detection of a possible complex formation between **11** and

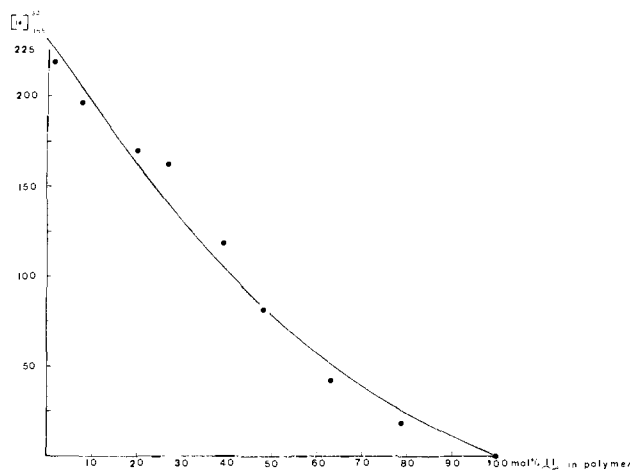
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**Figure 4.** Optical rotations after removal of the template of copolymers with varying amounts of **11** and methyl methacrylate calculated with respect to the amount of (4-vinylphenyl)boronic acid moieties present in the polymers. [E.g., at a weight percentage of 5% of the (4-vinylphenyl)boronic acid moieties in the copolymer, the measured specific optical rotation is multiplied by a factor of 20.] Points represent the experimental data, the solid line a compensated curve.

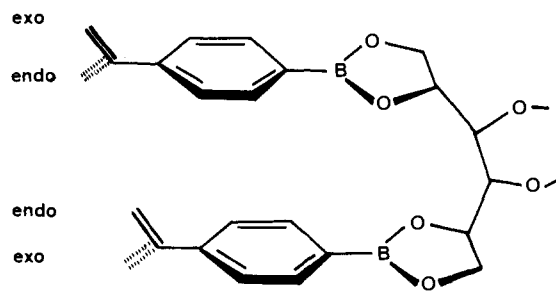
different comonomers was attempted by UV and NMR techniques, but in vain. A distinction between the two possibilities could be arrived at through the following approach. If polymerization proceeds via an insertion complex (type "a" mechanism), polymerization carried out with an excess amount of comonomer would produce copolymers containing isolated units of A [(4-vinylphenyl)boronic acid] and hence could not build a chiral main chain. This is due to the fact that alternating copolymers cannot generate the required chiral arrangements of monomers.<sup>5,7,33</sup>

Contrary to the foregoing, in the second type of mechanism (Figure 3b) with an excess of the B-containing comonomer in the polymerization mixture A-A dyads will still be produced. With a higher amount of A-A-forming monomer in the polymer chain, the generation of A tetrads and even A hexads will increase, for which a relatively lower contribution to the optical activity of the copolymer is expected. [A polymer containing 27 mol % **11** and 73 mol % methyl methacrylate units according to the copolymerization reactivity ratios should contain 78% dyads, 18% tetrads, and 3% hexads of (4-vinylphenyl)boronic acid units.] Therefore, with an excess of the B comonomer the optical activity with respect to the content of AA units should increase.

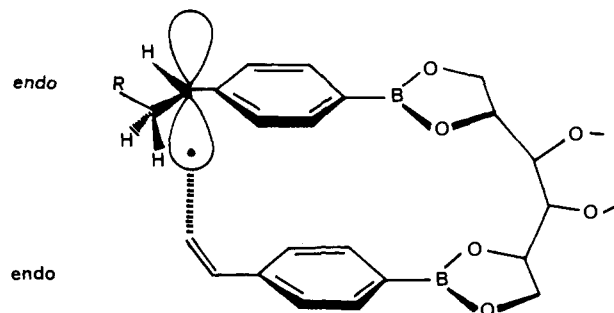
The optical rotation calculated with respect to the proportion of (4-vinylphenyl)boronic acid moieties present in the polymers with varying amounts of methyl methacrylate content is presented in Figure 4. It clearly illustrates a rise in the rotatory power of the polymers with increasing number of isolated distyryl dyads. These observations are sufficient for supporting the operation of a mechanism of the type "b" during this asymmetric copolymerization.

As the monomer **11** possesses  $C_2$  symmetry, it is immaterial which of the two vinyl groups of **11** is attacked first by the radical of the growing chain ( $R^*$ ) for asymmetric induction on the polymer chain. Each of the vinyl groupings of **11** may adopt one of two preferred conformations. Since the two phenyl rings in **11** are present in a terraced type of arrangement, the two conformations could be designated as *exo* and *endo* (see Figure 5). There seems to be no pronounced preference for one of the two conformations. Therefore, the attack of the radical of the growing chain at the vinyl group of **11** could occur in either the *exo* or *endo* conformation of the double bond with nearly equal probability.

Assuming an attack from an *endo* site (see Figure 6), a benzyl radical is formed, which in principle could attack the second double bond in its *endo* or in its *exo* conformation. In either case the benzyl radical reacts at the *si* face. Due to the resonance sta-

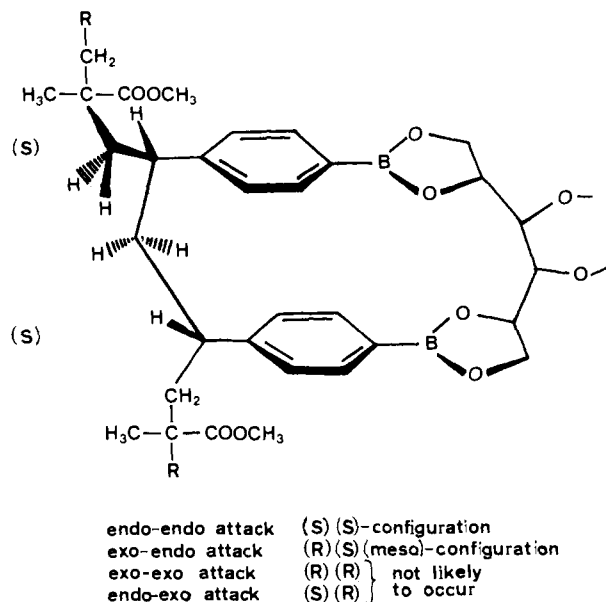


**Figure 5.** Different conformational arrangements in the vinyl group of **11**.



**Figure 6.** First attack of a radical ( $R^*$ ) at the *endo* position of **11**. Parts a and b are drawn by the program SCHAKAL. The main coordinates are taken from an X-ray analysis of D-mannitol 1,2:3,4:5,6-tris-*O*-(phenylboronate),<sup>32</sup> which have been partially replaced. Key: (a) ball and stick model, (b) space-filling model. For a better representation, the carbon atoms of the D-mannitol and of the two vinyl groups have been drawn in black, and in the ball and stick model, the hydrogens of the phenyl rings and the cyclohexane ring have been omitted.

bilization of the p orbital containing the unpaired electron there is a strong energy barrier of nearly 55–60 kJ/mol (13.1–14.3 kcal/mol)<sup>34</sup> to rotation about the benzylic bond, thus holding the



**Figure 7.** Endo-endo attack forming a 19-membered ring with asymmetric (*S,S*) configuration of the distyryl dyad. R's represent the polymer chain ends.

p orbital in a perpendicular position with respect to the aromatic ring. 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 the ring closure.

The steric requirements for an attack of the radical in the perpendicular position of the p orbital at the second double bond in the *endo* position are fulfilled, as can be seen from the appropriate model presented in Figure 6. On the other hand, an attack at the *exo*-positioned second double bond requires an unfavorable rotation around the benzyl radical bond as well as an out-of-plane rotation of the second double bond, resulting in a destabilized new benzyl radical. Therefore, only an endo-endo attack is likely to occur. For similar reasons, an *exo* attack at the first double bond will be followed by an *endo* attack at the second. As a result, only endo-endo and exo-endo attacks are expected.

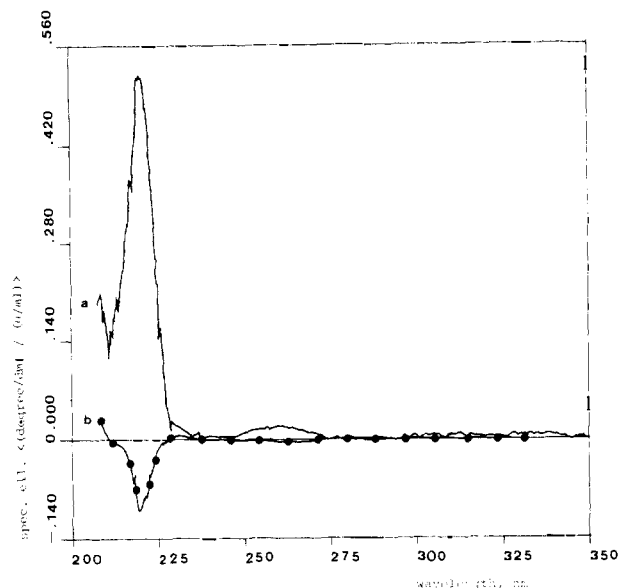
Through this type of attack at the second double bond of the template monomer the configuration at this carbon atom is predetermined prior to the attack of the comonomer, which can only react from beneath from the *si* face (see Figure 7; compare also Figure 6b). Therefore, an endo-endo attack results in the formation of a chiral and optically active (*S,S*)-distyryl dyad and an exo-endo attack in the formation of a *meso*-(*R,S*)-distyryl dyad. The optically active polymers obtained therefore should contain both of these two types of distyryl dyad units. Thus, the first step is not very selective, whereas the second one is strongly governed by the chirality of the D-mannitol template. As a result, enantiomeric (*R,R*) dyads annulling overall optical activity are not produced. The corresponding L-mannitol derivative of **11** produces polymers showing opposite optical rotations<sup>10b</sup> and having (*R,R*)- and (*S,R*)-distyryl dyads.

The evidence supporting the absolute configuration predicted for these copolymers was obtained by comparing their optical rotations with those of the synthesized model substances. **15a** with a (*R,R*) configuration shows an optical rotation of  $[\alpha]_{365}^{20} +85^\circ$ , whereas a deboronated copolymer containing 30 mol % styrene residues shows an optical rotation of opposite sign with  $[\alpha]_{365}^{30}$

(34) The barrier of rotation about the benzyl bond in the styrene radical has been found to be 56.3 kJ/mol (13.4 ± 1.0 kcal/mol).<sup>35,36</sup> In our case, the barrier might be slightly higher due to the electron-withdrawing effect of the boron and the bulkiness of the substituent.

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**Figure 8.** CD spectra of **15a** (a) and a copolymer of styrene and methyl methacrylate (b, 30:70), produced by copolymerization of **11** and methyl methacrylate, splitting off of the template, and deboronation. The ordinate shows the specific ellipticity in (deg·dm)/(g·mL).

**Table V.** Elemental Analysis of Polymers from Table I

polymer	B, %	N, %	<b>11</b> , mol %
1	6.02	2.83	59.1
2	5.62		53.0
3	5.58		48.5
4	5.52		59.8
5	5.85		65.9
6	5.12		64.2
7	5.86		58.8
8	5.36		52.4
9	4.60		40.4
10	5.86		64.8
11	5.47		58.3
12	3.91	2.95	52.4
13	4.78	2.67	57.2
14	4.17	2.54	60.1

$-30^\circ$ . In accordance, the CD spectra of both compounds show Cotton effects at 220 nm of opposite sign (see Figure 8). This attests to the presence of (*S,S*)-distyryl dyads in the optically active polymers. The lower optical rotation of the polymers can be ascribed to the following two effects: First, as Figure 4 shows, the maximum optical rotation of an individual distyryl unit is attained only at a low concentration of the styrene units (at higher concentration, tetrads, hexads, etc. will also be present). Second, in addition to optically active dyads, *meso* dyads are expected to be produced as well. <sup>13</sup>C NMR comparison of the model compounds **15a** and **17a** with a polymer containing only 8% styrene moieties in the chain shows that the optically active dyads and *meso* dyads are present with nearly equal intensity.<sup>21</sup>

The mechanism as shown in Figures 6 and 7 involves a cyclopolymerization, with the formation of a 19-membered ring. This is the first example of the formation of a large ring during cyclopolymerization, since the cyclopolymerization has been reported to occur normally through the formation of five and six-membered rings.<sup>31</sup> Although the formation of a 19-membered ring is involved, only two independent rotational axes (C-2-C-3 and C-4-C-5 in the mannitol moiety) are present that determine the relative position of the two styrene groups. Therefore this compound is comparable in rotational freedom with other cyclopolymerizable diene monomers (e.g., acrylic anhydride).

This investigation has enabled the elucidation of the mechanism of the asymmetric polymerization of vinyl monomers reported for the first time. The reaction yields copolymers showing optical activity due to configurational relationships in the main chain. The origin of the chirality has been clearly established, and the

**Table VI.** Composition of Copolymers of Methacrylonitrile with **11** (See Figure 1)

11 in monomer, mol %	11 in polymer						
	elemental anal.			<sup>1</sup> H NMR anal. (rel intens)			
	B, %	11, mol %	N, %	11, mol %	aryl protons	alkyl protons	11, mol %
4.0					79	266	20
9.7	4.40	25.6	7.32	29.5			
9.8	4.49	26.6	7.45	28.9			
10.8	4.53	27.0	7.45	28.9			
16.0	4.91	31.7	5.65	37.9			
19.2	5.12	34.7	5.11	41.1			
34.6	5.65	43.6	4.05	48.5			
49.3	6.02	51.5	2.83	59.1	277	331	58
50.2	5.73	45.2	2.52	62.3			
64.4	6.43	62.5	1.95	68.7	215	214	72
73.6	6.43	62.5	1.20	78.8	239	229	75
75.3	6.22	56.5	1.28	77.6			
86.0	6.20	56.0	0.50	90.0	218	195	81
88.8	6.89	79.0	0.80	85.0			

absolute configuration of the chiral distyryl dyad building blocks has been elucidated.

### Experimental Section

**General Procedures.** Elemental analyses were performed in the microanalytical laboratories of Dr. F. Pascher, Bonn (B analyses), and of the Faculty of Natural Sciences of the University of Düsseldorf. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian XL-100, VXR 300, and Bruker WP 360 spectrometers. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter. CD spectral measurements were carried out at 25 °C in 1,4-dioxane, using a Jasco J-20 automatic recording spectropolarimeter, interfaced with a DEC Microvax-2. Cell path lengths of 10 mm and 0.5 mm were used in the wavelength regions of 350–240 and 260–206 nm, respectively. Concentrations were chosen so as to obtain measurable UV absorbance.

**Preparation of 3,4-*O*-Cyclohexylidene-*D*-mannitol 1,2:5,6-Bis-*O*-[(4-vinylphenyl)boronate] (**11**).** 3,4-*O*-Cyclohexylidene-*D*-mannitol<sup>12</sup> (26.2 g, 0.1 mol) and 26 g (0.066 mol) of tris-*O*-(4-vinylphenyl)boroxin<sup>10b</sup> were heated in 150 mL of methylene chloride for 3 h, and the water formed was azeotropically distilled off. The solution was evaporated, and the residue was extracted with petroleum ether (60:80)/toluene (9:1, v/v). The crystals obtained were recrystallized three times from petroleum ether (60:80), giving 31 g (65%) of **11**: mp 113 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> +18°, at 365 nm +40.9°, at 436 nm +32.7°, at 546 nm +20.9°, at 578 nm +18.7° (c 4.0, THF). The NMR data agree with the predicted structure. Anal. Calcd for C<sub>28</sub>H<sub>32</sub>B<sub>2</sub>O<sub>6</sub>: C, 69.16; H, 6.65. Found: C, 68.89; H, 6.56.

**Comonomers.** The comonomers methyl methacrylate, methyl acrylate, isobutyl methacrylate, *n*-butyl methacrylate, *n*-decyl methacrylate, methacrylonitrile, and styrene were reagent grade and were purchased from E. Merck, Darmstadt. Similarly, 4-methylstyrene, 3-methylstyrene, and 4-vinylpyridine were obtained from Fluka, AG Buchs. The monomers were purified by refluxing for 1 h with calcium hydride followed by distillation prior to use. 4-Methoxystyrene,<sup>37</sup> 4-chlorostyrene,<sup>38</sup> 4-nitrostyrene,<sup>39</sup> and 4-cyanostyrene<sup>40</sup> were prepared according to reported literature procedures.

**Preparation of the Polymers. General Procedure.** Predetermined amounts of the monomers containing 0.5% azobis(isobutyronitrile) (w/w) were taken in a round-bottom flask and dissolved in toluene to make a solution of 0.5 mol/L. The polymerization mixture was subjected to repeated cool-thaw cycles to remove dissolved oxygen, and polymerization was carried out by keeping it at 60 or 70 °C in a thermostated shaker. At regular intervals, samples were taken out by a hypodermic syringe through a rubber septum and injected into a precipitating solvent. This method enabled us to monitor the percentage of conversion of monomers to polymers. After the desired conversion had been achieved, the reaction mixture was cooled to room temperature and precipitated into large volumes of vigorously stirred petroleum ether. The polymer was filtered off and washed with petroleum ether/toluene (5:1). The isolated polymer was dissolved in acetone/water (9:1, v/v) and was reprecipitated from weakly acidified methanol/water (3:1–1:3, v/v). This procedure

**Table VII.** Composition of Copolymers of Methyl Methacrylate and **11**

11 in monomer, mol %	11 in polymer by <sup>1</sup> H NMR anal. <sup>a</sup>		
	aryl protons	alkyl protons	11, mol %
0.5	18	1042	2
2.0	49	631	8
5.9	106	515	20
9.1	215	733	27
9.5	55	198	26
19.2	92	216	39
29.0	73	114	48
49.0	113	162	63
69.2	83	85	79

<sup>a</sup> Relative intensities of the peaks.

was repeated several times until the polymer showed constant optical rotation. In this manner the template can be split off quantitatively. The copolymers were finally precipitated from methylene chloride or were freeze dried from dioxane/water (9:1) to constant weight.

**Characterization of Polymers.** The compositions of the copolymers were determined by boron and nitrogen elemental analyses. While the results based on nitrogen analysis seem to be relatively reliable, results based on boron analysis seem to be less precise. In the case of copolymers of **11** with methacrylonitrile and methyl methacrylate, a third method was adopted for the determination of the composition. <sup>1</sup>H NMR spectra of the copolymers were used for such purpose by utilizing the peak areas due to aromatic protons and aliphatic protons. In copolymers, the monomeric unit of **11** (after splitting off the template) will result in eight aromatic and six aliphatic protons. Methacrylonitrile will result in five aliphatic and methyl methacrylate in eight aliphatic protons. By using the ratio of aromatic to aliphatic proton resonances, the mole ratio of the comonomers in the copolymers can be conveniently calculated. Problems sometimes arose due to interference of OH protons with the aliphatic protons. By addition of a trace amount of D<sub>2</sub>SO<sub>4</sub>, the OH signals were shifted to a downfield region. Results of composition analyses are summarized in Table V–VII. Molecular weight determination by membrane osmometry presented difficulties due to a relatively broad molecular weight distribution (see ref 10b). Values between 40 000 and 120 000 are obtained. GPC investigations were possible with the deboronated polymers.

**Investigation on Polymers Bearing the Template.** The course of the copolymerization reaction of **11** with methyl methacrylate or methacrylonitrile could be followed directly by three different methods. Polymerization of 15 mol % **11** and 85 mol % methacrylonitrile in toluene at 65 °C in a polarimeter cuvette showed increasing optical rotation during 3 h. The optical rotation increased from +1.1° to +1.6° (about 20% conversion). A quantitative analysis was not possible, since apparently long-term variations in optical activity occurred after this time. After 3 days of standing at room temperature, the optical rotation decreased nearly to the starting value. More reliable results were obtained by isolating a polymer with much lower content of **11** (see later).

Copolymerization mixtures containing 20, 30, and 70% **11**, which had been polymerized to the extent of 13–22%, were investigated by GPC. In all three cases a separate peak for the copolymer was obtained, which supports the formation of soluble polymers. Experimental conditions: column,  $\mu$ -Styragel 10<sup>4</sup> Å (25 cm); solvent, toluene; temperature, 50 °C; flow rate, 1 mL/min; pressure, 14 bar.

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Copolymers of methacrylonitrile or methyl methacrylate prepared with larger amounts of **11** were insoluble in anhydrous solvents. A copolymer prepared with 1.8 mol % **11** and methyl methacrylate (containing 7 mol % **11** in the copolymer according to NMR) was soluble in THF after the usual workup procedure. It showed  $[\alpha]_{365}^{30} +14^\circ$  ( $c$  1.0). After splitting off the template in the usual manner, an optical rotation of  $[\alpha]_{365}^{30} -38^\circ$  was observed.

**Deboronation of Polymers. General Procedure.** Copolymer (1.5 g) was suspended in 150 mL of acetone at room temperature, and just enough water was added to dissolve the copolymer. A 1.5 mol excess (calculated on the basis of boron content) of  $\text{AgNO}_3$  dissolved in 5 mL of concentrated  $\text{NH}_3$  was added with stirring. Copolymers with low boron content remained soluble, while those with higher boron content precipitated out. After the mixture was stirred for 10 min, 230 mL of water was added, and the reaction mixture was refluxed for 1 h. The solvent was decanted, and the precipitated polymer was purified by repeated dissolution and reprecipitation from THF or chloroform and petroleum ether or methanol, respectively. Removal of boron was verified by IR spectroscopy (absence of the B-O band at  $1350\text{ cm}^{-1}$ ). The procedure was repeated, when required, to remove the boronic acid residues completely. (For substances, see Table III.) For a compound prepared from 20 mol % **11** having after deboronation  $[\alpha]_{365}^{30} -21^\circ$ , a CD spectrum was measured: CD (0.8 mg in 1 mL of dioxane) specific ellipticity (deg·mL/dm·g)  $-0.11$  (220 nm),  $-0.003$  (260 nm) (see Figure 8).

**Synthesis of the Distyryl Unit. meso-1,5-Dibromo-2,4-diphenylpentane (16b).** meso-1,5-Dihydroxy-2,4-diphenylpentane (**16a**)<sup>22</sup> 3.5 g, 14 mmol) and tetrabromomethane (18.5 g, 36 mmol) were dissolved in 50 mL of methylene chloride in a 500-mL flask under a nitrogen atmosphere and cooled to 0 °C. Triphenylphosphine (14.7 g, 56 mmol) dissolved in 100 mL of methylene chloride was added dropwise. The reaction mixture was slowly allowed to warm to room temperature and stirred for another 2 h. Methanol was added to decompose the excess of the  $\text{CBr}_4/\text{P}(\text{C}_6\text{H}_5)_3$  complex, and the solvent was removed under reduced pressure. The resulting residue was treated with ether/methylene chloride (80:20, v/v) and finally filtered through a pad of aluminum oxide (neutral) to separate the triphenylphosphine oxide. The filtrate was concentrated and purified by vacuum distillation (Kugelrohr, 180 °C,  $10^{-2}$  Pa), yielding 4.0 g (76%) of **16b**:  $^1\text{H NMR } \delta$  2.24 (m, 2 H,  $\text{CH}_2$ ), 2.9 (septet,  $J_{1,2} = J_{2,3} = J_{2,3'} = 6$  Hz, 2 H, CH), 3.52 (d,  $J_{1,2} = J_{4,5} = 6$  Hz, 4 H,  $\text{CH}_2\text{Br}$ ), 7.13 (m, 10 H, phenyl); mass spectrum,  $m/e$  382 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{18}\text{Br}_2$ : C, 53.43; H, 4.75. Found: C, 53.06; H, 4.75.

**(S,S)-1,5-Dibromo-2,4-diphenylpentane (14b).** This compound was synthesized in the analogous manner as described for the meso compound above:  $^1\text{H NMR } \delta$  2.33 (m, 2 H,  $\text{CH}_2$ ), 2.64 (m, 2 H, CH), 3.44 (d,  $J_{1,2} = 6$  Hz, 4 H,  $\text{CH}_2\text{Br}$ ), 7.12 (m, 10 H, phenyl); mass spectrum,  $m/e$  382 ( $\text{M}^+$ ); specific rotation  $[\alpha]_{20}^{20} +32^\circ$  ( $\text{CHCl}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{18}\text{Br}_2$ : C, 53.43; H, 4.75. Found: C, 53.42; H, 4.80.

**Oligomers of Methyl Methacrylate.** The oligomers were prepared by anionic polymerization of methyl methacrylate with sodium methoxide as initiator in the presence of methanol, analogous to the procedure described by Völker et al.<sup>25</sup> Up to the pentamer, the oligomers were separated by vacuum distillation.

**Coupling Reaction.** Dimethyl 2-(methoxymethyl)-2,4-dimethylglutarate (**12a**);<sup>25</sup> 3.7 g, 16 mmol, the oligomer with  $P_n = 2$ , was converted to the ester enolate according to the procedure described by Lochmann<sup>24</sup> (LDA, THF,  $-78^\circ\text{C}$ ). A solution of meso-1,5-dibromo-2,4-diphenylpentane (**16b**; 3 g, 7 mmol) in 20 mL of DMPU (1,3-di-

methyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone)<sup>27</sup> was added at  $-70^\circ\text{C}$ , stirred for 1 h, allowed to warm to  $-40^\circ\text{C}$ , and stirred at this temperature for 3 days. During this period, samples were taken at regular intervals to check the completion of the reaction by GPC analysis. After completion, methanol was added to decompose the unreacted anions. The reaction mixture was worked up in the following manner: 100 mL of water was added and the mixture was stirred for 1 h and extracted with diethyl ether. The combined organic extracts were dried over  $\text{MgSO}_4$ , filtered, and concentrated. The pure product **17a** was isolated by preparative GPC (Ostion LGC 6%, Chemapol Praha, eluent THF) (80% yield analyzed by GPC):  $^1\text{H NMR } \delta$  0.96 (m, 12 H,  $\text{CH}_3$ ), 1.83 (m, 14 H,  $\text{CH}_2$ ), 2.88 (s, 6 H,  $\text{OCH}_3$ , ester), 3.3 (s, 6 H,  $\text{OCH}_3$ , ether), 3.6 (m, 6 H,  $\text{OCH}_3$ , ester), 7.06 (m, 10 H, phenyl); mass spectrum,  $m/e$  682 ( $\text{M}^+$ ), 651 ( $\text{M} - 31$ ). Anal. Calcd for  $\text{C}_{39}\text{H}_{56}\text{O}_{10}$ : C, 68.48; H, 8.24. Found: C, 67.32; H, 8.32.

**Reaction of (S,S)-1,5-Dibromo-2,4-diphenylpentane (14a) with Dimethyl 2-(Methoxymethyl)-2,4-dimethylglutarate.** The procedure employed for this case is analogous to that used for the meso component **17a**. Product **15a**:  $^1\text{H NMR } \delta$  0.85 (m, 12 H,  $\text{CH}_3$ ), 1.75 (m, 14 H,  $\text{CH}_2$ ), 2.9 (s, 6 H,  $\text{OCH}_3$ , ester), 3.2 (s, 6 H,  $\text{OCH}_3$ , ether), 3.48 (m, 6 H,  $\text{OCH}_3$ , ester), 7.08 (m, 10 H, phenyl); mass spectrum,  $m/e$  682 ( $\text{M}^+$ ), 651 ( $\text{M} - 31$ ); specific rotation  $[\alpha]_{20}^{20} +21.2^\circ$  ( $\text{CHCl}_3$ ); CD (2 mg in 1 mL of dioxane) specific ellipticity (deg·mL/dm·g)  $+0.52$  (220 nm),  $+0.02$  (260 nm). Anal. Calcd for  $\text{C}_{39}\text{H}_{56}\text{O}_{10}$ : C, 68.46; H, 8.24. Found: C, 68.36; H, 8.33.

**Reaction of meso- and (S,S)-1,5-Dibromo-2,4-diphenylpentanes with Higher Oligomers.** The procedure employed for these reactions is analogous to the coupling reaction with the dimer described above. The coupling reaction carried out with the trimeric methyl methacrylate did not give an appreciable amount of disubstituted product, while with the tetramer, 10% of the disubstituted product and 60% of monosubstituted product were obtained (HPLC analysis).

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**Registry No.** **11**, 110590-40-4; (**11**)(methacrylonitrile) (copolymer), 110590-41-5; (**11**)(methyl methacrylate) (copolymer), 110590-54-0; (**11**)(methyl acrylate) (copolymer), 110590-42-6; (**11**)(isobutyl methacrylate) (copolymer), 110590-43-7; (**11**)(butyl methacrylate) (copolymer), 110590-44-8; (**11**)(decyl methacrylate) (copolymer), 110590-45-9; (**11**)(styrene) (copolymer), 110590-46-0; (**11**)(3-methylstyrene) (copolymer), 110590-47-1; (**11**)(4-methylstyrene) (copolymer), 110590-48-2; (**11**)(4-methoxystyrene) (copolymer), 110590-49-3; (**11**)(4-chlorostyrene) (copolymer), 110590-50-6; (**11**)(4-nitrostyrene) (copolymer), 110590-51-7; (**11**)(4-cyanostyrene) (copolymer), 110590-52-8; (**11**)(4-vinylpyridine) (copolymer), 110590-53-9; **14b**, 110658-91-8; **15a**, 110590-58-4; **16a**, 20698-77-5; **16b**, 110590-57-3; methacrylonitrile, 126-98-7; methyl methacrylate, 80-62-6; 3,4-*O*-cyclohexylidene-D-mannitol, 110590-55-1; tris-*O*-(4-vinylphenyl)boroxin, 110590-56-2; dimethyl-2-(methoxymethyl)-2,4-dimethylglutarate, 13423-03-5.