No. DMR-7926048). Thanks are also extended to the University of Lowell and to the Fulbright–Hays Program for partial support of M.M.

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Chirality of Polyvinyl Compounds. 2. An Asymmetric Copolymerization

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Received November 17, 1981

ABSTRACT: Optically active polymers or copolymers of 1-substituted olefins with structural chirality in the main chain were previously unknown and not expected to occur. By symmetry considerations, three types of structure are deduced where optical activity due to chirality of the main chain is to be expected. One of these, the structure resulting from asymmetric copolymerization, was realized. For this, two monomeric units were fixed stereospecifically at a chiral template molecule and during radical polymerization another comonomer was polymerized diastereoselectively with these two. After the template was split off, linear optically active copolymers with asymmetric triads were obtained. D-Mannitol 1,2:3,4:5,6-tris-*O*-[(4-vinylphenyl)boronate] (**5a**), 3,4-*O*-isopropylidene-D-mannitol 1,2:5,6-bis-*O*[(4-vinylphenyl)boronate] (**6**), and D-mannitol 3,4-*O*-carbonate 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**7**) were thus successfully used in copolymerization with methyl methacrylate or styrene. D-Mannitol 3,4-di-*O*-benzyl ether 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**8**), methyl α-D-mannopyranoside 2,3:4,6-bis-*O*-[(4-vinylphenyl)boronate] (**9**), or D-glucitol tris-*O*-[(4-vinylphenyl)boronate] (**10**), which have another conformational arrangement of the (4-vinylphenyl)boronate residues, did not give optically active copolymers after the template was split off. A possible reaction mechanism for this new type of copolymerization is discussed.

I. Introduction

During our investigations on enzyme analogue built polymers,[1] the question arose as to whether vinyl monomers in the presence of optically active templates can form optically active polymers whose optical activity depends on the chirality of the main chain. According to previous findings[2] optical activity is not expected to occur in usual polyvinyl compounds, since in each step of the polymerization of a 1-substituted olefin, a chiral center is formed from a prochiral center, but in atactic polymers with an irregularly alternating *R* and *S* configuration and in syndiotactic polymers with a regularly alternating *R* and *S* configuration. Chains of this type could indeed be chiral, but the optical activity is intramolecularly compensated and therefore not measurable. Isotactic polymers (**1**, Chart I) could begin with an *R* or with an *S* configuration, with formation of two enantiomorphic chains. If, however, the difference in the end groups can be neglected ($RCH_2 \simeq R'$), as is always permissible in the case of longer chain lengths, the molecule possesses a reflection plane (i.e., it is a mesoform) and does not show any optical activity.[2]

In accordance with this, as yet no optically active polyvinyl or polyvinylidene compounds are known whose optical activity depends on the chiral structure of the main chain;[3] indeed, there are numerous examples where the optical activity arises from chiral side chains.[2]

On the other hand, for polymers from 1,2-disubstituted olefins like homopolymers from benzofuran[2,4] or alternating copolymers from maleic acid,[2,5] the occurrence of chirality in the main chain is to be expected, and many optically active polymers have already thus been obtained by asymmetric induction.[2]

The same holds true with polymers from substituted 1,3-dienes,[2,6] where also optical activity due to chirality of the main chain can be achieved.

Recently, we deduced by symmetry considerations three types of structure where optical activity due to chirality of the main chain is expected in vinyl or vinylidene polymers.[7] One possibility would be the head-to-head polymerization of the monomers, in which 1,2-disubstituted chiral segments can be formed (**2**) with a structure similar to that of the copolymers of the 1,2-disubstituted monomers. Chirality in the main chain would also be possible if the substituents near the center of an isotactic polymer chain change to the other side of the main chain with respect to the Fischer projection (**3**). Since each part of the chain has in itself a strong isotactic structure, we propose the designation inverse-diblock isotacic for this type of arrangement. With identical chain ends, **3** has one twofold symmetry axis and is therefore chiral as a whole. Whether this type of polymer can exhibit a measurable optical activity is now investigated by an attempted directed synthesis of this type.

While the concept inverse-diblock isotactic applies for homo- as well as copolymers, there should also be a type of chirality of polymer chains that can occur only in copolymers. **4** represents one example of several possibilities. In these copolymers triad I, as well as the other two possible triads, is asymmetric, and polymers of this type should show optical activity. In this context, it must be remembered that optical activity should already occur if the structures **2**, **3**, and **4** are only partially realized in the chains.

Another quite different possibility of chirality in polymer chains has been realized very recently. Okamoto et al.[8a] described the preparation of optically active, isotactic poly(triphenylmethyl methacrylate) in a one-handed helical conformation by anionic polymerization in the

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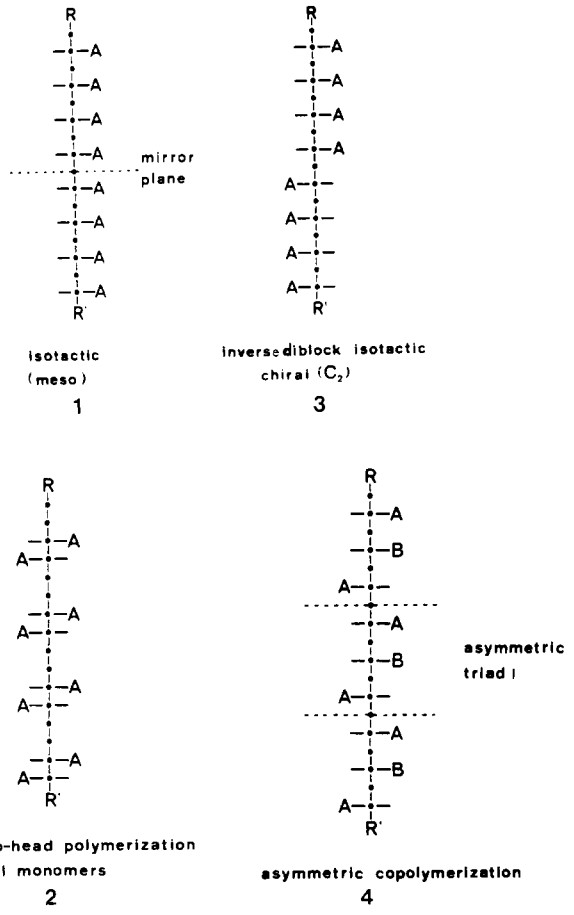
Chart I



presence of (−)-sparteine. On substitution of the trityl by the less bulky methyl ester group, optically inactive (meso) poly(methyl methacrylate) was obtained.

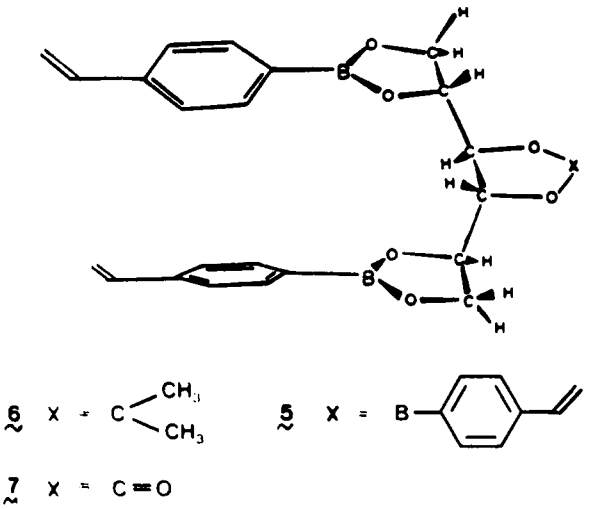
In this paper, we report on the realization of the concept of the asymmetric copolymerization. Parts of this investigation have already been described in two short communications.[7]

II. Results

1. Selection and Preparation of the Monomers. Looking at the triad I of **4**, one notes that a monomeric unit with a B substituent is neighbored by two others with an A substituent. To prepare such triads in the right stereochemistry, we attempted to fix two monomeric units stereospecifically at a chiral template molecule and to insert diastereoselectively another monomer between these two during polymerization. After polymerization, the template molecule was intended to be split off.

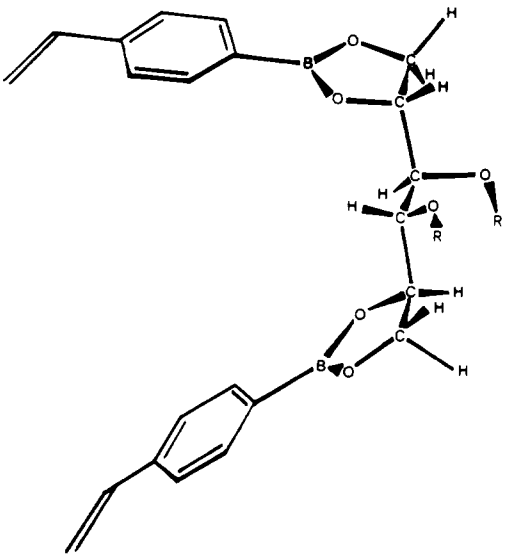
For this purpose D-mannitol 1,2:3,4:5,6-tris-*O*-[(4-vinylphenyl)boronate] (**5a**), which was prepared earlier,[1a,c] was used. The conformation given in formula **5a** is supported by an X-ray analysis of D-mannitol 1,2:3,4:5,6-tris-*O*-phenylboronate.[9] A comonomer can easily be inserted between the styrene residues in the 1,2- and 5,6-positions of **5a** in the given conformation. The corresponding derivatives of D-[1-^{14}C]mannitol (**5b**) and L-mannitol (**5c**) were also prepared.

Since the polymerizable residue in the 3,4-position is not necessary for the assigned purpose, it was replaced by other groups. For this, the 3,4-*O*-isopropylidene compound **6** and the 3,4-carbonate **7** were prepared. **6** could be obtained by esterification of 3,4-*O*-isopropylidene-D-mannitol[10] and **7** by esterification of D-mannitol 3,4-*O*-carbonate[11] with (4-vinylphenyl)boronic acid. The conformations of **5**–**7**



should be fairly similar; in all cases they are fixed by a five-membered ring in the 3,4-position. Insignificant differences may be possible by replacement of boron by carbon and by the different hybridization of the carbon (sp^3 and sp^2).

For control experiments, bifunctional monomers with different steric arrangements of the (4-vinylphenyl)boronate residues should be used. For this, the five-membered ring in **5**–**7** was replaced by a 3,4-di-*O*-benzyl grouping. The whole molecule will become much more flexible by this structural change, and the most probable conformation should be that with a planar zigzag arrangement[12] of the mannitol chain as is shown in formula **8**. For the synthesis



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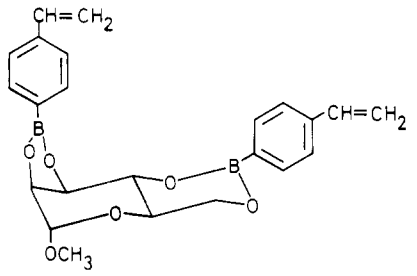
of **8**, 1,2:5,6-di-*O*-isopropylidene-D-mannitol[13] was benzylated in the 3,4-position to give **11a**, from which the isopropylidene groups were split off by weak acid. The resulting **11b** was then esterified with 2 equiv of (4-vinylphenyl)boronic acid to give the desired **8**.

Likewise, another spatial arrangement of the two (4-vinylphenyl)boronate residues in **5**, **6**, or **7** gives **9**. This compound, which was prepared earlier by us,[1b] is conformationally restricted by a pyranoid sugar ring.

In addition to D-mannitol, D-glucitol was transformed to the tris[(4-vinylphenyl)boronate] (**10**). In this case, the position of the boronic ester residues has not been proved. Whereas the structure of the known D-glucitol tris-*O*-phenylboronate[14] is not clarified, tri-*O*-isopropylidene-D-glucitol has a 1,2:3,4:5,6-substitution pattern.[15] In view of



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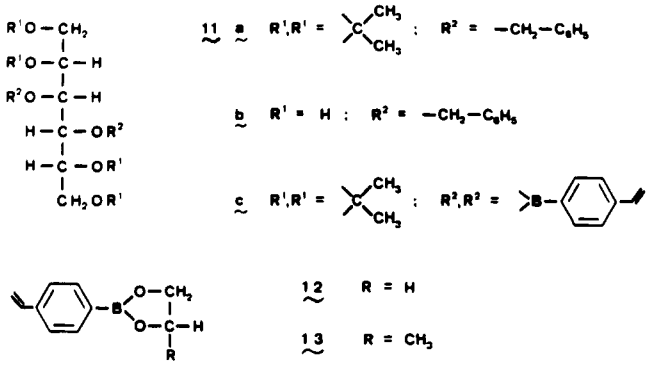
the similarity in the substitution pattern between isopropylidene and phenylboronate derivatives,[16] **10** should possess a 1,2:3,4:5,6 substitution pattern as well.

In addition, experiments with chiral monomers containing only one (4-vinylphenyl)boronate residue were performed. For this, the mannitol 3,4-*O*-[(4-vinylphenyl)boronate] **11c** was used, which was prepared by



esterification of 1,2:5,6-di-*O*-isopropylidene-D-mannitol with (4-vinylphenyl)boronic acid. Likewise the monomers **12** and **13**[1c] contain only one (4-vinylphenyl)boronate residue.

2. Preparation and Properties of the Polymers. The described monomers **5**–**13** were copolymerized radically with varying amounts of comonomer, mostly methyl methacrylate (for composition of the polymerization mixtures, see Tables I and II.) In the case of the monomers **5**–**10**, cross-linked, insoluble polymers were normally[17] obtained, from which the template D-mannitol (with polymers from **5a**, **5b**), L-mannitol (with polymers from **5c**), 3,4-*O*-isopropylidene-D-mannitol (from **6**), D-mannitol 3,4-*O*-carbonate (from **7**), 3,4-di-*O*-benzyl-D-mannitol (from **8**), methyl α-D-mannopyranoside (from **9**), and D-glucitol (from **10**) could be split off by methanol–water. As a result of this, the polymers became soluble and could be completely freed from the template by repeated precipitation from 10:1 acetone–water in water.

These polymers, mostly poly[4-vinylphenyl)boronic acid-*co*-methyl methacrylate], showed molecular weights (M_n) on the order of 44 000–120 000 (membrane osmometric). According to their osmometric behavior, they possessed a broad molecular weight distribution. They were soluble only in solvent mixtures containing some protic solvent. On drying, apparently –B–O–B– anhydride structures with cross-linking are formed. With water or alcohols, these bonds are broken. Elemental analysis was therefore strongly dependent upon the drying conditions and hence not very reliable. Furthermore, in boron-containing cross-linked polymers the carbon content is usually found to be too low, as was discovered in previous experiments.[17]

The polymerization was carried out in such a way as to obtain a quantitative conversion. Actually the yields were in the range 60–90%. This type of polymerization gives a high amount of polymer from valuable starting materials. This procedure could be applied with methyl methacrylate and styrene as comonomers, since the observed optical rotations compared to those obtained in experiments with only 10% conversion did not differ markedly. With other comonomers having strongly differing reactivity ratios, as with methacrylonitrile, there are strong differences in optical rotation depending on the conversion.[18] The ratio of the monomeric units in the polymerization mixture and in the resulting polymers with high conversion is nearly the same, as can be judged from the boron elemental analysis (see Table IV).

3. Optical Rotation of the Polymers. The optical rotations were measured in 10:1 acetone–water solution (*c* 0.2). The results are given in Tables I and II.[19] As can be seen, copolymers from **5a**,**b**, **6**, and **7** show strong negative rotations. In contrast, the optical rotations of the starting monomers are strongly positive: **5a**, $[\alpha]^{20}_{365}$ +270° (chloroform); **6**, $[\alpha]^{20}_{365}$ +17.3° (acetone); **7**, $[\alpha]^{20}_{365}$ +408° (acetone). The optical rotations of the templates are as follows: D-mannitol, $[\alpha]^{22}_{365}$ –3.5° (water); 3,4-*O*-isopropylidene-D-mannitol, $[\alpha]^{20}_{365}$ +73.3° (water); D-mannitol-3,4 *O*-carbonate, $[\alpha]^{20}_{365}$ +92.1° (acetone). It can therefore be concluded that the rotations of the polymers do not originate from adhering starting material or template. Polymer A-14 from the L-mannitol monomer **5c** showed optical rotation of the opposite sign.

Templates not completely split off result in a positive rotation of the polymer obtained. On mixing a solution of polymer H-1 (not optically active) with a solution of D-mannitol, the optical rotations quickly became strongly positive. Under these conditions, the polymer can form boronic esters with D-mannitol.[1c] After some time the solution became turbid and, as a result of cross-linking, the polymer subsequently precipitated.

In order to exclude optical activity brought about by incorporation of D-mannitol by chain transfer reactions, we repeated the experiments with monomer **5b** prepared from D-[1-^{14}C]mannitol. Under the same conditions given before, polymers A-11, A-12, and A-13 showed optical rotation in the same order as with monomer **5a** (see Table III). By determination of the radioactivity by liquid scintillation counting, it was found that only 0.2% and 0.4%, respectively, of the total D-mannitol was still present in the polymers showing strong negative rotation, thus ruling out the possibility of its having any significant influence on the optical rotation.

In accordance with our concept, polymers obtained by homopolymerization of **5a** (A-7), **6** (B-5), or **7** (C-5) showed practically no or only very weak optical rotation. The attempt to polymerize **5a** slightly below the melting temperature gave polymers with no optical activity (polymer A-7). In order to obtain conditions more comparable with those of the previous copolymerizations, we carried out a copolymerization of **5a** with ethylene glycol *O*-[(4-vinylphenyl)boronate] (**12**). After removal of the templates D-mannitol and ethylene glycol, we thus obtained by a copolymerization technique homopolymers of (4-vinylphenyl)boronic acid (A-8 and A-9). These polymers showed only a weak positive rotation, possibly because of small amounts of D-mannitol still present.

Copolymers prepared from the monomers **8** (polymer D), **9** (polymers E-1 to E-4), and **10** (polymer F) gave no negative rotation. Small positive rotations may result from some residue of the template. The same is true with polymers and copolymers from monomers with only one (4-vinylphenyl)boronate grouping (polymers G and H). In this case, the polymers with templates still bound were

Table I
Composition of the Polymerization Mixture for the Preparation of the Polymers A-1 to A-14 and the Specific Rotation of the Polymers after Removal of the D- and L-Mannitol

polymer	monomer	mmol of monomer	comonomer[a]	mmol of co-monomer	solvent	mL of solvent	equiv % of 5 in monomer mixture[b]	$[\alpha]^{20}_{365}$ in 10:1 acetone–water, deg
A-1	5a	3.0	MMA	19.3	benzene	9	31.8	−26.4
A-2	5a	5.8	MMA	30.0	benzene	12	36.7	−29.4
A-3	5a	5.8	MMA	24.0	benzene	15	42.0	−28.8
A-4	5a	5.8	MMA	18.0	benzene	18	49.2	−28.3
A-5	5a	5.8	MMA	12.0	benzene	21	59.2	−26.0
A-6	5a	5.8	MMA	6.0	benzene	24	74.4	−18.4
A-7	5a	6.0			solid state		100	+1.7
A-8	5a	5.8	12	30.2	benzene	24	36.6	+1.5
A-9	5a	5.8	12	29.8	benzene	20	36.9	+1.6
A-10	5a	5.8	styrene	28.6	toluene	25	27.8	−16
A-11	5b	4.2	MMA	51.0	toluene	25	19.8	−7.6
A-12	5b	5.6	MMA	30.0	toluene	30	35.9	−21.7
A-13	5b	11.0		0	toluene	45	100	0
A-14	5c	6.0	MMA	30.0	benzene	10	37.5	+28.8

[a] MMA = methyl methacrylate. [b] 1 equiv of 5a = 1/3 mol of 5a.

Table II
Composition of the Polymerization Mixture for the Preparation of the Polymers B to I and the Specific Rotation of the Polymers after Removal of the Templates

polymer	monomer	mmol of monomer	comonomer	mmol of comonomer	solvent	mL of solvent	equiv % of boronic esters in the monomer mixture	$[\alpha]^{20}_{365}$ in 10:1 acetone–water, deg
B-1	6	6.5	MMA[a]	32.5	toluene	15	28.6	−29.8
B-2	6	11.0	MMA	54.7	toluene	21	28.7	−29.5
B-3	6	7.3	MMA	58.3	toluene	18	20.0	−23.5
B-4	6	11.0	MMA	27.3	toluene	15	44.6	−36.5
B-5	6	15.0		0	toluene	13	100	0
C-1	7	2.5	MMA	20.0	DMF[b]	50	20	−27.8
C-2	7	2.5	MMA	12.5	DMF	45	28.6	−36.5
C-3	7	2.5	MMA	6.2	DMF	33	44.6	−40.0
C-4	7	5.0	MMA	7.5	DMF	55	57.1	−41.7
C-5	7	5.0	MMA	5.0	DMF	50	66.7	−35.4
C-6	7	2.3		0	DMF	20	100	−2.4
D	8	3.0	MMA	15.4	toluene	10	28.0	+3.4
E-1	9	1.2	MMA	52.6	toluene	10	4.4	+1.2
E-2	9	2.6	MMA	52.6	toluene	10	9.0	−0.2
E-3	9	5.0	MMA	51.9	toluene	15	16.2	+0.9
E-4	9	9.7	MMA	21.5	toluene	30	47.4	+2.0
F	10	6.0	MMA	30.0	toluene	10	37.5	+2.9
G	11	10.0	MMA	16.7	toluene	10	37.5	+0.9
H-1	12	30.5		0	toluene	40	100	0
H-2	12	19.0	MMA	39.4	toluene	10	32.5	0
I	13	10.4	MMA	20.4	benzene	5	33.8	+0.4

[a] MMA = methyl methacrylate. [b] DMF = dimethylformamide.

Table III
Content of D-[1-^{14}C]Mannitol and Optical Rotation of Polymers A-11, A-12, and A-13

polymer	equiv % of 5b in monomer mixture	$[\alpha]^{20}_{365}$, deg	rest of D-mannitol in the polymers, %
A-11	19.8	−7.6	0.38
A-12	35.9	−21.7	0.22
A-13	100	0	1.17

soluble and showed rotations in the order expected from the rotation of the monomer.

III. Discussion

The strong negative rotation of the copolymers prepared from monomers **5–7** clearly indicates an asymmetric induction by the chiral template. As the results with ^{14}C-labeled D-mannitol show, the optical rotations do not originate from pendant templates but from the chirality of the main chain of the polymer. This is also demonstrated by a comparison of the CD spectra of the starting monomer **5a** and the resulting polymer A-1. These spectra show marked differences: the polymer exhibits a negative Cotton effect at 236 nm and a positive Cotton effect at 220 nm, whereas the monomer shows a positive Cotton effect at 224 nm. This strong difference cannot only be attributed to a somewhat different chromophore in **5a**. A detailed discussion of some of the interesting features of the CD spectra—especially the temperature dependence—will be given in another paper.

Indications for an asymmetric copolymerization are given by the unsuccessful efforts to prepare an optically active homopolymer by the same procedure. Further on, there is a strong dependence of the specific rotation on the molar ratio of the comonomers in the polymerization mixture. Figure 1 shows as an example the specific rotation of copolymers prepared from **7** and varying amounts

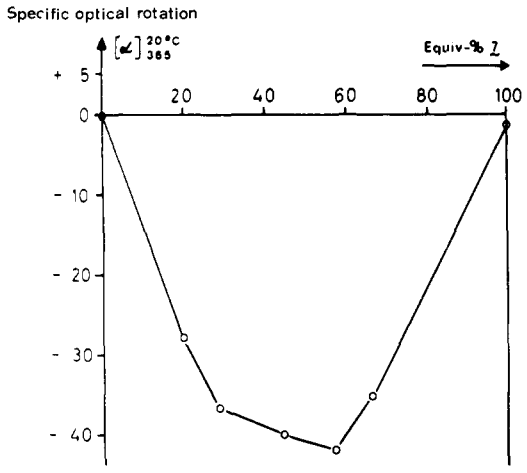


Figure 1. Specific optical rotation at 365 nm of copolymers of methyl methacrylate with 7 after removal of the template. Equivalent percent of 7 (1 equiv of 7 = $^1/_2$ mol of 7) in the polymerization mixture and the optical rotation of the resulting copolymers are given.

of methyl methacrylate after removal of D-mannitol. The maximum negative rotation is reached at 40 mol% (57 equiv %) boronic acid groups. With ideal copolymerization, the maximum is expected at 66.6 equiv % (a 2:1 ratio of the 4-vinylphenyl)boronic acid and methyl methacrylate moieties) for an asymmetric copolymerization of the type discussed earlier.

Apparently, the 3,4-[(4-vinylphenyl)boronate] group in **5** is not necessary for an asymmetric induction, since monomers **6** and **7** yielded polymers with comparable or even stronger optical activity. On the other hand, the steric arrangement of the two residues in the 1,2- and 5,6-positions is decisive, as polymer D from **8** clearly shows. No optical rotation was found in this case as with polymers E and F from monomers **9** and **10**, respectively.

The structure of the monofunctional comonomer is less critical. Polymer A-**10** with styrene as comonomer shows a negative rotation, too. Solvent effects during polymerization seem not to be very pronounced.

From these results, an asymmetric copolymerization with insertion of the comonomer between two styrene residues is likely to occur. A possible mechanism is shown in Figure 2. Since monomers **5–7** possess C_2 symmetry, radical attack of a growing chain at the (4-vinylphenyl)-boronate groups of the 1,2-position as well as the 5,6-position of the D-mannitol will yield the same product. It should be mentioned that this prerequisite is also true with monomer **8** but not with monomers **9** and **10**. In this latter case, the first attack could occur at two nonequivalent styrene moieties. Therefore, principally two different triads with different or even opposite signs in optical rotation could be formed.

It is surely justified to assume that the first radical attack at one of the vinyl groups of **5**, **6** or **7** occurs predominantly from the outside conformation of the vinyl grouping (see Figure 2). The newly formed radical then, in a second step, attacks a comonomer, which should be situated between the two (4-vinylphenyl)boronate moieties. This attack yields the asymmetric induction of the triad I, induced by the chiral environment of the template molecule. The third step is the attack of the comonomer radical at the second (4-vinylphenyl)boronic ester residue. This attack produces a pseudoasymmetric center in the resulting triad I. The fourth step, attack of the second (4-vinylphenyl)boronate residue at another monomer, establishes the triad. There are two possibilities of this

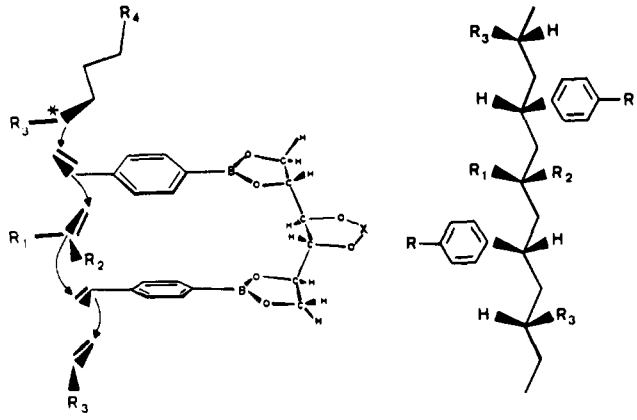


Figure 2. Possible mechanism for the asymmetric copolymerization.

attack, one yielding triad I, the other a triad with a meso configuration. Only triad I yields an optically active polymer. It should be mentioned that the monomeric units adjacent to triad I have to consist of monomers other than the comonomer used. Otherwise an alternating copolymer with no optical activity will be formed.

In accordance with this mechanism, it was possible on copolymerization of bifunctional monomers of the types **6** and **7** with methacrylonitrile to obtain soluble polymers without removal of the template.[17] The extent of branching or cross-linking can therefore only be low. From a bifunctional monomer, highly cross-linked polymers are expected under normal conditions.

At the moment another mechanism cannot be ruled out. This is a copolymerization whereby the comonomer is not inserted between the two styrene moieties but the two fixed styrene moieties are directly linked (cyclopolymerization) and the comonomer is situated between these dyads.

The exact configuration of the asymmetric triad yielding the optical activity of our polymers has yet to be ascertained, as well as the degree to which these active triads are present in the polymer.

IV. Experimental Section

General Procedures. Elemental analyses were performed in the microanalytical laboratories of Dr. F. Pascher, Bonn, of the Institute of Organic Chemistry and Biochemistry of Bonn University and of the Faculty of Natural Science of Düsseldorf University. ^{1}H NMR spectra were obtained on Varian HX-100 and EM-390 instruments and a Bruker 360-MHz instrument, and CD spectra were taken on a Dichrographe III (Jobin Yvon Division d'Instruments S.A.). Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. Differential thermal analysis was performed with a DuPont Model 990 thermal analyzer. The NMR data of the prepared monomers corresponded with the assumed structures.

Preparation of the Monomers. D-Mannitol 1,2:3,4:5,6-tris-*O*-[(4-vinylphenyl)boronate] (**5a**) was prepared according to ref 1c, methyl α-D-mannopyranoside 2,3:4,6-bis-*O*-[(4-vinylphenyl)-boronate] (**9**) according to ref 1b, and L-1,2-propanediol *O*-[(4-vinylphenyl)boronate] (**13**) according to ref 1c.

D-[1-^{14}C]Mannitol 1,2:3,4:5,6-Tris-*O*-[(4-vinylphenyl)boronate] (5b). The preparation followed the procedure for **5a**.[1c] To the reaction mixture of 7.28 g (0.04 mol) of D-mannitol and 15.6 g (0.04 mol) of tris[*O*-(4-vinylphenyl)boroxin] was added 40 μCi (10–30 mCi/mmol) of D-[1-^{14}C]mannitol (Amersham-Buchler) such that the D-mannitol contained 1 μCi/mmol: yield 85%; mp 160 °C; $[\alpha]^{22}_{365}$ +269° (*c* 0.8, $CHCl_3$).

L-Mannitol 1,2:3,4:5,6-Tris-*O*-[(4-vinylphenyl)boronate] (5c). This compound was prepared as **5a**.[1c] The optical purity of the L-mannitol[20] used was less than that of the D-mannitol: yield 83%; mp 152–155 °C; $[\alpha]^{22}_{365}$ −222° (*c* 0.6, $CHCl_3$).

Anal. Calcd for $C_{30}H_{29}B_3O_6$: C, 69.56; H, 5.64. Found: C, 69.80; H, 5.70.

D-Glucitol Tris-*O*-[(4-vinylphenyl)boronate] (10). Preparation was analogous to that of **5a**[1c]: yield 75%; mp 172–174 °C (from toluene–petroleum ether); $[\alpha]^{20}_{365}$ +373° (*c* 0.7, $CHCl_3$).

Anal. Calcd for $C_{30}H_{29}B_3O_6$: C, 69.56; H, 5.64. Found: C, 69.66; H, 5.70.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-Di-*O*-benzyl Ether (11a).[21] To a flask with 250 mL of freshly distilled benzyl chloride were added 40 g of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[13] and 62.5 g of powdered KOH in portions. After stirring overnight at room temperature, the excess benzyl chloride was distilled off under vacuum. The residue was subjected to a steam distillation. The upper layer of the distillate was separated, and the lower water layer was extracted twice with $CHCl_3$. The combined organic layers were dried (Na_2SO_4), concentrated, and distilled, giving 50 g (74%) of the dibenzyl ether **11a**: bp 190 °C (0.1 mm); mp 41–42 °C; $[\alpha]^{22}_{365}$ +110.2° (*c* 0.48, acetone).

Anal. Calcd for $C_{26}H_{34}O_6$: C, 70.50; H, 7.74. Found: C, 70.40; H, 7.74.

D-Mannitol 3,4-Di-*O*-benzyl Ether (11b).[21] **11b** can be obtained by hydrolysis of **11a** with Amberlyst 15.[21] It proved to be more favorable to start directly from a benzylation mixture to prepare **11a**. Thus after benzylation 200 mL of water was added to the reaction mixture as in the foregoing experiment; and the mixture was heated until it turned weakly acidic (otherwise more benzyl chloride was added). Then the solution was evaporated and the residue recrystallized from ethanol, giving 33 g (59.7%) of **11b**: mp 74–75 °C; $[\alpha]^{22}_{365}$ +18.6° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.15; H, 7.16.

D-Mannitol 3,4-Di-*O*-benzyl Ether 1,2:5,6-Bis-*O*-[(4-vinylphenyl)boronate] (8). **11b** (2 g, 5.5 mmol) was heated 3 h with 1.4 g (3.7 mmol) of tris[*O*-(4-vinylphenyl)boroxin] in 200 mL of CH_2Cl_2, and the water formed was azeotropically distilled off. The solution was filtered and evaporated. The residue yielded crystals on treatment with petroleum ether. Recrystallization from toluene–petroleum ether gave 2.6 g (82%) of **8**: mp 110–112 °C; $[\alpha]^{20}_{365}$ +298.5° (*c* 0.5, $CHCl_3$); 360-MHz ^1H NMR ($CDCl_3/Me_4Si$) δ 4.00 (H-3 mannitol), 4.74 (H-2 mannitol) ($J_{2,3}$ = 4.52 Hz, $J_{3,3'}$ = 4.34 Hz).

Anal. Calcd for $C_{36}H_{36}B_2O_6$: C, 73.72; H, 6.15; B, 3.75. Found: C, 73.31; H, 6.14; B, 3.85.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-*O*-[(4-Vinylphenyl)boronate] (11c). As described for **8**, 4.0 g (73%) of **11c** was obtained from 3.93 g (15 mmol) of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[13] and 1.95 g (5 mmol) of tris[*O*-(4-vinylphenyl)boroxin]: mp 137–138 °C (from ethanol–petroleum ether); $[\alpha]^{20}_{365}$ −66.2° (*c* 1.0, $CHCl_3$); mass spectrum, *m/z* 374 (M^+) (calcd *m/z* 374.2).

Anal. Calcd for $C_{20}H_{27}BO_6$: C, 64.19; H, 7.27. Found: C, 64.14; H, 7.25.

3,4-*O*-Isopropylidene-D-mannitol 1,2:5,6-Bis-*O*-[(4-vinylphenyl)boronate] (6). As described for the preparation of **8**, 3.3 g (74%) of **6** was obtained from 2.22 g (10 mmol) of 3,4-*O*-isopropylidene-D-mannitol[10] and 2.6 g (6.6 mmol) of tris[*O*-(4-vinylphenyl)boroxin]: highly viscous oil, which solidified to a crystalline mass on standing, mp 55–60 °C; $[\alpha]^{22}_{365}$ +17.3° (*c* 1.8, acetone); mass spectrum, *m/z* 446 (M^+) (calcd *m/z* 446.1); 360-MHz ^1H NMR ($CDCl_3/Me_4Si$) δ 4.10 (H-3 mannitol), 4.74 (H-2 mannitol) ($J_{2,3}$ = 5.80 Hz, $J_{3,3'}$ = 6.66 Hz).

Anal. Calcd for $C_{25}H_{28}B_2O_6$: C, 67.31; H, 6.33; B, 4.85. Found: C, 67.24; H, 6.31; B, 4.82.

D-Mannitol 3,4-*O*-Carbonate 1,2:5,6-Bis-*O*-[(4-vinylphenyl)boronate] (7). As described for the preparation of **8**, 10.9 g (63%) of **7** was obtained from 8.9 g (40 mmol) of D-mannitol 3,4-*O*-carbonate[11] and 11.1 g of tris[*O*-(4-vinylphenyl)boroxin]: mp 228–231 °C (from dioxane–diethyl ether); $[\alpha]^{20}_{365}$ +407.9° (*c* 0.2, acetone); mass spectrum, *m/z* 432 (M^+) (calcd *m/z* 432.3).

Anal. Calcd for $C_{23}H_{22}B_2O_7$: C, 63.94; H, 5.13. Found: C, 63.88; H, 4.91.

Ethylene Glycol *O*-[(4-Vinylphenyl)boronate] (12).[21] As described for the preparation of **8**, 19 g (75%) of **12** was obtained on distillation from 20 g (50 mmol) of tris[*O*-(4-vinylphenyl)-boroxin] and 0.9 g (145 mmol) of ethylene glycol: bp 84 °C (0.5 mm), viscous oil.

Anal. Calcd for $C_{10}H_{11}BO_2$: C, 69.03; H, 6.37. Found: C, 69.10; H, 6.38.

Preparation of the Polymers. General Procedure. A mixture of the boronic ester containing monomer, the comonomer, azobis(isobutyronitrile) (1.5% of the monomeric mixture), and the solvent (for composition, see Tables I and II) was placed into a tube, carefully degassed by evacuating three times, sealed under argon, and polymerized every 24 h at 60, 80, and 100 °C. Afterward the tube was cooled and broken, and the polymer was directly milled (Janke-Kunkel A10). After the polymer was dried in a vacuum-drying cupboard at 40–50 °C, the templates were split off continuously for 24 h by 1:3 methanol–water in a special cleavage apparatus.[1b] Then the polymers were dissolved in 9:1 acetone–water (~10–20 mg/mL) and precipitated by dropping into 20 volumes of weakly acidified water. The polymers were separated by filtration or centrifugation. After three reprecipitations, the final isolation was accomplished through freeze-drying from acetone–water. All experiments were carried out with polymers purified this way. The yield was 60–90%.

Polymer A-7. Differential thermal analysis of **5a** showed that it melted at 160 °C but an exothermic polymerization followed immediately. In order to get a polymerization in a crystalline state, 3 g of **5a** was sealed under N_2 in a tube and heated 3 weeks at 145 °C. The reaction product was treated several times with CH_2Cl_2 to remove unreacted **5a**. Afterward it was worked up in the usual manner. Yield was only 60 mg.

Polymers A-11 to A-13. Work up of these polymers followed the general procedure. The amount of D-[1-^{14}C]mannitol present after cleavage was determined by liquid scintillation counting. Calibration was done with solutions of known amounts of D-[1-^{14}C]mannitol in the presence of polymer A-2. The measurements were made in a scintillation cocktail containing 250 mg of 1,2-bis[2-(5-phenyloxazolyl)]benzene, 4 g of 2,5-diphenyloxazole, 60 g of naphthalene, 20 mL of ethylene glycol, and 100 mL of methanol made up to 1000 mL with 1,4-dioxane. Calibrations were made at four different concentrations and the polymers were measured at two different concentrations. The measured radioactivity of the polymers was in the range of 30–400 counts/min, and results for 10-mg samples are given in Table III.

Polymers G and I. The polymerizations yielded soluble polymers. The measured optical rotations of the polymers containing the template without any previous purifications are as follows: polymer G, $[\alpha]^{20}_{365}$ +29.8° (*c* 0.11, acetone); polymer I $[\alpha]^{20}_{365}$ +45.30° (*c* 1.5, acetone). In this case the cleavage of the template could be affected by reprecipitation.

Addition of D-Mannitol to Polymer H-1. D-Mannitol (14.1 mg) in 1 mL of water was added to 13.1 mg of polymer **H-1** in 5 mL of 9:1 acetone–water, and the optical rotation was measured. Time, $[\alpha]^{22}_{365}$: 10 min, +81.3°; 25 min, +95.8°; 40 min, +100.8°; 60 min, +103.8°; 85 min, +105.7°; 115 min, +107.6°. After 115 min no further measurement was possible because of the onset of turbidity and subsequent precipitation.

Molecular Weight Determinations. The polymers obtained were only soluble in solvents containing some water, alcohols, or glycols. Good solvents were, for example, 9:1 acetone–water, 85:15 acetone–methanol, and 9:1 2-butanone–ethylene glycol. Molecular weight determinations by membrane osmometry suffered from the fact that the molecular weight distribution is usually broad. With the work up procedure used, oligomers and medium molecular weight fractions are not fully removed; therefore their influence on the molecular weight is rather pronounced. Furthermore, in some cases, parts of the samples under investigation penetrated through the membrane, giving rise to erroneous results. Therefore only in some representative examples the molecular weight was determined as a rough measure of its size. In this work no attempt was made to investigate the dependence of optical activity upon the molecular weight.

Measurements were made with a Knauer membrane osmometer with a no. 010007 membrane (finest) of regenerated cellulose: polymer A-2 gave M_n = 120 000 (9:1 acetone–water); polymers A-2 to A-6 gave M_n = 70 000–120 000 (9:1 acetone–water), polymer

Table IV
Boron Content of Polymers

polymer	% B[a] found	equiv % in polymer[b]	equiv % in monomer mixture[c]
A-1	3.00	33	31.8
A-2	3.38	37	36.7
A-3	3.71	41	42.0
A-4	4.21	48	49.2
A-5	4.97	59	59.2
A-6	5.42	67	74.4
A-7	nd	nd	100
A-8	6.85	91	36.6 + 63.4
A-9	6.42	83	36.9 + 63.1
A-10	3.22	35	37.8
A-11	nd	nd	19.8
A-12	nd	nd	35.9
A-13	nd	nd	100
A-14	3.19	34	37.5
B-1	2.78	28	28.6
B-2	2.62	28	28.7
B-3	1.85	19	20.0
B-4	3.64	41	44.6
B-5	6.54	85	100
C-1	2.06	21	20
C-2	2.76	28	28.6
C-3	4.01	45	44.6
C-4	4.84	57	57.1
C-5	nd		
C-6	6.84	91	100
D	1.88	19	28
E-1	0.56	5	4.4
E-2	0.89	9	9.0
E-3	1.52	17	16.2
E-4	3.79	42	47.4
F	2.90	31	37.5
G	2.50	26	37.5
H-1	6.88	91	100
H-2	2.89	31	32.5
I	2.94	32	33.8

[a] Boron analyses were performed in the microanalytical laboratory of Dr. F. Pascher, Bonn. [b] Equivalent percent of boron-containing monomer in the polymer as calculated from the elemental analysis. [c] Equivalent percent of boron-containing monomer in the monomeric polymerization mixture.

B-1 yielded M_n = 59 000 (85:15 acetone–methanol), and polymer H-2 gave M_n = 44 000 (85:15 acetone–methanol). The estimated error of this determination in acetone–water is ±10 000 and in acetone–methanol ±5000.

Acknowledgment. Thanks are due to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

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