Chirality of Polyvinyl Compounds. 18.[1] Preparation and Characterization of New Optically Active Copolymers with Main Chain Chirality Carrying Naphthyl Chromophores

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Received February 8, 1995⊗

ABSTRACT: Optically active copolymers were obtained by radically initiated asymmetric cyclocopolymerization of two new monomers, 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(4-vinylnaphthyl-1)]-boronate] (**2**) and 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(2-vinylnaphthyl-1)boronate] (**3**), with comonomers (e.g. methyl methacrylate) and subsequent splitting off the chiral D-mannitol template. The copolymers are optically active due to the chirality of the configuration of the main chain. Because of the spatial proximity of the two naphthalene units in the side chain of the copolymers circular dichroism (CD) spectra show strong CD with exciton couplets. The configurations of the (4-vinylnaphthyl-1)boronic acid and (2-vinylnaphthyl-1)boronic acid diad, respectively, in the copolymer chains could be determined with the aid of the "exciton chirality method". In both cases the diads possess (*S*,*S*) configuration. The mechanisms of cyclopolymerization of the two monomers are discussed on the basis of their conformations of lowest energy obtained by calculations with semiempirical methods (AM1).

Introduction

During the last decade there has been growing success in preparing optically active polymers by asymmetric cyclopolymerization. The optical activity of these polymers arises from the chirality of the main chain (main chain chirality).[2]

Two approaches have to be distinguished. In a more recent method a suitable achiral monomer may be cyclopolymerized with the help of a chiral catalyst/initiator system.[3] Therefore, the chiral catalyst/initiator system determines the information on the chirality of the produced polymer. The best example is the asymmetric cyclopolymerization of 1,5-hexadiene with a chiral metallocene catalyst such as (*R*)-ethylenebis-(tetrahydroindenyl)zirconium (*R*)-binaphtholate by Waymouth and co-workers;[3] up to 68% of chiral threo-diisotactic units of methylene-1,3-cyclopentane are formed in the polymer chain during polymerization.

The first asymmetric cyclopolymerizations have been performed in our group using an achiral initiator and a chiral template molecule, 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(4-vinylphenyl)boronate], to which the monomeric units are attached.[2,5−9] The same approach has been used by Kakuchi et al.[4] to build polymeric chiral crown ethers.

By radically initiated copolymerization of **1** (see Figure 1) with different comonomers we were able to synthesize a number of copolymers that were still optically active after splitting off the chiral template, 3,4-*O*-cyclohexylidene-D-mannitol. A chiral diad of two (4-vinylphenyl)boronic acid residues is formed which is separated from other diads by comonomeric units (see Figure 2 for possible arrangements). The two stereogenic centers of the diad causing optical activity in the copolymers both have (*S*) configuration (in the case of methyl methacrylate (MMA) as the comonomeric unit).[5] The stereochemistry of the carbon atom connected to substituent A (side chain of the monomer) does not influence the chiroptical properties.

The chiroptical properties of these copolymers have been investigated by circular dichroism spectroscopy (CD) and optical rotation. The CD spectra always show a negative Cotton effect with a maximum at about 230 nm due to the $^{1}L_{a}$ chromophore of the phenylboronic acid unit. As a result of the chiral diad the chromophores of the comonomeric units are in a chiral environment and give rise to additional Cotton effects. Signs and values of these Cotton effects depend on the distance and the orientation of the chromophores relative to the polymer backbone[7] and the amount of the chromophore in the copolymer. Up to now, only the influence of different comonomers on the chiroptical properties of these copolymers has been investigated systematically.

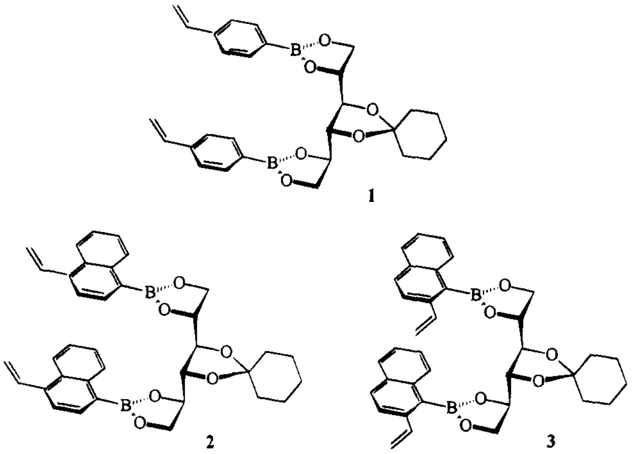

Figure 1. 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(4-vinylphenyl)boronate] (**1**), 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(4-vinylnaphthyl)boronate] (**2**), and 3,4-*O*-cyclohexylidene-D-mannitol 1,2;5,6-bis-*O*-[(4-vinylnaphthyl-1)-boronate] (**3**).

The present paper describes our research into two new bifunctional monomers, **2** and **3**, that have a structure related to **1** but a different chromophore, the styrene units having been replaced by vinylnaphthalene units. This changes the symmetry properties of the polymerizing units considerably: there is no rotational symmetry with regard to the aryl−boron bond. This should influence the mechanism of the cyclopolymerization. The naphthalene chromophores also account for different chiroptical properties. The photochemical intramolecular [2 + 2] cycloaddition of monomer **2** and

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⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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Table 1. Polymerization Conditions and Properties of Polymers

polymer	monomer	comonomer[b]	polym temp (°C)	polym time (h)	yield (%)	**2** or **3**, mol fraction in reaction mixture	**2** or **3**, mol fraction in copolymer[c]	$[\alpha]^{30}{}_{436}$[g] (deg cm^2 dag^{-1})	M_w[h]	M_n[h]
P1	**2**	MMA	65	7	34	11.11	31	+32	58 000	31 000
P2	**2**	MAN	65	24	19	11.08	38	+74	16 000	10 000
P3	**2**	ST	65	7	8	11.11	34[d]	+29	47 500	30 000
P4	**2**	MAN	65	42	32	50.00	*e*	+19	5 000	3 600
P5	**2**	PhMI	65	18	35	50.00	53	~0[i]	4 000	3 000
P6	**2**	VS	65	5	37	28.49	*e*	+169	*e*	*e*
P7	**3**	MMA	75	24	78	20.00	24[f]	−255	*e*	*e*
P8	**3**	ST	75	24	36	20.00	*e*	−278	*e*	*e*

[a] **P1−P6**, 1 weight % AIBN per monomer; **P7** and **P8**, 2 mol % AIBN per monomer. [b] MMA = methyl methacrylate; MAN = methacrylonitrile; ST = styrene; MAN = maleic anhydride; PhMi = *N*-phenylmaleimide; VS = 4-vinylstilbene. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by IR spectroscopy of the deboronated copolymer. [e] Not determined. [f] Determined by elemental analysis (B). [g] Measured in THF/H_2O (9/1, v/v); concentration approximately 1 mg/mL. [h] Obtained for deboronated copolymers by GPC (calibrated with polystyrene standards). [i] At this wavelength nearly no optical rotation, but see Table 2.

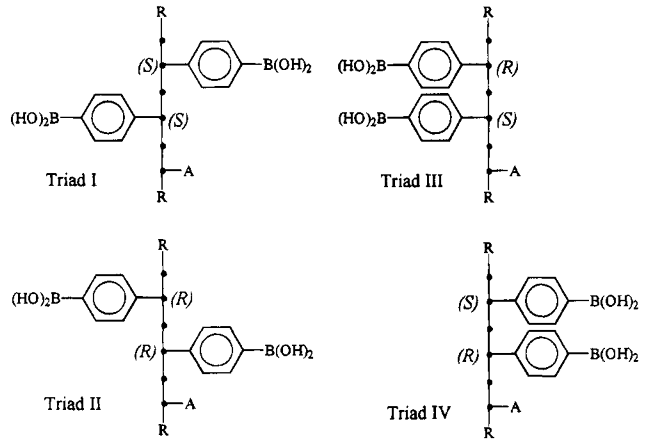


Figure 2. Possible triads formed during cyclopolymerization of **1** (R = polymer chain). The assignment of absolute configuration (*R*,*S*) according the CIP rules is based on the assumption that substituent A has a higher priority than the 4-(dihydroxyboranyl)phenyl residue, i.e. methyl methacrylate units.

the chiroptical properties of the cycloaddition product have been described recently in a short communication.[10]

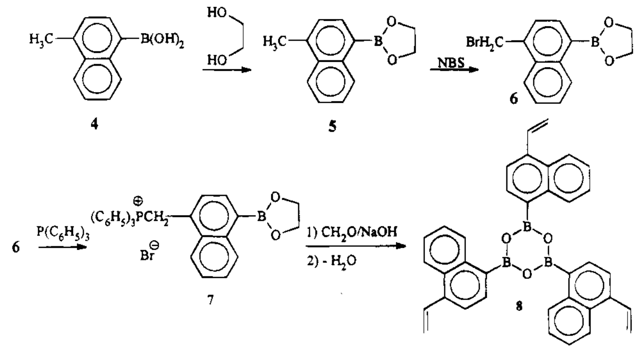
Results

Preparation of the Monomers. The new monomers **2** and **3** have been prepared similarly to **1**[5] by esterification of 3,4-*O*-cyclohexylidene-D-mannitol[11] with tris-*O*-(4-vinylnaphthyl-1)boroxine (**8**) or (2-vinylnaphthyl-1)boronic acid (**11**) through azeotropic removal of the water formed. Both compounds could be obtained in good yields.

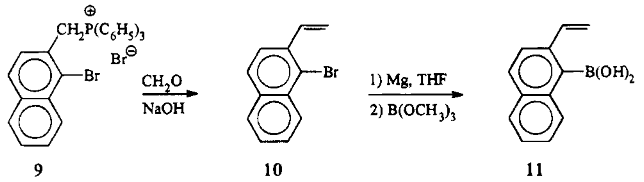
The boronic acid derivatives **8** and **11** were also unknown and prepared for the first time. **8** was prepared (see Scheme 1) starting from (4-methylnaphthyl-1)boronic acid (**4**).[12] **4** was brominated with *N*-bromosuccinimide in CCl_4 in the form of its ethylene glycol ester **5** to yield 4-bromomethyl compound **6**. This compound was transformed by the method of Anteunis et al.[13,14] (*via* the triphenylphosphonium salt **7** with formaldehyde in the presence of NaOH) into the desired (4-vinylnaphthyl-1)boronic acid, which was isolated as the trimeric boroxine **8**. Boroxines can directly be used to form esters of boronic acid with diols, as in the case of **2**.

(2-Vinylnaphthyl-1)boronic acid (**11**) was prepared in a similar way. Starting with (1-bromonaphthyl-2)-methyltriphenylphosphonium bromide **9**[15] the vinyl group was introduced again by Wittig reaction to yield **10**. Formation of the Grignard compound from **10** and reaction with trimethyl borate provides the desired boronic acid **11**.

Scheme 1. Preparation of Tris-*O*-(4-vinylnaphthyl-1)-boroxine (8)



Scheme 2. Preparation of (2-Vinylnaphthyl-1)boronic Acid (11)



Preparation and Properties of the Polymers. Copolymers were prepared in a way similar to that reported for monomer **1**,[5,9] choosing common comonomers such as methyl methacrylate, methacrylonitrile, styrene, and 4-vinylstilbene (Table 1). In general, the copolymerization was performed by radical initiation and was stopped after relatively low conversion in order to obtain a more homogeneous copolymer. It is known that **1** (compared to MMA) is preferably incorporated into the copolymer. Therefore, an excess of comonomer has to be used to separate the diads from each other.[5] Similar proportions of the comonomers have been used for **2** and **3**. It is known that maleic anhydride as well as *N*-phenylmaleimide tend to form alternating copolymers with styrene. This explains why copolymerization of **1** with maleic anhydride or *N*-phenylmaleimide resulted in copolymers with alternating sequences having distyryl diads and comonomeric units (maleic anhydride or *N*-phenylmaleimide).[9] Therefore, copolymerizations of **2** with maleic anhydride as well as with *N*-phenylmaleimide have been performed in a 1:1 molar ratio of the monomers.

No precipitation was observed for any of the copolymers shown in Table 1, indicating that cross-linking does not occur and that nearly complete cyclopolymerization may be expected. The template (3,4-*O*-cyclohexylidene-D-mannitol) could be removed from the resulting copolymers quantitatively by repeated dissolution in THF/H_2O (9/1, v/v) and precipitation in an excess of methanol/H_2O/HCl. The ^{1}H NMR spectra of

Table 2. CD Absorption Maxima and Zero Crossings[a]

	^1B_b					^1L_a				
polymer	λ_{max}	$[\psi]$	$\lambda_{[\psi]=0}$	λ_{max}	$[\psi]$	λ_{max}	$[\psi]$	$\lambda_{[\psi]=0}$	λ_{max}	$[\psi]$
P1	223	−22 400	229	235	+33 060	276	+1000	291	306	−1300
P2	223	−27 100	229	235	+44 900	273	+1300	292	304	−1600
P3	225	−15 300	231	237	+25 600	282	+1200	295	309	−1000
P4	219	−13 800	227	235	+16 300	277	+800	291	304	−1000
P5	219	−6 900	228	236	+7 800	281	+500	294	304	−500
P6	221	−7 000	230	236	+13 100				318[b]	+2100[b]
P7	224	+13 200	231	239	−29 800	272	−2400			
P8	226	+12 500	231	238	−27 100	271	−2100			

[a] CD spectra measured in THF/H_2O (9/1, v/v); concentration approximately 1 mg/mL; $[\psi]$ (deg cm^2 dag^{-1}); λ (nm). [b] ^1B transition of 4-vinylstilbene.

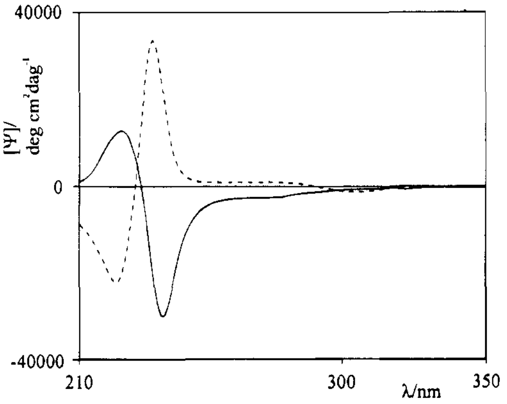


Figure 3. CD spectra of copolymer **P1** (- - -) and copolymer **P7** (—), measured in THF/H_2O (9/1, v/v), concentration approximately 1 mg/mL.

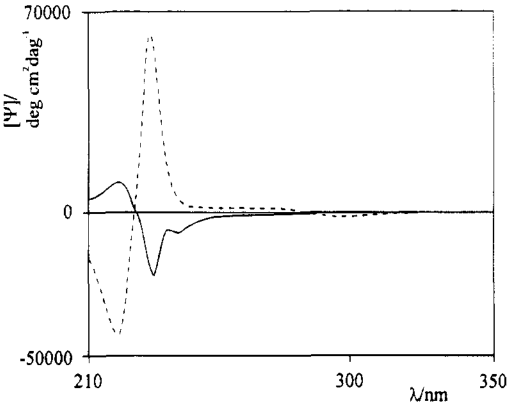


Figure 4. CD spectra of deboronated copolymers **P1** deboronated (- - -); **P7** partially deboronated (—), measured in THF/H_2O (9/1, v/v), concentration approximately 1 mg/mL.

the deprotected copolymers showed no proton signals belonging to the mannitol backbone. **2** and **3** were preferentially incorporated into the copolymer similarly to monomer **1**. The observed molecular weights were not very high since relatively large amounts of initiator AIBN have been used. Furthermore, vinylnaphthalenes tend to give polymers of lower molecular weight. Especially copolymers with maleic anhydride or *N*-phenylmaleimide showed relatively low molecular weights with M_w 4000–5000. Unlike copolymers of **1** that had rather broad molecular weight distributions,[5] copolymers of **2** and **3** presented in Table 1 showed relatively narrow molecular weight distributions. Apparently, in these cases the low molecular weight part has been removed by repeated reprecipitation.

Optical rotations of the copolymers are presented in Table 1. All copolymers made of **2** with one exception exhibit positive optical rotations, while polymers of **3** have strong negative optical rotations. Copolymers of **3** show the highest absolute optical rotations we ever measured for copolymers with this type of main chain chirality.

A more detailed investigation of the chiroptical properties is possible with the aid of CD spectroscopy. Figure 3 shows typical CD spectra of copolymers of **2** and **3**. The CD spectra are governed by a strong CD couplet at about 230 nm (zero crossing) corresponding to the ^1B_b transition of the naphthalene chromophore. The CD couplet is caused by dipole–dipole interaction of the electric transition moments of the ^1B_b transitions polarized along the long axis of the two neighboring naphthalene rings in the diad. In the case of copolymers of **2** a positive CD couplet is always observed while it is negative for copolymers of **3**. Furthermore, copolymers of **2** have a second negative CD couplet at ca. 290 nm (zero crossing) corresponding to the ^1L_a transition with an electric transition moment polarized along the short axis of the naphthalene rings. Additional Cotton effects for the chromophores of the comonomers could not be detected by CD spectroscopy because their Cotton effects are in the same wavelength area (210–300 nm) and much weaker than those of the chromophores of the diad. One exception is copolymer **P6** obtained from **2** and 4-vinylstilbene. The CD spectrum indicates an additional induced positive Cotton effect with a maximum at 318 nm similarly as in copolymers of **1** with vinylstilbene[6] (see Table 2). This Cotton effect belongs to the ^1B transition of stilbene.

The boronic acid units in copolymers of **1** could be removed completely with $AgNO_3/NH_3$.[5] In the case of copolymers of **2** and **3** deboronation would lead to copolymers of 1- or 2-vinylnaphthalene. Only copolymers of **2** could be deboronated quantitatively, as had been proved by IR and ^1H NMR spectroscopy. The IR spectra of the deboronated polymers **P1** and **P7** did not show any absorption between 1390 and 1310 cm^{-1} (B–O stretch vibration). In addition, the IR and ^1H NMR spectra were nearly identical with those obtained for an achiral poly(1-vinylnaphthalene-*co*-methyl methacrylate) copolymer.

The CD spectrum of deboronated copolymer **P1** is presented in Figure 4. The signs of both CD couplets are the same as in the corresponding boron-containing copolymers; this shows that the boronic acid units do not have a strong influence on the conformation of the copolymers. The zero crossings of the CD couplets are shifted to about 225 nm (^1B_b) and 290 nm (^1L_a).

As can be seen from the CD spectrum of a copolymer of **3** (see Figure 4) that has been treated with $AgNO_3/NH_3$, deboronation is incomplete. As a result of the ortho position of the boronic acid units to the polymeric backbone, steric hindrance occurs. The CD couplet is centered at about 225 nm due to the deboronated diad, but a small CD couplet (shoulder) still remains, stemming from unreacted naphthyl boronic acid units. The

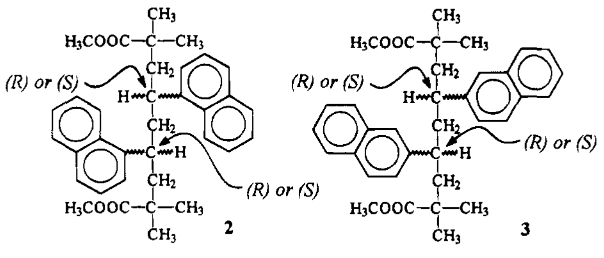


Figure 5. Theoretical model compounds of copolymers of **2** and **3**.

sign of the CD couplet of the ^1B_b transition does not change after deboronation either.

Discussion

Copolymers of **2** and **3** show extremely strong circular dichroism and, in contrast to copolymers of **1**, the naphthalene chromophores give rise to CD couplets. The deboronated copolymers of **2** have 1-substituted naphthalenes as substituents; the copolymers of **3**, 2-substituted naphthalenes. The different orientation of the chromophores with regard to the polymeric chain should give rise to distinct chiroptical properties, as has been proven for copolymers of **1** with 1- or 2-vinylnaphthalene.[6]

The prevailing chiral diad in the copolymers of **2** and **3** can be determined with the aid of the qualitative "exciton chirality method" of Nakanishi[16,17] and the knowledge of the optimal relative conformation of the two naphthalene rings in the diad for both possible chiral configurations, (*S*,*S*) and (*R*,*R*). The copolymer conformations are estimated by comparison with related theoretical model compounds (see Figure 5). The model compounds represent a part of the copolymer chain with the diad being flanked by two methyl methacrylate units.

The comonomer units do not have a strong influence on the relative spatial arrangement of the two naphthalene rings. This can be deduced from comparison of the CD couplets in different copolymers that do not change their signs when the comonomer is varied (see Table 2).

The optimal conformations of the two theoretical model compounds with both chiral configurations are drawn as Newman projections in Figure 6. They have been approximated by force field calculations (CHARMm).[18] Table 3 shows the calculated signs of the CD couplets for every model structure according to the "exciton chirality method" and compares them with the observed values for the related copolymer.

Therefore, from these data one can assume that both monomers **2** and **3** yield preferentially (*S*,*S*) diads by cyclopolymerization. This finding is supported by the fact that **P6** with 4-vinylstilbene as comonomer shows an induced positive Cotton effect at 318 nm similarly as in copolymers of **1** with 4-vinylstilbene.[6] In polymers of **1** the absolute configuration of the distyryl diad has been proven to be (*S*,*S*). For a definite proof of the configuration of polymers of **2** and **3** suitable model compounds have to be prepared as in case of copolymers of **1**.[5]

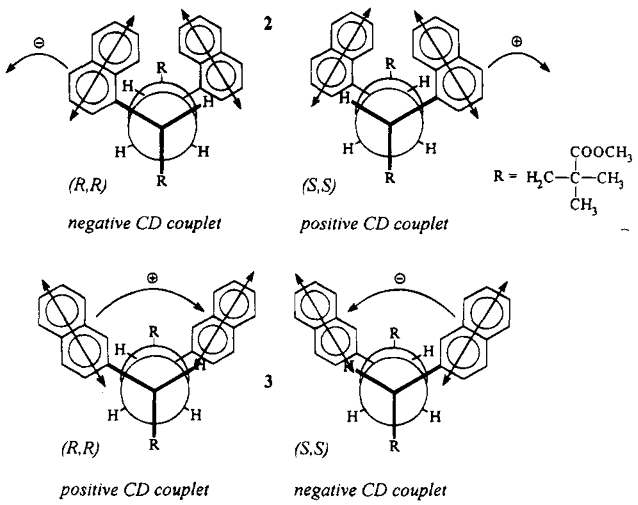


Figure 6. Theoretical model compounds of copolymers of **2** and **3** (configuration of diads in brackets) and application of the "exciton chirality method" of Nakanishi: straight arrows are transition moments of ^1B_b transition; bent arrows determine the sign of the CD couplet belonging to the ^1B_b transition.

Table 3. Comparison of Calculated (According to the "Exciton Chirality Method") and Measured Signs of the CD Couplets for Both Types of Copolymers

	calcd for model compound with (*R*,*R*) diad	calcd for model compound with (*S*,*S*) diad	measured signs
copolymer of **2**	−	+	+
copolymer of **3**	+	−	−

Table 4. UV Absorption Maxima of Copolymers[a]

polymer	λ_{max}	[ϵ]	λ_{max}	[ϵ]
P1	229	134.1	293	23.5
P2	229	160.7	293	27.8
P3	230	117.8	293	21.5
P4	225	112.0	292	18.8
P5[b]				
P6	229	128.0	302[c]	75.5[c]
P7	229	187.5	279	26.2
P8	230	169.2	276	24.0

[a] Measured in THF/H_2O (9/1, v/v); concentration approximately 0.1 mg/mL; [ϵ] (L g^{-1} cm^{-1}); λ (nm). [b] Not determined. [c] Overlap of ^1L_a band of naphthalene and ^1B band of stilbene.

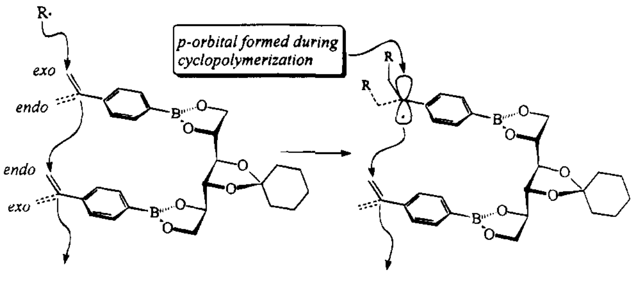


Figure 7. Possible conformations of **1** and the course of its cyclopolymerization. The second preferred conformation of the double bond is drawn with dotted lines.

The opposite signs of the CD couplets for the polymers of monomers **2** and **3** are related to the different orientations of the electric transition moments of the naphthalene rings with regard to the backbone in both types of copolymers. A similar observation has been made by Ciardelli and co-workers[19] who copolymerized (*S*)-3,7-dimethyl-1-octene, a monomer with a definite configuration in the side chain, with 1- or 2-vinylnaphthalene. Although the chirality in both copolymers had the same origin, both show CD couplets for the ^1B_b transition with opposite sign.

The question arises whether the identical configurations of the diads produced from the three monomers **1**−**3** are originated by the same mechanistic pathway of the cyclopolymerization or whether all monomers yield the same preferred diad only by accident. The mechanism of cyclopolymerization of **1** had already been described earlier.[5] Figure 7 displays the optimal conformations of **1** for cyclopolymerization. A radical

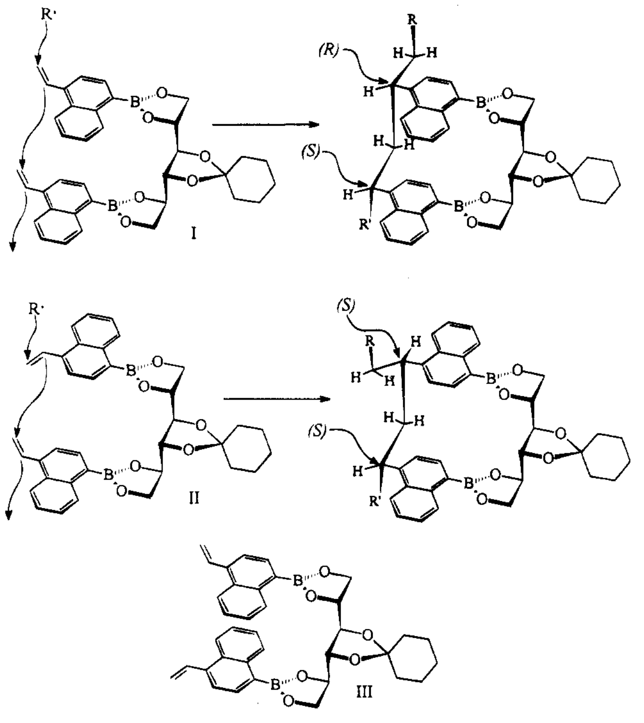


Figure 8. Conformations I–III of lowest energy of **2** and course of cyclopolymerization of **2**: R = beginning of chain; R′ = end of chain.

(initiator or growing polymer chain) attacks one double bond of **1** (since **1** possesses C_2 symmetry, the two vinyl groups are equivalent) in "exo" or "endo" conformation such that the decisive carbon atom becomes (*R*)- or (*S*)-configurated after cyclization. There seems to be no preference for either of the two attacks. The second double bond is attacked nearly exclusively in its "endo" conformation because the p-orbital, which contains the radical, is in perpendicular position to the decisive carbon atom of the second double bond. An attack in "exo" conformation would require a totally different conformation of the whole monomer which would be much more unstable. An (*S*)-configurated carbon atom results from "endo" attack provided that the next monomer (comonomer such as MMA) approaches from below.

The conformation of **2** and **3** with lowest energy have been approximated with semiempirical calculation methods (AM1).[20,21] In comparison with **1** it was found that the aromatic rings are no longer in plane with the dioxaborolane rings, whereas the conformation of the template part does not change significantly. In the case of **2** the aromatic rings are rotated about 15° and in the case of **3** about 60° out of the dioxaborolane plane. This rotation is due to the protons in the naphthalene units which are in peri position to the dioxaborolane ring. In **3** this is emphasized due to the vinyl substituents in the ortho position. Furthermore, in **2** the vinyl substituents have only one preferred possibility of arrangement compared with **1** ("exo" or "endo") because of the peri protons. In the case of **3** the parallel alignment of aromatic rings and dioxaborolane rings is too high in energy. The best conformations for cyclopolymerization taking accout of the distance of both vinyl groups would be the perpendicular arrangements. In the case of **2** both parallel and perpendicular arrangements are of comparable energies. Figures 8 and 9 show all conformations with parallel (for **2**) and perpendicular arrangements (for **3**), which originate from our calculations. The differences in energy between actual and perpendicular conformations are less than 20 kJ/mol.

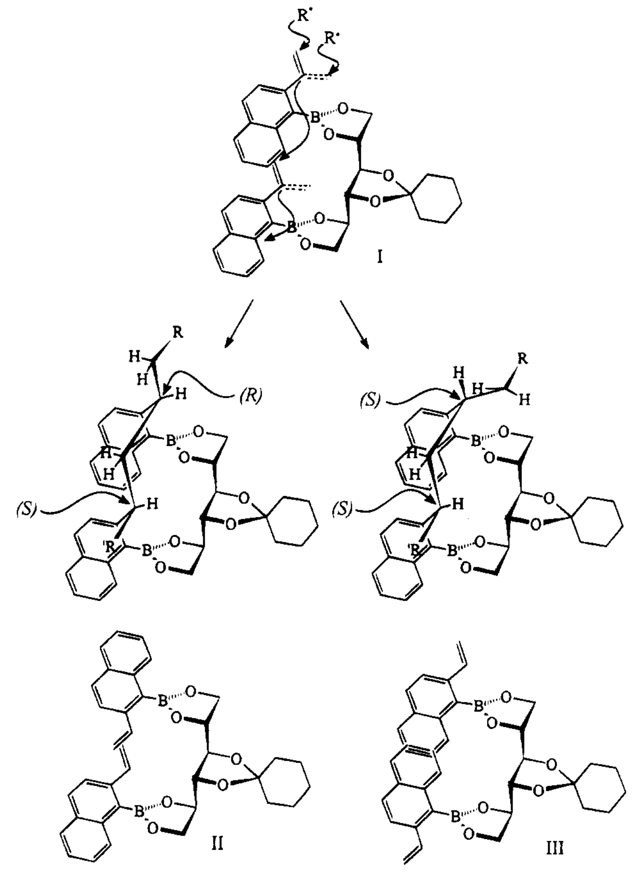


Figure 9. Conformations I–III of lowest energy of **3** and course of its cyclopolymerization: R = beginning of chain; R′ = end of chain.

The difference between the preferred conformations I–III is the mutual arrangement of the naphthalene rings (conformational rotamers). The template is not influenced by the different arrangements of the aromatic units. While the cyclopolymerization of **2** has to pass through a 19-membered transition state (as for **1**), it goes through a 15-membered transition state for **3** because of the position of the vinyl groups.

The arrows in Figure 8 indicate the possible course of the cyclization of monomer **2**. A cyclopolymerization is possible only in conformations I and II. In conformation III on the other hand the vinyl substituents are too far away from each other. Cyclocopolymerizations involving conformations I and II can explain the formation of meso (*R*,*S*) diads and (*S*,*S*) diads which is in accordance with the CD spectroscopical investigations. At present the ratio of (*S*,*S*) to (*R*,*S*) diads in the copolymers has not been determined directly. It should be mentioned that a perpendicular arrangement of aromatic rings and dioxaborolane rings would give the same results. Detailed information on the microstructure of these polymers as well as on the enantiomeric excess in the different reaction steps could be obtained by a radical ring closure reaction of **2** and a detailed investigation of the products formed.[22] It should further be mentioned that the presence of the meso diads (*R*,*S*) does not contribute to the CD spectra and does not affect the interpretation of the absolute stereochemistry, since only the (*S*,*S*) or (*R*,*R*) diads are causing Cotton effects.

The conformations of **3** for cyclopolymerization are analogous to those of monomer **2** with respect to the template and the aromatic units; only the vinyl groups are in the ortho position and the rings are more stable in the perpendicular orientation. Inspection of molecular models shows that conformations II and III do not

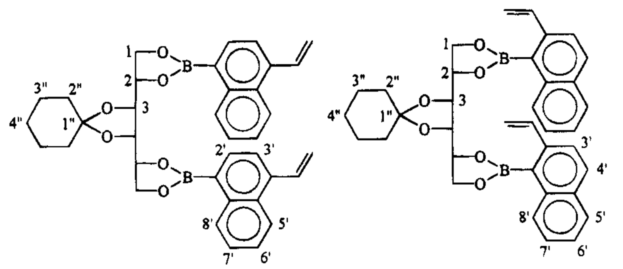


Figure 10. Numbering of positions of atoms for experimental section.

allow a cyclopolymerization (see Figure 9). A cyclopolymerization is, however, possible starting from conformation I.

As for monomer **1**, the vinyl groups have two preferred arrangements. The first attack can take place in both positions of the vinyl substituent. The second attack forming the cycle occurs much easier in the exo-conformation of the second vinyl substituent. The arrows in Figure 9 describe this course of cyclization of monomer **3**. Therefore, again two diads, (*R*,*S*) and (*S*,*S*), are favored by conformation I.

In spite of differences in mechanisms of cyclization for both monomers, both yield the same preferred diad.

Conclusions

The cyclocopolymerization of **2** and **3** with methyl methacrylate yield optically active copolymers containing an excess of chiral (*S*,*S*) diads with two 4-boronylnaphthyl-1 or 4-boronylnaphthyl-2 side chains in the copolymer backbone. Therefore, the CD spectra show a strong positive CD couplet in the case of **2** and a strong negative one in the case of **3**. The preferred configuration of the diads could be determined by the "exciton chirality method" of Nakanishi. The formation of the (*S*,*S*) diads can be explained in either case from the calculated optimal conformations of **2** and **3**.

Experimental Section

General Procedures. Elemental analyses were performed in the microanalytical laboratories of Dr. F. Pascher, Remagen (boron analysis), and of the Faculty of Natural Sciences of the Heinrich-Heine-University Düsseldorf (C, H, N). ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 (for numbering of positions of atoms see Figure 10). IR spectra (KBr disks) were recorded on a Perkin-Elmer ratio recording infrared spectrophotometer 1420. Optical rotations were measured with a Perkin-Elmer Model 241 MC polarimeter. CD spectral measurements were carried out at 25 °C in a 0.1 mm cuvette, using a Jasco J600 spectropolarimeter. UV spectral measurements were carried out at 25 °C in a 1 mm cuvette, using a Perkin-Elmer spectrophotometer 554. Melting points were measured with a Büchi 510 melting point apparatus.

Materials. All solvents were reagent grade and were purified by standard procedures prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Other reagents were used without further purification.

Comonomers. The comonomers methyl methacrylate, styrene, methacrylonitrile, and maleic anhydride were commercially available. Liquid monomers were purified by refluxing for 1 h with calcium hydride, followed by distillation. Maleic anhydride was purified by sublimation.

The other comonomers were prepared according to known literature procedures: *N*-phenylmaleimide,[23] 4-vinylstilbene.[24]

Template Monomers. 3,4-*O*-Cyclohexylidene-D-mannitol 1,2;5,6-Bis-*O*-[(4-vinylphenyl)boronate] (1) was prepared as described earlier.[5]

(4-Methylnaphthyl-1)-1,3,2-dioxaborolane (5). (4-Methylnaphthyl-1)boronic acid (**4**)[12] (137.6 g, 0.74 mol) and ethylene glycol (45.9 g, 0.74 mol) were heated in toluene, and the reaction water formed was removed by azeotropic distillation. Toluene was evaporated under reduced pressure, and the residue was recrystallized from *n*-hexane to give 138.4 g (88.2%) of (4-methylnaphthyl-1)-1,3,2-dioxaborolane (**5**) as colorless needles: mp 101−102 °C; ^{1}H NMR ($CDCl_3$) δ 2.68 (d, 3H, $-CH_3$, $^4J_{HH3}$ = 0.7 Hz), 4.38 (s, 4H, $-(CH_2)_2-$), 7.31 (dd, 1H, H3, $^3J_{H3H2}$ = 7.1 Hz, $^4J_{H3H}$ = 0.7 Hz), 7.48−7.54 (m, 2H, H6, H7), 8.00 (m, 1H, H2), 7.97−8.02 (m, 1H, H5), 8.75−8.79 (m, 1H, H8); ^{13}C NMR ($CDCl_3$) δ 19.94 (1C, $-CH_3$), 65.81 (2C, $-(CH_2)_2-$), 124.25, 125.41, 126.04, 126.09, 128.81, 132.42, 136.07, 136.87, 138.55 (9C, aromatic C). The signal of C1' could not be observed due to quadrupole relaxation by boron. Anal. Calcd for $C_{13}H_{13}BO_2$: C, 73.63; H, 6.18. Found: C, 73.65; H, 6.24.

[4(Bromomethyl)naphthyl-1]-1,3,2-dioxaborolane (6). (4-Methylnaphthyl-1)-1,3,2-dioxaborolane (**5**) (83.4 g, 0.393 mol), *N*-bromosuccinimide (73.5 g, 0.413 mol) and 0.1 g of AIBN in 800 mL of dry CCl_4 were irradiated with a UV lamp for 5 h. Succinimide was removed by filtration, and the solvent was distilled off. The solid residue was recrystallized from *n*-hexane/$CHCl_3$ to yield 95.5 g (83.5%) of [4-(bromomethyl)naphthyl-1]-1,3,2-dioxaborolane (**6**) as colorless needles: mp 99−101 °C; ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 4H, $-(CH_2)_2-$), 4.90 (s, 2H, $-CH_2Br$), 7.50 (d, 1H, H3, $^3J_{H3H2}$ = 7.0 Hz), 7.55−7.59 (m, 2H, H6, H7), 8.01 (d, 1H, H2), 8.12−8.15 (m, 1H, H5), 8.78−8.81 (m, 1H, H8); ^{13}C NMR ($CDCl_3$) δ 31.52 (1C, $-CH_2Br$), 65.93 (2C, $-(CH_2)_2-$), 123.81, 126.20, 126.65, 126.78, 129.13, 130.62, 135.50, 136.73, 137.31 (9C, aromatic C). Anal. Calcd for $C_{13}H_{12}BrBO_2$: C, 53.67; H, 4.16. Found: C, 53.58; H, 4.21.

[4-(1,3,2-Dioxaborolan-2-yl)naphthyl-1]methyltriphenylphosphonium Bromide (7). [4-(Bromomethyl)naphthyl-1]-1,3,2-dioxaborolane (81.1 g, 0.279 mol) and triphenylphosphine (73.1 g, 0.279 mol) were dissolved in 600 mL of $CHCl_3$ and heated at reflux for 2 h. The cooled reaction mixture was poured into 1.5 L of diethyl ether. The precipitated white powder of **7** (151.7 g (98%)) was dried in vacuum: mp 242 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.45 (s, 4H, $-(CH_2)_2-$), 5.58 (d, 2H, $-CH_2P$, $^2J_{HP}$ = 14.4 Hz), 6.95−7.00 (m, 1H, H6), 7.26−7.31 (m, 1H, H7), 7.34 (d (broad), 1H, H5, $^3J_{H5H6}$ = 8.5 Hz), 7.38 (dd, 1H, H3, $^3J_{H3H2}$ = 7.2 Hz, $^4J_{H3P}$ = 3.6 Hz), 7.45−7.69 (m, 15H, $-P(C_6H_5)_3$), 7.75 (d, 1H, H2), 8.59 (d, 1H, H8, $^3J_{H7H8}$ = 8.2 Hz). Anal. Calcd for $C_{31}H_{27}BBrO_2P$: C, 67.30; H, 4.92. Found: C, 67.34; H, 5.14.

Tris-*O*-(4-vinylnaphthyl-1)boroxine (8). [4-(1,3,2-Dioxaborolan-2-yl)naphthyl-1]methyltriphenylphosphonium bromide (**7**) (60.0 g, 0.108 mol) was suspended in a formaldehyde solution (360 mL, 37% in water) and water (50 mL). A solution of NaOH (60 g) in 200 mL of water was added. The solution was stirred for 3 h and diluted with 2 L of water. After suction filtration the solution was acidified with concentrated HCl and the boronic acid was crushed out. The precipitate was filtered off and dried over P_4O_{10}. The crude product was dissolved in 600 mL of CH_2Cl_2 and heated at reflux. The formed water was removed by azeotropic distillation. After filtration through a charcoal/Celite pad, the volume of the solution was reduced to about 200 mL, so that the product started to precipitate. Complete precipitation was achieved by cooling to −22 °C overnight. The white crystalline product of **8** (13.3 g, 70%) was filtered off. It still contained 24% of (4-vinylnaphthyl-1)boronic acid according to its ^{1}H NMR spectrum: mp 191 °C (polym); ^{1}H NMR (DMSO-d_6) δ 5.53 (dd, 3H, =HCH, $^3J_{cis}$ = 11.0 Hz, $^2J_{gem}$ = 1.6 Hz), 5.91 (dd, 3H, =HCH, $^3J_{trans}$ = 17.2 Hz), 7.50−7.80 (m, 6H, H6, H7), 7.63 (dd, 3H, −CH=), 7.78 (d, 3H, H3, $^3J_{H3H2}$ = 7.2 Hz), 8.23 (dd, 3H, H5, $^3J_{H5H6}$ = 8.0 Hz, $^4J_{H5H7}$ = 1.6 Hz), 8.33 (d, 3H, H2), 9.28 (dd, 3H, H8, $^3J_{H7H8}$ = 8.7 Hz, $^4J_{H8H6}$ = 1.4 Hz); ^{13}C NMR (DMSO-d_6) δ 117.44 (3C, =HCH), 134.22 (3C, −CH=), 122.52, 123.67, 125.40, 125.56, 129.14, 130.64, 133.52, 136.38, 136.88 (27C, aromatic C). For C1' see **5**.

3,4-*O*-Cyclohexylidene-D-mannitol 1,2:5,6-Bis-*O*-[(4-vinylnaphthyl-1)boronate] (2). Tris-*O*-(4-vinylnaphthyl-1)boroxine (**8**) (11.82 g, 22 mmol) and 3,4-*O*-cyclohexylidene-D-mannitol[11] (8.61 g, 32.8 mmol) were heated in 200 mL of CH_2Cl_2 for 3.5 h, and the water formed was removed by azeotropic distillation. The solution was filtered through a charcoal/Celite pad, and the solvent was removed under reduced pressure. The residue was recrystallized from toluene/petroleum ether (60/80) to give 14.7 g (76%) of colorless needles of **2**: mp 109−111 °C; $[\alpha]^{30}_{D} = +16.3°$ (c = 1.0 in THF); ^{1}H NMR ($CDCl_3$) δ 1.34−1.38 (m, 2H, $CH_2(4'')$), 1.55−1.61 (m, 4H, $CH_2(3'')$), 1.64−1.66 (m, 4H, $CH_2(2'')$), 4.22−4.24 (m, 2H, H3), 4.49−4.53 (m, 4H, H1), 4.74−4.78 (m, 2H, H2), 5.49 (dd, 2H, =HCH, $^{3}J_{cis}$ = 10.9 Hz, $^{2}J_{gem}$ = 1.5 Hz), 5.78 (dd, 2H, =HCH, $^{3}J_{trans}$ = 17.2 Hz), 7.41−7.45 (m, 4H, H6′ H7′), 7.46 (dd, 2H, −CH=), 7.48 (d, 2H, H3′, $^{3}J_{H2'H3'}$ = 7.3 Hz), 8.02 (d, 2H, H2′), 8.07−8.10 (m, 2H, H5′), 8.70−8.73 (m, 2H, H8′); ^{13}C NMR ($CDCl_3$) δ 23.85 (2C, $CH_2(3'')$), 24.94 (1C, $CH_2(4'')$), 37.09 (2C, $CH_2(2'')$), 68.09 (2C, C1), 77.52 (2C, C2), 80.30 (2C, C3), 111.33 (1C, C1″), 118.06 (2C, $=CH_2$), 134.49 (2C, −CH=), 122.73, 123.89, 125.66, 126.30, 128.64, 130.76, 136.04, 136.93, 139.21 (18C, aromatic C). Anal. Calcd for $C_{36}H_{36}B_2O_6$: C, 73.75; H, 6.19. Found: C, 73.61; H, 6.18.

1-Bromo-2-vinylnaphthalene (10). (1-Bromonaphthyl-2)methyltriphenylphosphonium bromide[15] (**9**) (112.5 g, 0.20 mol) and some 4-*tert*-butylcatechol were dissolved in 400 mL of CH_2Cl_2. First, a formaldehyde solution (160 mL, 37% in water) and then a saturated solution of 42.4 g of Na_2CO_3 (0.40 mol) were added to the rapidly stirred reaction mixture within 2 h. After stirring for an additional 3 h, the emulsion was diluted with 300 mL of water. The organic layer was separated, washed with water, and dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was extracted several times with petroleum ether (40/60) to remove most of the triphenylphosphine oxide. The solvent was evaporated under reduced pressure. The solid residue was recrystallized from methanol to yield 35.9 g (77%) of slightly yellow crystals of **10**: mp 56 °C; ^{1}H NMR ($CDCl_3$) δ 5.47 (dd, 1H, =HCH, $^{3}J_{cis}$ = 11.0 Hz, $^{2}J_{gem}$ = 0.95 Hz), 5.81 (dd, 1H, =HCH, $^{3}J_{trans}$ = 17.5 Hz), 6.38 (m, 1H, −CH=), 7.5−7.8 (m, 5H, aromatic H), 8.3−8.35 (m, 1H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 117.30 (1C, =HCH), 136.67 (1C, −CH=), 123.67, 123.76, 126.49, 127.47, 127.62; 127.66, 127.96, 132.46, 133.95, 134.83 (10C, aromatic C). Anal. Calcd for $C_{12}H_9Br$: C, 61.83; H, 3.89. Found: C, 61.69; H, 3.76.

(2-Vinylnaphthyl-1)boronic Acid (11). (2-Vinylnaphthyl-1)magnesium bromide was prepared from 1-bromo-2-vinylnaphthalene (**10**) (11.7 g, 50 mmol) and magnesium (1.33 g, 55 mmol) in dry THF according to standard procedures. The cooled reaction mixture was added to a solution of 22 mL of trimethyl borate (*ca.* 200 mmol) in 100 mL of dry THF in such a manner that the temperature did not rise above −60 °C. After complete addition, the cooling bath was removed and the reaction mixture was stirred until it warmed to room temperature. The mixture was stirred for an additional 2 h and then poured into 100 mL of water containing 20 mL of concentrated HCl. After addition of 100 mL of diethyl ether and 100 mL of water, the organic layer was separated and washed with water. The solvents were evaporated under reduced pressure. The solid residue was dried over P_4O_{10} and recrystallized twice from CH_2Cl_2 (crystallization at −25 °C) to yield 3.6 (37%) of small colorless needles of **11**: mp 121 °C; ^{1}H NMR (DMSO-d_6) δ 5.33 (dd, 1H, =HCH, $^{3}J_{cis}$ = 11.0 Hz, $^{2}J_{gem}$ < 1 Hz), 5.90 (dd, 1H, =HCH, $^{3}J_{trans}$ = 17.4 Hz), 6.92 (m, 1H, −CH=), 7.42−7.51 (m, 2H, aromatic H), 7.76−7.86 (m, 4H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 114.30 (1C, =HCH), 137.74 (1C, −CH=), 121.82, 125.47, 125.78, 127.50, 127.77, 128.72, 131.98, 134.67, 135.75 (9C, aromatic C). Anal. Calcd for $C_{12}H_{11}BO_2$: C, 72.78; H, 5.60. Found: C, 72.54; H, 5.45.

3,4-*O*-Cyclohexylidene-D-mannitol 1,2;5,6-Bis-*O*-[(2-vinylnaphthyl-1)boronate] (3). (2-Vinylnaphthyl-1)boronic acid (**11**) (3.96 g, 20 mmol) and 3,4-*O*-cyclohexylidene-D-mannitol (2.62 g, 10 mmol) were heated in 100 mL of CH_2Cl_2 for 4 h, and the water formed was azeotropically distilled off. The solution was filtered, and solvent was removed. The white amorphous residue could not be recrystallized, but analytical results were satisfactory. Yield: nearly quantitative. $[\alpha]^{30}_{D} = +101.6°$ (c = 1.132 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.4−1.5 (m, 2H, $CH_2(4'')$), 1.6−1.8 (m, 8H, $CH_2(2'')$, $CH_2(3'')$), 4.16 (m, 2H, H4), 4.55 (m, 4H, H1, H2), 4.80−4.87 (m, 2H, H3), 5.33 (dd, 2H, =HCH, $^{3}J_{cis}$ = 10.9 Hz, $^{2}J_{gem}$ = 0.8 Hz), 5.80 (dd, 2H, =HCH, $^{3}J_{trans}$ = 17.3 Hz), 7.13 (dd, 2H, −CH=), 7.39−7.45 (m, 4H, H6′, H7′), 7.68 (d, 2H, H4′, $^{3}J_{H3'H4'}$ = 8.8 Hz), 7.81 (d, 2H, H3′), 7.71−7.78 (m, 2H, H8′), 8.00−8.05 (m, 2H, H5′). ^{13}C NMR ($CDCl_3$): δ 23.81 (2C, $CH_2(3'')$), 24.98 (1C, $CH_2(4'')$), 36.66 (2C, $CH_2(2'')$), 67.49 (2C, C1), 77.51 (2C, C2), 79.80 (2C, C3), 111.36 (1C, C1″), 115.54 (2C, $=CH_2$), 137.61 (2C, −CH=), 122.49, 125.68, 126.31, 128.14, 128.37, 130.01, 132.42, 136.14, 140.39 (18C, aromatic C). For C1′ see **5**. Anal. Calcd for $C_{36}H_{36}B_2O_6$: C, 73.75; H, 6.19. Found: C, 73.59; H, 6.20.

Preparation of Copolymers. Predetermined amounts of the monomers and AIBN (see Table 1) were dissolved in toluene to make a solution of 0.4 mol/L. The polymerization mixture was subjected to repeated cool−pump−thaw cycles to remove dissolved oxygen and at least flushed with nitrogen. Polymerization was carried out by stirring it at the given temperature (65 or 75 °C). After the time given in Table 1, the polymers were precipitated in a mixture of acetone/petroleum ether 60/80 (1/5, v/v). The polymers were dried in vacuum to constant weight. Yields of polymerization are determined by weighing the dried copolymers.

The template was removed by repeated dissolution in THF/water (9/1, v/v) and precipitation in a slightly acidified (HCl) mixture of methanol/water (1/1, v/v) or water. At last the copolymers were precipitated in CH_2Cl_2 and dried in vacuum to a constant weight.

Deboronation of the copolymers was performed as described earlier.[5]

Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft, the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and the Fonds der Chemischen Industrie is gratefully acknowledged.

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MA9501454