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Chirality of Polyvinyl Compounds. 10.[1] Asymmetric Perturbation of Side-Chain Chromophores Caused by the Main-Chain Configuration of Optically Active Vinyl Polymers

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ABSTRACT: After removal of the D-mannitol template, copolymers of 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (1) with comonomers having aromatic chromophores obtained by free radical polymerization were investigated for their chiroptical properties. As comonomers, usually those containing aromatic systems of benzene, naphthalene, biphenyl, and stilbene with a varying distance of the chromophores from the polymerizable group were used. The copolymers are optically active due to the chirality of the configuration of the main chain. While the (*S*,*S*)-(4-vinylphenyl)boronic acid diads cause a strong negative Cotton effect at 233 nm, the aromatic comonomeric units generally bring about a positive Cotton effect at higher wavelength. Depending on the extent to which these two influences are operating, optical rotations varying from strongly negative to strongly positive were observed for the copolymers of different comonomers. The aromatic comonomeric unit shows the highest influence on the chiroptical properties if it is present as an isolated entity directly bound to the main chain. The asymmetry of the aromatic chromophore is caused by a conformational perturbation through the neighboring (*S*,*S*) diads.

Introduction

Much of the interest in optically active polymers stems from the potential of these materials for several specialized uses, viz., (i) chiral matrices for asymmetric synthesis, (ii) chiral stationary phases for the resolution of racemates, (iii) synthetic molecular receptors, and (iv) chiral liquid crystals for ferroelectric and nonlinear optical applications.[2-5] This has stimulated a considerable amount of research directed toward designing improved synthetic procedures for obtaining optically active polymers with well-defined molecular and supermolecular structural ordering of the polymer chain and the functional groups.

Based on molecular symmetry considerations, we have recently developed a novel synthetic strategy for obtaining optically active vinyl polymers whose chirality arises from the configurational relationships in the main chain. Our approach toward constructing such a chiral polymer chain involves stereoregular placement of two monomeric units in a defined absolute configuration (asymmetric diads), which are separated from one another by one or more nonstereoregular comonomer units.[2,6] Hence by polymerization of the appropriate template monomer 1 with another comonomer such as styrene, methacrylonitrile, etc. and subsequent removal of the chiral template units, one is furnished with polymers showing appreciable optical activity.[7] Our detailed synthetic and mechanistic investigations revealed the absolute configuration of the asymmetric diad units to be (*S*,*S*), showing negative optical rotations.[8] Furthermore, since the asymmetric configurations and hence the optical activity are mainly

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influenced by the template monomer, the comonomeric part was varied to prepare new optically active vinyl copolymers by copolymerizing with the appropriate monomers. In the majority of cases, the copolymers showed negative optical rotations, in agreement with what was expected from the absolute configuration of the asymmetric diad repeating units. However, the copolymers obtained from styrene derivatives bearing cyano, aldehyde, methoxycarbonyl, and nitro groups directly linked to the phenyl ring showed appreciable positive optical rotations.[8,9]

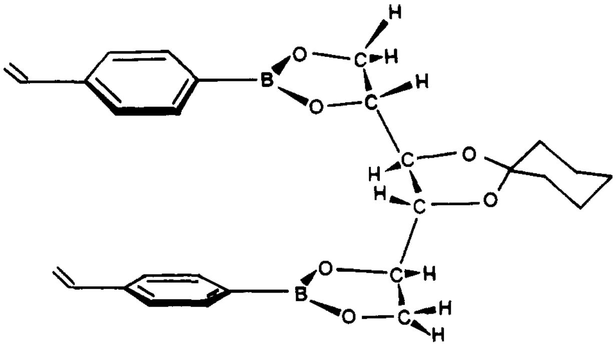
Chemical and chiroptical studies showed that regardless of their direction of rotation, both the positively and negatively rotating polymers possess the same absolute configuration. For example, a polymer with 4-vinylbenzaldehyde as the comonomer gave, after reduction with $LiAlH_4$, a polymer that had a structure corresponding to that obtained with 4-vinylbenzyl alcohol as comonomer. Since both possessed nearly identical values of optical rotation, the same degree of asymmetric induction occurred as well. Similar results were obtained in other cases,[9] so it can safely be assumed that regardless of the comonomeric part, all asymmetric diads possess (*S*,*S*) configuration. The observed positive optical rotations of the copolymers obtained with these comonomers is a consequence of asymmetric perturbation of the side-chain chromophoric groups of atactic comonomeric units.[9]

In order to gain a deeper understanding on this induced optical activity from the side-chain chromophores of comonomers, a detailed investigation of this effect was undertaken. In this respect the transmission of chirality from the asymmetric configuration of the main chain (asymmetric diads) to the configurationally irregular side-chain chromophores present in the comonomer part is compared with the previously known transmission of chirality from optically active side chains to achiral side-chain chromophores in isotactic or atactic polymers. This latter effect has been extensively studied in previous years, particularly by the Pisa school.[10–13] In our investigation the following questions were addressed: (a) Is the induced opposite optical rotation a general feature for all comonomers having conjugated aromatic chromophores? (b) What is the influence of the arrangement of the chromophores (distance, orientation) at the main chain on their asymmetric perturbation? (c) Can the optical rotation be changed by light-induced structural changes of the chromophores?

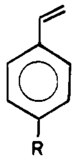
Results and Discussion

(a) Influence of the Nature of the Comonomeric Chromophores on the Induced Chirality. As in our earlier investigations, free radical initiated copolymerizations of 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**1**) with different comonomers were performed. In order to obtain copolymers having substantially homogeneous composition, the polymerization reactions were stopped at low conversions (<15%). After quantitative removal of the 3,4-*O*-cyclohexylidene-D-mannitol templates, the chemical compositions and molecular properties, in particular the optical rotation and circular dichroism, of these copolymers were investigated. In order to investigate the influence of the comonomeric chromophores on the induced chirality in the copolymers, we have choosen vinyl compounds bearing different types of aromatic chromophoric systems as the comonomers. The comonomers thus used were styrene (**2a**), 4-chlorostyrene (**2b**), 1-vinylnaphthalene (**3**), 2-vinylnaphthalene (**4**), 4-vinylbiphenyl (**5**), and 4-vinylstilbene (**6**). It is anticipated that in case of optical rotation and circular dichroism the effect of these copolymers it is a consequence of a superimposition of the influences of (*S*,*S*)-(4-vinylphenyl)boronic acid diads and those of the comonomer units. This is further complicated since these two effects can be separately observed but they are not independent of each other.

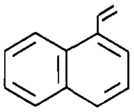
In order to elucidate the influence of the (*S*,*S*)-(4-vinylphenyl)boronic acid diad on the optical activity, a comonomer was first used for comparison purposes that itself does not contribute to Cotton effects in the accessible region of the CD spectrum. For this purpose, methacrylonitrile was choosen as comonomer (see Table I). Copolymers with **1** after removal of the template show a strong negative Cotton effect (232 nm, $[\psi] = -4051°$) and two positive ones (216 nm, $[\psi] = +777°$, and 206 nm, $[\psi] = +1410°$) (see Figure 1, Table II). This spectrum differs somewhat in the lower wavelength region from our earlier published results.[9] In the present case it has been measured with a new instrument (JASCO 600) covering a larger wavelength region and having a better quality of performance at lower wavelengths.



1



2a R=H
2b R=Cl



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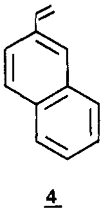

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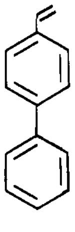

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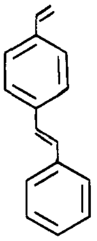


6

In order to ensure that the nitrile group does not influence the CD spectrum, previously synthesized[14] copolymers **7a** and **7b** were compared. **7a** contains a nitrile group, while **7b** is the modified analogue of **7a** where the nitrile group is reduced to a CH_2NH_2 group. Both the copolymers showed nearly identical CD spectra (see Table II, entries 2 and 3). Therefore the CD spectrum of the methacrylonitrile-containing copolymer can be used as a reference material for studying the influence of the (*S*,*S*)-(4-vinylphenyl)boronic acid diads in the main chain. Thus, the optical rotation of $[\alpha]^{30}_{365} = -85°$ should mainly be attributed to the distyryl diads.

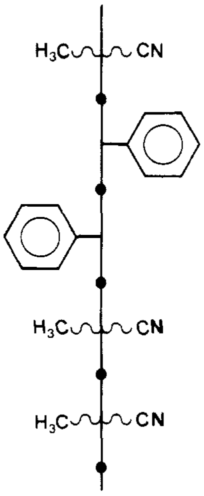
In contrast to the methacrylonitrile-based copolymers, those containing 4-vinylbiphenyl and 4-vinylstilbene as comonomers show strong positive optical rotations with values up to $[\alpha]^{30}_{365} = +89°$ and $[\alpha]^{30}_{365} = +145°$, respectively (see Table I, entries 5 and 10). The CD spectra (see Table II and Figure 2) of the 4-vinylbi-

Table I
Optical Activities of Copolymers of 1 and Vinyl Aromatic Monomers after Splitting Off the Templates[a]

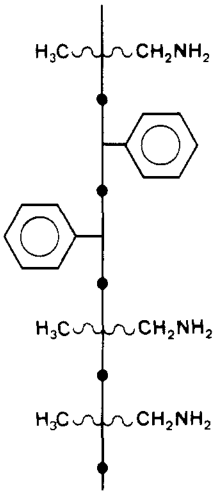
entry	comonomer	1, mole fractn in reactn mixt	1, mole fractn in copolym	$[\alpha]^{30}_{365}$, deg
1	methacrylonitrile	0.15	0.30	-85[8]
2	4-vinylbiphenyl (**5**)	0.14	0.28	+49
3		0.25	0.34	+57
4		0.41	0.52	+65
5		0.52	0.63	+89
6		0.59	0.71	+74
7	4-vinylstilbene (**6**)	0.16	0.26	+61
8		0.26	0.38	+86
9		0.41	0.54	+121
10		0.50	0.62	+145
11		0.59	0.70	+136
12	styrene (**2a**)	0.11	0.18	-25
13		0.15	0.23	-28
14		0.24	0.38	-34
15		0.35	0.47	-24
16		0.48	0.59	-22
17	4-chlorostyrene (**2b**)	0.50	0.58	+1.5[8]
18	1-vinylnaphthalene (**3**)	0.15	0.27	-34
19		0.26	0.36	-41
20		0.38	0.52	-49
21		0.49	0.59	-56
22		0.62	0.71	-52
23	2-vinylnaphthalene (**4**)	0.21	0.36	+42
24		0.32	0.47	+50
25		0.40	0.56	+58
26		0.51	0.61	+63
27		0.62	0.69	+57

[a] The composition of the copolymers was calculated from the elemental analyses (see Table VI) and in some cases controlled by ^{1}H NMR spectroscopy.

phenyl copolymers show a strong and broad positive Cotton effect with a maximum centered at 255 nm and a broad negative one with a maximum at 230 nm. This CD is mainly determined by the biphenyl chromophore whose UV spectrum (see the UV spectrum of the copolymer in Figure 3) shows a broad absorption band at 257 nm, corresponding to a ${}^{1}L_a$ transition.[15] The positive Cotton effect at 255 nm appears to be responsible for the observed positive optical rotations of these copolymers. These results are indicative of the significant amounts of asymmetric induction in these groups during polymerization or of an asymmetric conformational perturbation of these groups induced by the optically active (*S*,*S*) diads.



7a



7b

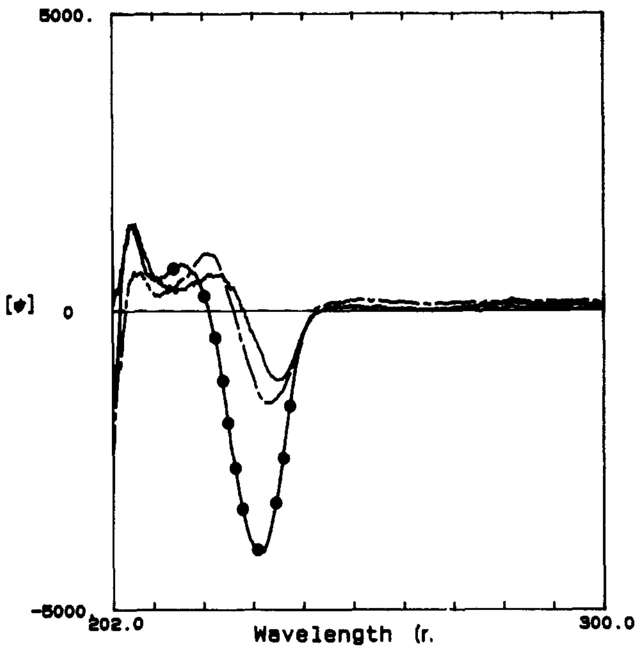


Figure 1. CD spectra of the copolymers of 1 with different comonomers after splitting off the template: $[\psi]$ = specific ellipticity at 25 °C (deg/dm)/(g/mL); (●) copolymer with 68 mol % methacrylonitrile; (- - -) copolymer with 52 mol % styrene; (—) copolymer with 42 mol % 4-chlorostyrene.

For the copolymers carrying stilbene moieties the CD spectral pattern is also determined by the conjugated aromatic chromophore (see Figure 4). The UV spectrum of the copolymer (see Figure 5) consists of two absorption bands in the regions 340–260 and 248–220 nm due to the ${}^{1}L_b$ electronic transition of *trans*-stilbene chromophores and the ${}^{1}L_b$ transition of *trans*-stilbene together with the ${}^{1}L_b$ benzenoid transitions, respectively.[16] The CD spectrum shows a very broad positive band over the wavelength range 350–250 nm followed by a negative band with its maximum centered at 233 nm. The positive band in the longer wavelength region is thus a consequence of the asymmetric arrangement of the stilbene chromophore along the copolymer chain.

In the foregoing cases the conjugated aromatic chromophores show strong CD bands at higher wavelength. Thus the CD effects of the (*S*,*S*)-(4-vinylphenyl)boronic acid diads are partially dominated by these comonomer chromophores and the typical negative Cotton effect at 233 nm is reduced in the case of the 4-vinylbiphenyl copolymers. The UV absorption bands of the comonomer units for the copolymers based on styrene and 4-chlorostyrene appear in the same regions as those of (4-vinylphenyl)boronic acid units [UV absorption maxima: (a) polystyrene, λ_{max} = 218 nm; (b) poly(4-chlorostyrene), λ_{max} = 222 nm; (c) poly[(4-vinylphenyl)boronic acid], λ_{max} = 229 nm]. This implies if any positive Cotton effect is induced in the comonomeric parts of these copolymer systems, it would result in a reduction of the negative Cotton effect of the (*S*,*S*) diads at 233 nm. Furthermore, lower negative optical rotations are expected. The results in Table I and II and Figure 1 verify these assumptions.

These analyses reasonably explain the results using a large variety of comonomers,[8,9] where optical rotations ranging from strongly negative to positive were observed. In certain cases very small rotations are obtained. It now becomes clear that the asymmetric inductions in the main chain in all cases may be of similar order, but the overall optical rotation seems to be a combined outcome of the influences of two opposite effects: first due to the

Table II
Results of the CD Spectral Pattern of the Optically Active Copolymers

			CD absorption maxima			
entry	comonomer	1, mole fractn in copolym	λ_1	$[\psi]_1$	λ_2	$[\psi]_2$
1	methacrylonitrile	0.32	232	−4062	216	+777
2	methacrylonitrile (**7a**) (after deboronation)	0.32	218	−894		
3	polymer **7b** (after reduction of polymer **7a**)	0.32	219	−885		
4	styrene (**2a**)	0.48	234	−1554	222	+890
5	4-chlorostyrene (**2b**)	0.58	235	−1161	223	+585
6	1-vinylnaphthalene (**3**)	0.59	231	−6562	216	+787
7	2-vinylnaphthalene (**4**)	0.61	231	+4845	215	−618
8	4-vinylbiphenyl (**5**)	0.28	255	+1067	231	−1157
9	4-vinylbiphenyl (**5**)	0.52	255	+1256	229	−912
10	4-vinylbiphenyl (**5**)	0.63	253	+1361	232	−1244
11	4-vinylbiphenyl (**5**)	0.71	253	+1478	229	−1391
12	4-vinylstilbene (**6**)	0.54	315	+816	234	−1852
13	4-biphenyl methacrylate (**10a**)	0.62	251	+1051	232	−2109
14	4-biphenylmethyl methacrylate (**10b**)	0.56			233	−2875

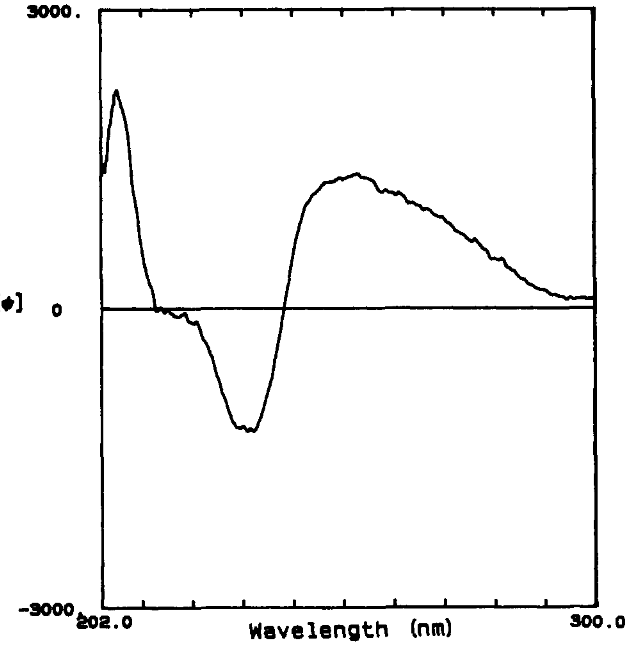


Figure 2. CD spectrum of the copolymer of 1 and 4-vinylbiphenyl (37 mol %).

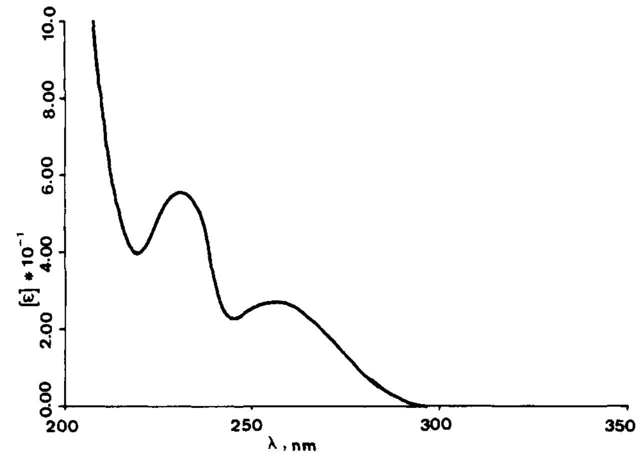


Figure 3. UV spectrum of the copolymer of 1 with 4-vinylbiphenyl (37 mol %). [ε] = specific extinction at 25 °C [log (I_0/I)/ (cm·g)/L].

chromophore of the (*S*,*S*) diads and second to the comonomeric part. For example 4-methoxystyrene gives only a small negative ($[\alpha]^{30}{}_{365} = -3.5°$) and 4-chlorostyrene a small positive optical rotation ($[\alpha]^{30}{}_{365} = +1.5°$).

With 1-vinylnaphthalene and 2-vinylnaphthalene as comonomers a surprising result was obtained. Copolymers from 1-vinylnaphthalene showed negative optical rotations ($[\alpha]^{30}{}_{365} = -56°$), while those based on 2-vinylnaphthalene were positively rotating ($[\alpha]^{30}{}_{365} = +63°$). The CD spectra of these copolymers are presented in Figure 6. The UV spectrum (see Figure 7) shows an absorption maximum in the region 305–270 nm, corresponding to a ^1L_a transition, followed by a strong band around 240–215 nm due to the ^1B_b electronic transition of the naphthyl chromophores along with the ^1L_a electronic transition of the phenylboronic acid units.[15]

The CD spectra show for the positively rotating 2-vinylnaphthalene based copolymer a positive band with its maximum at 234 nm, followed by a weaker negative band at 215 nm. On the other hand, negatively rotating 1-vinylnaphthalene containing copolymers present nearly a mirror image CD curve (see Figure 6). Taking a negative Cotton effect for the (*S*,*S*) diad in both cases into consideration, the ellipticities of the bands stemming from the 1- and 2-vinylnaphthalene moieties of the copolymers seem to have nearly the same absolute value. This result indicates the formation of two different chiral structures for the copolymers of the two regioisomers of vinylnaphthalene, although in both cases the (*S*,*S*)-(4-vinylphenyl)boronic acid diads should remain identical. Earlier investigations on asymmetric perturbation of naphthyl chromophores in copolymers of 1- and 2-vinylnaphthalene with optically active α-olefins[17] revealed that with α-olefins of the same absolute configuration the CD spectra exhibited opposite Cotton effects for copolymers of 1- and 2-vinylnaphthyl chromophores. Such behavior was ascribed to the influence of the relative orientations of the transition moments of the chromophores with respect to the polymeric chain on their chiroptical properties. Similar results were obtained with 1- and 2-naphthyl derivatives of cyclic dipeptides.[18]

Important information can be drawn from the dependence of optical rotation and circular dichroism on the ratio of the monomers in the copolymers. It has been reported earlier that for the copolymers of 1 with methacrylonitrile and methyl methacrylate, maximum optical rotations were observed for ca. 25–30 mol % (4-vinylphenyl)boronic acid diad content in the copolymer chain (see Figure 8).[8] The optical rotation was also calculated with respect to the proportion of (4-vinylphenyl)boronic acid diads present in the polymers with varying amount of comonomer. It clearly illustrated a rise in the rotatory power of the polymers with increasing number of isolated distyryl diads.[8] In contrast, for polymers prepared from 4-vinylbiphenyl, 4-vinylstilbene, and 2-vinylnaphthalene, as can be seen from Table I and Fig-

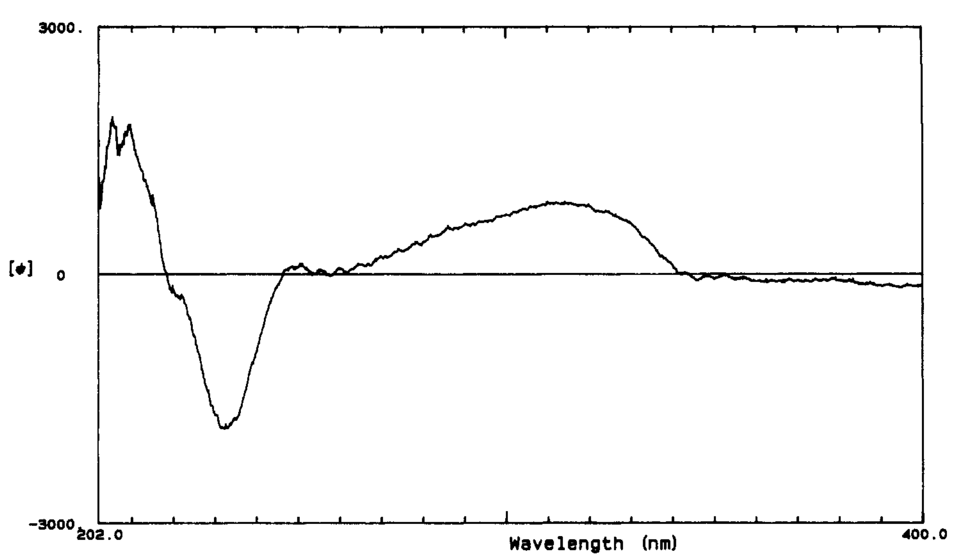


Figure 4. CD spectrum of the copolymer of 1 with 4-vinylstilbene (46 mol %).

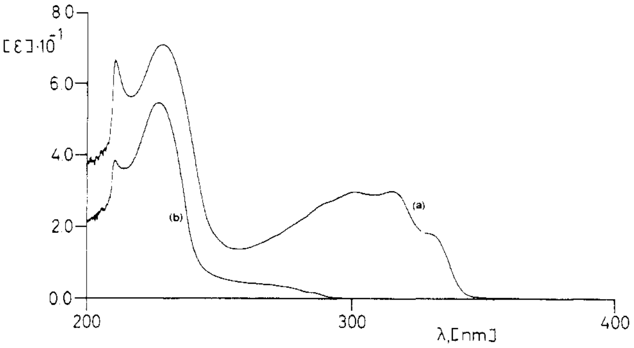


Figure 5. UV spectra of the copolymers of 1 with (a) 4-vinylstilbene (46 mol %) and (b) methacrylonitrile (68 mol %).

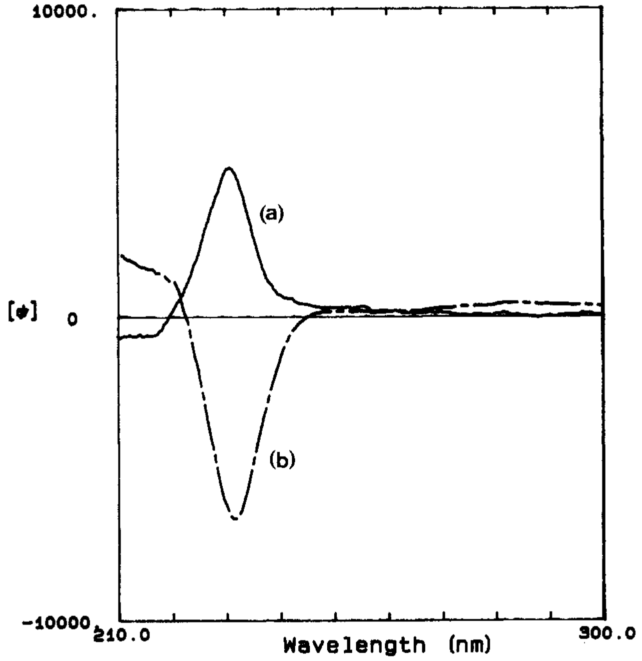


Figure 6. CD spectra of the copolymers of 1 with (a) 2-vinylnaphthalene (39 mol %) and (b) 1-vinylnaphthalene (41 mol %).

ure 8, the specific optical rotation values show a maximum at 60–65 mol % of distyryl diads. A similar behavior is shown for the negatively rotating copolymers of 1-vinylnaphthalene. Figure 9 shows the CD spectra of copolymers of 4-vinylbiphenyl containing different mole fractions of the comonomers. The strongest positive Cotton effect per mole of 4-vinylbiphenyl units is observed with only 28 mol % 4-vinylbiphenyl units in the copolymer (specific ellipticities are given in Figure 9). This suggests that the comonomeric part appears to govern the observed optical rotation. The significant contributions to the optical rotations in these copolymers, on the other hand, would therefore appear to arise from isolated comonomeric units in the polymer chain.

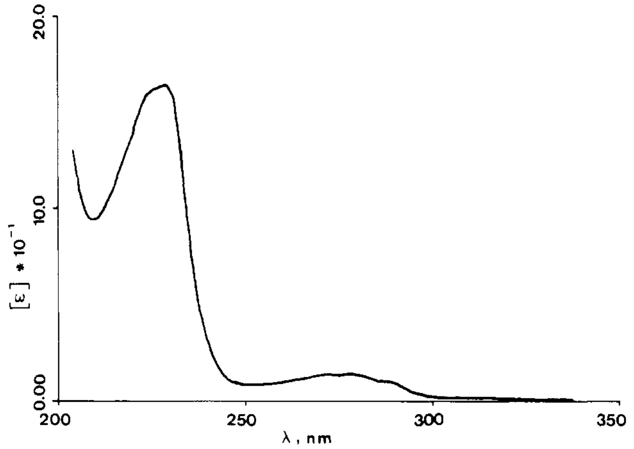
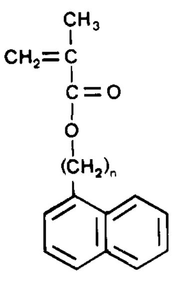
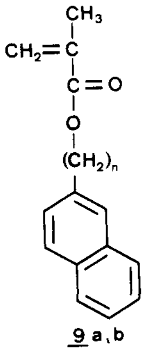


Figure 7. UV spectrum of the copolymer of 1 with 2-vinylnaphthalene (39 mol %).

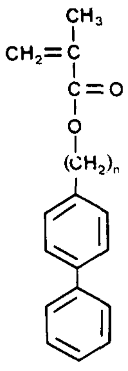
(b) Effect of Distance between Polymer Main Chain and Chromophoric Groups on Induced Chirality. In order to gain further information with regard to the origin of the induced chirality in the comonomer part of the polymers, it was of interest to determine to what extent the distance between the polymer backbone and the chromophoric group would influence this induced optical activity and the circular dichroism characteristics of these copolymers. Toward this end, we have synthesized two sets of methacrylate derivatives bearing the same aromatic chromophores described earlier. One set of these comonomers consists of the methacrylic group directly bound to the aromatic rings through an ester linkage (structures **8a**–**11a**), and for the other set an additional methylene spacer was introduced between them (structures **8b**–**11b**). Copolymerization of these comonomers with the template monomer 1 and removal of the template also furnished optically active copolymers. The results on their composition and specific optical rotations are presented in Tables III and IV. A perusal of the data reveals that the copolymers prepared by using the methacrylate monomers with chromophoric units directly linked to the ester group (Table III) exhibit similar behavior to the vinyl compounds with respect to optical activity. This, too, holds good for the composition dependence of their optical rotation (see Figure 10). However, their specific optical rotation values are somewhat lower compared with their vinyl aromatic based counterparts. The reduction is somewhat less pronounced for the extended aromatic system of stilbene.



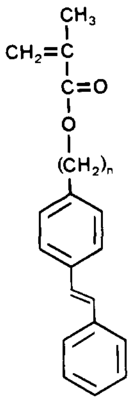
8 a, b



9 a, b



10 a, b



11 a, b

In Formula **8**–**11**

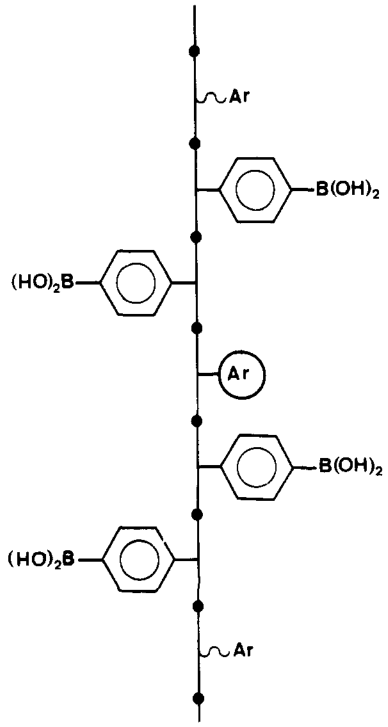
For a, n=0
For b, n=1

In contrast, the copolymers obtained with the methacrylate monomers having the aromatic moieties separated from the ester group through a methylene spacer, as can be seen from Table IV, mostly exhibit negative optical rotations. Moreover, as Figure 10 shows, composition versus optical activity for these copolymers follows a trend similar to those obtained with comonomers having no such chromophoric system (viz., methyl methacrylate, methacrylonitrile[8]). However, the specific negative optical rotation values of the present copolymers are smaller than those of the previously investigated copolymers. The copolymers bearing the stilbene chromophore show small positive optical rotation (Table IV), indicating nearly nulification of the two oppositely operating effects due to the (*S*,*S*) diads and due to the comonomer.

These two opposite effects are clearly demonstrated in the CD spectra of these compounds. Figure 11 shows the CD spectra of the biphenyl group containing copolymers of 4-vinylbiphenyl (**5**), 4-biphenyl methacrylate (**10a**) and 4-biphenylmethyl methacrylate (**10b**). Compared to copolymers of **5** those of **10a** show a smaller positive Cotton effect in the range 290–250 nm. The negative Cotton effect at 233 nm originating from the (*S*,*S*) diads is less overlapped and can be clearly identified. Copolymers with **10b** are lacking a positive Cotton effect at 290–250 nm but show a strong negative one at 233 nm, similar to that (or even stronger) of copolymers of methacrylonitrile or styrene. From these observations it appears that there is a critical distance between the chromophore and the main chain beyond which the main-chain chirality of the (*S*,*S*) diads is not able to induce a measurable dissymmetry in the chromophores of the comonomers.

It remains debatable whether this dissymmetry induced in the chromophoric systems of the comonomers arises from a conformational perturbation of the comonomer chromophores by the (*S*,*S*) diads in the main chain or whether the comonomer units are present in an asymmetric configuration in the main chain.

The latter can occur by an asymmetric induction during chain growth by the optically active template at the growing polymer chain end. As has already been described in the preceding section, the observed positive optical rotations were strongest for the chain containing isolated comonomer units. This implies that the aromatic group (Ar) is situated in the manner shown in **12** (in circle). The center at which this aromatic group is situated is chirotopic, i.e., it is in a chiral neighborhood. But it is not stereogenic, if only five carbon atoms are regarded at both sides of the chain. It becomes only stereogenic if the carbon atoms with aromatic groups are taken into consideration in a six-carbon distance. It is quite unlikely that there is a strong asymmetric induction over this long distance. On the other hand, it seems quite plausible that the (*S*,*S*)-(4-vinylphenyl)boronic acid diads induce a dissymmetric perturbation in the chromophores present on either side of it. If the distance of the chromophore from the main chain becomes longer, the dissymmetric perturbation diminishes.



12

Similar behavior has been observed by Ciardelli et al.[19-21] and others[22,23] with copolymers of vinyl aromatic monomers and vinyl monomers carrying optically active side

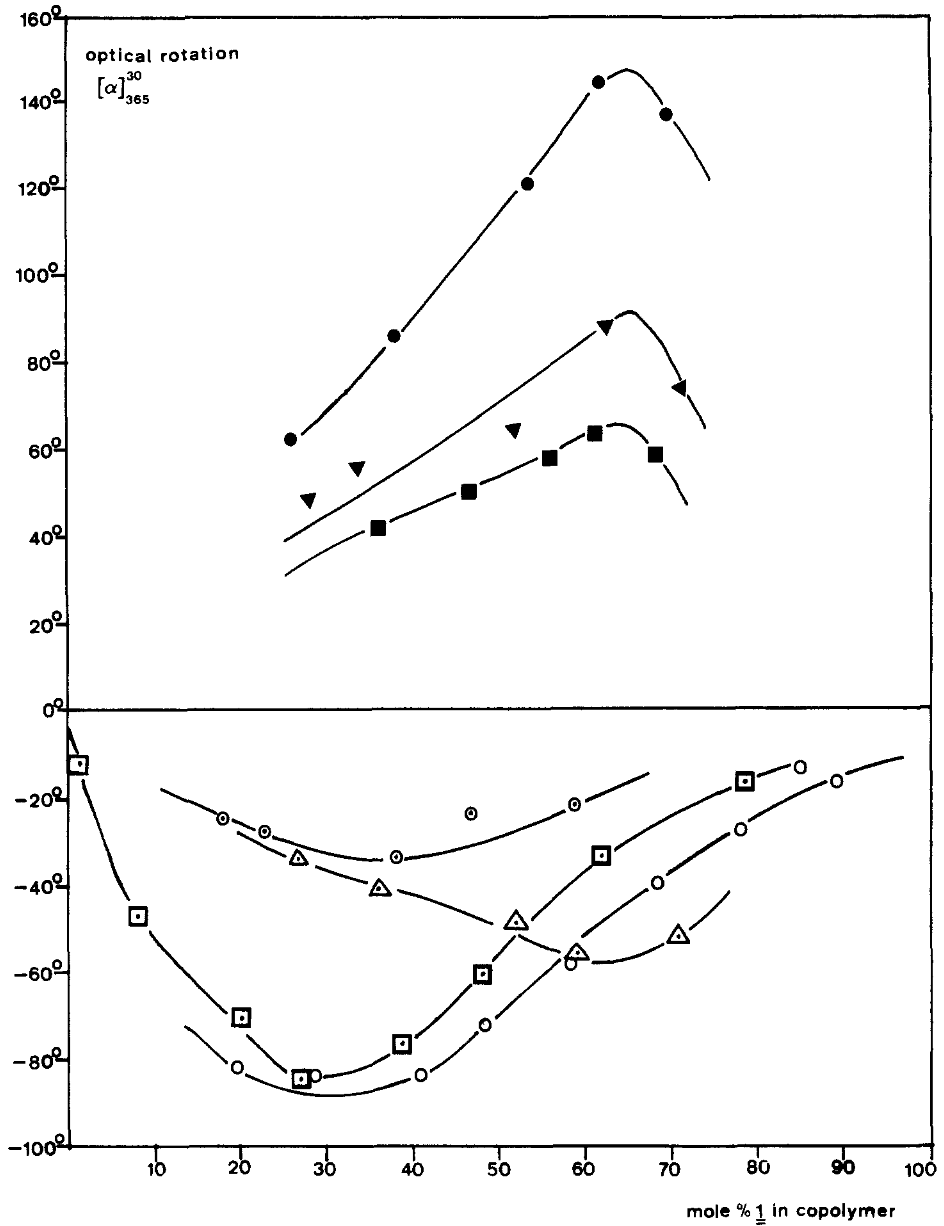


Figure 8. Composition-dependent specific optical rotation values of the copolymers of **1** with different comonomers: (●) 4-vinylstilbene; (▲) 4-vinylbiphenyl; (■) 2-vinylnaphthalene; (⊙) styrene; (◬) 1-vinylnaphthalene; (⊡) methyl methacrylate; (○) methacrylonitrile.

chains. Induced chirality in those systems was ascribed to originate from dissymmetric perturbations of isolated chromophores and/or from a dipole–dipole interaction between at least two identical chromophores disposed in a chiral geometry with a single skewness. For the later type of effect, a couplet due to exciton splitting[24] in the CD should be present. In our polymers a detailed study was difficult due to overlapping of bands originating from the (*S*,*S*) diads and the aromatic chromophore of the comonomer in the lower wavelength region. Solaro et al.[25] have reported the occurrence of exciton coupling in the 350–250-nm region of π–π^* electronic transitions of *trans*-stilbene chromophores for copolymers of 4-vinylstilbene and (+)-menthyl acrylate. In our case, although appreciable dichroic bands were observed in this region, there was no indication of exciton coupling. Analysis of the CD spectra of copolymers with **6** containing varying amounts of the comonomers, as can be seen from Figure 9, does not show any exciton coupling, even for higher amounts of **6** in the copolymer. This appears to attest to the fact that the optical activity and the circular dichroism in the present case are mainly caused by isolated comonomers. It is to be expected that the isolated (*S*,*S*)-(4-vinylphenyl)boronic acid diads would give rise to an exciton coupling. But even in copolymers with methacrylonitrile there is no clear indication of a couplet. It needs to be investigated further whether there is no couplet or whether there is an overlap of different bands.

(c) Light-Regulated Variation of Optical Activities of Copolymers Bearing *trans*-Stilbene Side Chains. In order to further investigate the two oppositely operating effects of the (*S*,*S*)-(4-vinylphenyl)boronic acid diads and chromophoric systems of the comonomer on the observed optical activity of these copolymers, the photoisomerization of *trans*-stilbene containing copolymers was pursued. While *trans*-stilbene moieties show a strong absorption band between 360 and 250 nm with a maximum at 302 nm, the cis compound shows an absorption at low wavelength (maximum at 280 nm) with only one-third of the extinction of the trans compound. The effect of the later isolated chromophore should therefore be less pronounced with respect to optical rotation.

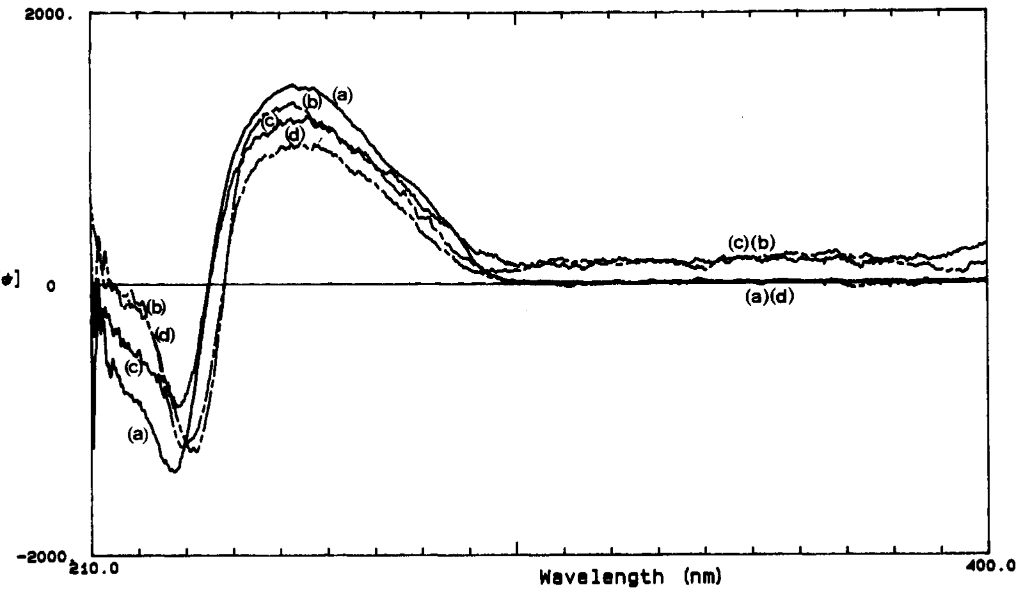


Figure 9. CD spectra of copolymers of **1** with 4-vinylbiphenyl containing different mole fractions of the comonomers: (a) 71 mol % **1**; (b) 63 mol % **1**; (c) 52 mol % **1**; (d) 28 mol % **1**.

Table III
Optical Activities of the Copolymers of 1 with Aryl Methacrylate Monomers after Removal of the Template

entry	comonomer	1, mole frctn in reactn mixt	1, mole fractn in copolym	$[\alpha]^{30}_{365}$, deg
1	1-naphthyl methacrylate (**8a**)	0.16	0.26	-18
2		0.29	0.38	-27
3		0.41	0.53	-31
4		0.51	0.58	-34
5	2-naphthyl methacrylate (**9a**)	0.25	0.34	+18
6		0.40	0.52	+23
7		0.49	0.57	+32
8		0.58	0.64	+29
9	4-biphenyl methacrylate (**10a**)	0.26	0.40	+45
10		0.35	0.48	+51
11		0.41	0.54	+57
12		0.50	0.62	+65
13	4-stilbenyl methacrylate (**11a**)	0.22	0.32	+105
14		0.35	0.47	+116
15		0.41	0.52	+124
16		0.51	0.59	+133

Table IV
Optical Activities of Copolymers of 1 with Arylmethyl Methacrylate Monomers after Removal of the Template

entry	comonomer	1, mole fractn in reactn mixt	1, mole fractn in copolym	$[\alpha]^{30}_{365}$, deg
1	1-naphthylmethyl methacrylate (**8b**)	0.15	0.27	-18
2		0.24	0.37	-28
3		0.37	0.49	-23
4		0.48	0.63	-20
5	2-naphthylmethyl methacrylate (**9b**)	0.18	0.32	-22
6		0.33	0.48	-27
7		0.42	0.54	-22
8		0.49	0.68	-19
9	4-biphenylmethyl methacrylate (**10b**)	0.15	0.28	-17
10		0.28	0.42	-25
11		0.36	0.56	-23
12		0.47	0.65	-15
13	4-stilbenylmethyl methacrylate (**11b**)	0.20	0.32	+3
14		0.27	0.43	+4
15		0.39	0.58	+3
16		0.50	0.67	+3

Copolymers containing **6**, **11a**, and **11b** were irradiated at 334–328 nm for different periods of time and the UV spectra and the optical rotations of the irradiated samples were measured (see Figures 12 and 13 and Table V). The UV absorption maxima decreases with increasing irradiation time. After a certain time, further irradiation does not bring about changes in the UV absorption maxima, thus indicating the attainment of a photostationary state of the isomerization process.[26,27]

With this decrease in the UV absorption maximum in the 350–250-nm region as a function of irradiation time, the specific optical rotation values of these positively rotat-

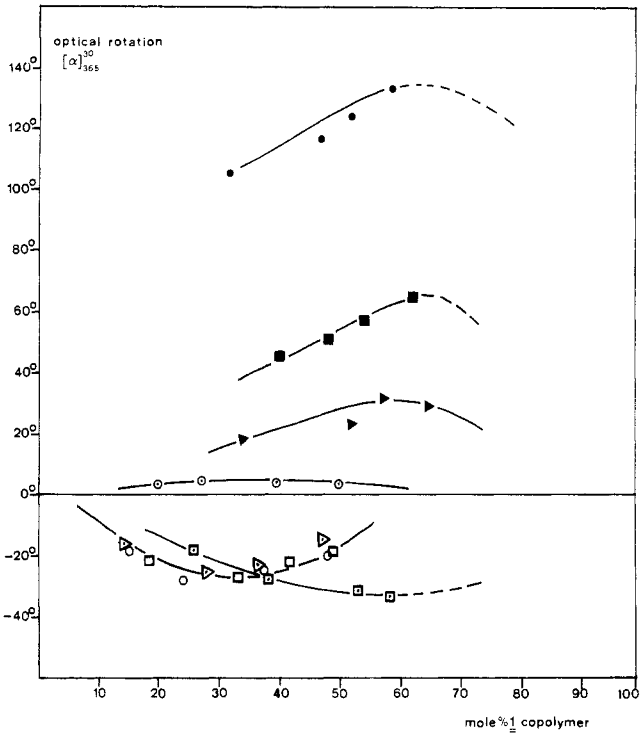


Figure 10. Composition-dependent specific optical rotation values of the copolymers of 1 with comonomers having spacers between the aromatic chromophore and the double bond: (●) 4-stilbenyl methacrylate; (■) 4-biphenyl methacrylate; (▲) 2-naphthyl methacrylate; (⊙) 4-stilbenylmethyl methacrylate; (⊡) 1-naphthyl methacrylate; (◬) 4-biphenylmethyl methacrylate; (O) 1-naphthylmethyl methacrylate; (□) 2-naphthylmethyl methacrylate.

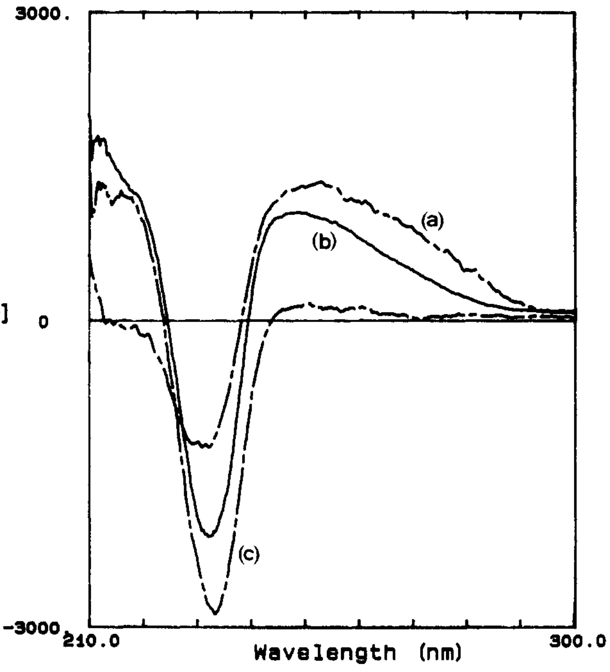


Figure 11. CD spectra of the copolymers of 1 with (a) 4-vinylbiphenyl, (b) 4-biphenyl methacrylate, and (c) 4-biphenylmethyl methacrylate.

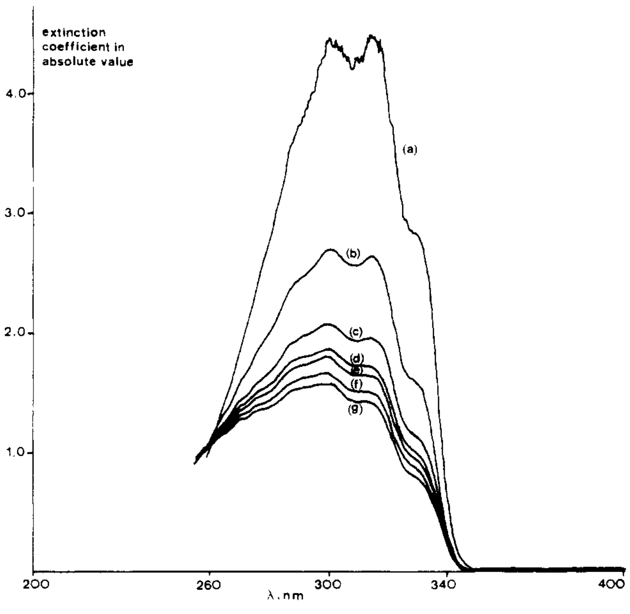


Figure 12. Typical UV spectral pattern of an irradiated copolymer of 1 containing stilbene chromophore (4-vinylstilbene) (a) at the beginning, (b) after 10 min, (c) after 20 min, (d) after 30 min, (e) after 40 min, (f) after 50 min, and (g) after 60 min.

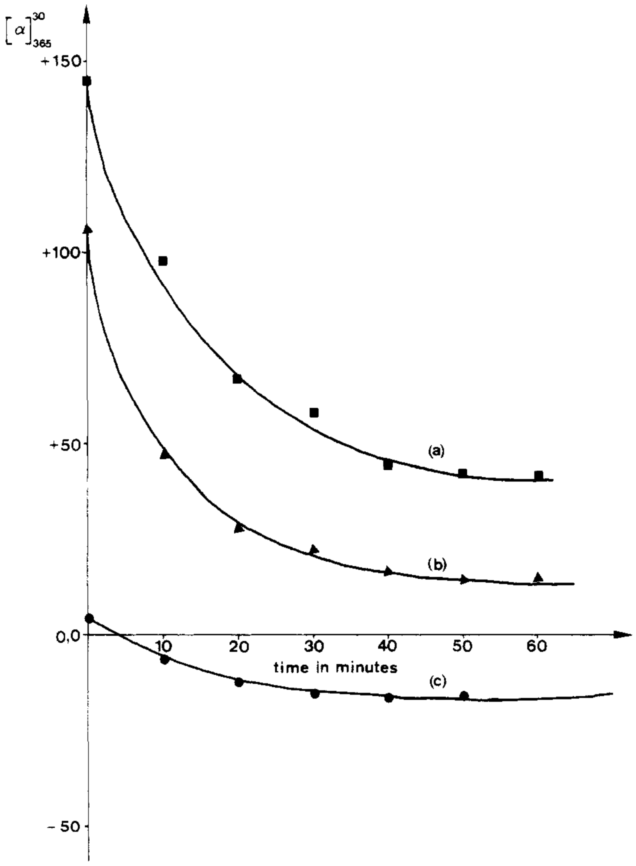


Figure 13. Specific optical rotations versus irradiation times for the copolymers of 1 with (a) 4-vinylstilbene, (b) 4-stilbenyl methacrylate, and (c) stilbenylmethyl methacrylate.

ing copolymers correspondingly decreased. After the photostationary state is reached, any further irradiation did not affect the specific optical rotation values. Interestingly, copolymers of **11b**, which showed initially a low positive rotation, became negatively rotating upon irradiation. This implies, in all these cases the observed specific optical rotations are influenced by residual *trans*-stilbene units and the (*S*,*S*) diads and to a much lesser extent by the *cis*-stilbene moieties. It remains unclear at the present time whether the influence of the *cis*-stilbene moieties is less effective on the optical rotations only due to the lower UV absorption at lower wavelength or because the asymmetric perturbation of the *cis*-stilbene groups is much less pronounced as was suggested in photoisomerization studies of copolymers with

Table V
Results on the Specific Extinction Coefficients and Specific Optical Rotations of the Irradiated Copolymers Bearing Stilbene Chromophores

irradn time, min	$[\epsilon]_{302\mathrm{nm}}$	$[\alpha]^{30}_{365}$, deg
1-4-Vinylstilbene (6) (62:38) Copolymer		
0	7.500	+145
10	4.500	+98
20	3.520	+67
30	3.150	+58
40	3.000	+44
50	2.790	+42
60	2.620	+41
1-4-Stilbenyl Methacrylate (11a) (47:53) Copolymer		
0	7.760	+116
10	3.550	+48
20	2.460	+28
30	2.180	+22
40	1.700	+16
50	1.470	+15
60	1.390	+15
1-4-Stilbenylmethyl Methacrylate (11b) (27:73) Copolymer		
0	6.730	+4
10	3.800	−3
20	2.820	−6
30	2.460	−8
40	2.230	−8
50	2.020	−9
60	1.980	−9

trans-stilbene moieties and optically active side chains.[27–29]

Conclusion

The optical rotation and the circular dichroism of copolymers consisting of (*S*,*S*)-(4-vinylphenyl)boronic acid diads and comonomers of different types can be influenced by both the partners. If the comonomer does not possess a UV absorption band above 210 nm, optical rotation and CD are mainly determined by the (*S*,*S*) diads. These copolymers are strongly negatively rotating. The rotational power is highest from isolated (*S*,*S*) diads. In case of comonomers having strong UV absorptions above 250 nm, the comonomer mostly causes an additional positive Cotton effect giving rise to positively rotating polymers. This influence diminishes sharply with increasing distance between the chromophore and the main chain. An exception is the case of 1-vinylnaphthalene, which causes an additional negative Cotton effect and gives negatively rotating polymers. The comonomeric units show highest influence on the chiroptical properties if they are present as isolated units along the main chain. Due to borderline cases (i.e., UV absorptions of the comonomers between 210–250 nm), all optical rotations between strongly negative and strongly positive can be obtained depending on the chemical structure of the comonomers. The asymmetry of the comonomer chromophore apparently does not arise from the configurational arrangement of these units in the main chain but from a conformational perturbation through the neighboring (*S*,*S*) diads.

Experimental Section

All the solvents were reagent grade and were purified by standard procedures prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. All the reagents were of analytical grade, obtained either from Fluka AG or E. Merck, and were used as received.

Monomers. (i) Template Monomer (1). Detailed procedures dealing with the synthesis of the template monomer, 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] have been reported elsewhere.[8]

(ii) Comonomers. Styrene (**2a**) was obtained from Fluka AG and was purified by distillation immediately before use. The comonomers 4-chlorostyrene (**2b**),[30] 4-vinylstilbene (**6**),[31] 1- and 2-naphthyl methacrylate (**8a** and **9a**),[32] 4-biphenyl methacrylate (**10a**),[33] and 1- and 2-naphthylmethyl methacrylate (**8b** and **9b**)[34] were synthesized following known literature procedures. Syntheses of other comonomers are described in brief as follows.

(iii) 1- and 2-Vinylnaphthalene (3 and 4). These two monomers were obtained by phosphine–nickel complex catalyzed cross-coupling of the Grignard reagent of the respective naphthyl bromide with vinyl bromide.[35] The 1-vinylnaphthalene was obtained as a colorless liquid, bp 95–97 °C (3 mm) [lit.[36] 115–116 °C (4 mm)] and 2-vinylnaphthalene as a light yellow solid, mp 65 °C (lit.[36] 67 °C). ^{1}H NMR spectra were in accordance with the desired structure.

(iv) 4-Vinylbiphenyl (5). This compound was synthesized through Wittig reaction of 4-biphenylcarbaldehyde with methyltriphenylphosphonium bromide following an analogous procedure adopted for the preparation of 4-hydroxystyrene,[37] mp 117 °C (lit.[38] 119 °C).

(v) 4-Stilbenyl Methacrylate (11a). Following a procedure employed for stilbenyl acrylate,[39] this monomer was synthesized in an analogous manner: mp 151–153 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–7.0 (m, 11 H, stilbene H), 6.25 (s, 1 H, cis =CH), 5.7 (s, 1 H, trans, =CH), 1.95 (s, 3 H, CH_3).

(vi) 4-Biphenylylmethyl Methacrylate (10b). The synthesis of this monomer from 4-(hydroxymethyl)biphenyl and methacryloyl chloride was similar to that of naphthylmethyl methacrylates.[34] After workup, the product was obtained in the form of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.7–7.3 (m, 9 H, biphenyl ring H), 6.23 (s, 1 H, cis =CH), 5.62 (s, 1 H, trans = CH), 5.32 (s, 2 H, biphenyl-CH_2O), 1.94 (s, 3 H, CH_3).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.45; H, 6.21.

(vii) 4-Stilbenylmethyl Methacrylate (11b). This monomer was synthesized by condensing potassium methacrylate with 4-(bromomethyl)stilbene, the later being obtained by *N*-bromosuccimide-based bromination of 4-methylstilbene.[30] Mp 129–130 °C; ^{1}H NMR ($CDCl_3$) δ 7.8–7.2 (m, 11 H, stilbene H), 6.22 (s, 1 H, cis =CH), 5.64 (s, 1 H, trans =CH), 5.23 (s, 2 H, stilbene–CH_2O), 2.12 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.96; H, 6.52. Found: C, 81.98; H, 6.44.

Polymer Synthesis. The copolymerization reactions were carried out at 60 °C under N_2 atmosphere by mixing the appropriate amounts of monomers and AIBN in toluene. The conversion of monomers to polymers was always restricted to below 15%. Detail procedures dealing with analogous polymer synthesis, isolation, and purification are described elsewhere.[8]

Analysis and Characterization. Elemental analysis was carried out at Faculty of Natural Science, University of Düsseldorf. The melting point was measured with Büchi 510 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded with Varian EM 390 and Varian VXR 300 spectrometers, respectively, using $CDCl_3$ as solvent and TMS as internal standard.

UV spectra were recorded at 25 °C in dioxane/water (9:1 v/v) by using a Varian CARY 2300 spectrophotometer. The path length of the cell was 0.1 cm and the sample concentrations were ca. 2 mg/mL. Optical rotations were measured at 30 °C with a Perkin-Elmer 241 polarimeter. CD spectral measurements were carried out at 25 °C in dioxane/water (9:1 v/v) at a sample concentration of ca. 1 mg/mL by using a JASCO-600 automatic recording spectropolarimeter. The path length of the cell was 0.1 cm. (For elemental composition data of the copolymers, see Table VI).

Irradiation experiments were carried out in dioxane/water (9:1 v/v) solution of the polymer by using a Grantzel 400 photochemical reactor equipped with suitable cutoff filters to select emissions at 334–328 nm. Photoisomerization reactions were followed by recording UV absorptions at different irradiation times on a Perkin-Elmer UV-visible spectrophotometer.

Acknowledgment. This investigation was supported by financial grants from Minister für Wissenschaft and Forschung des Landes Nordrhein-Westfalen

Table VI
Elemental Composition Data of Copolymers

				elem. comp	
entry	comonomer	1, mole fractn in reactn mixt	1, mole fractn in copolym	% C	% H
1	styrene (**2a**)	0.11	0.18	81.88	7.11
2		0.15	0.23	79.82	7.02
3		0.24	0.38	74.92	6.71
4		0.35	0.47	72.58	6.58
5		0.48	0.59	70.41	6.45
6	1-vinylnaphthalene (**3**)	0.15	0.27	81.76	6.37
7		0.26	0.36	78.63	6.28
8		0.38	0.52	74.35	6.22
9		0.49	0.59	72.64	6.18
10		0.62	0.71	70.08	6.08
11	2-vinylnaphthalene (**4**)	0.21	0.36	78.61	6.32
12		0.32	0.47	75.15	6.43
13		0.40	0.56	73.21	6.24
14		0.51	0.61	71.35	6.09
15		0.62	0.69	70.36	6.17
16	4-vinylbiphenyl (**5**)	0.14	0.28	82.23	6.48
17		0.25	0.34	80.25	6.42
18		0.41	0.52	75.33	5.78
19		0.52	0.63	71.48	6.29
20		0.59	0.71	70.61	6.23
21	4-vinylstilbene (**6**)	0.16	0.26	83.85	6.61
22		0.26	0.38	79.88	6.52
23		0.46	0.54	75.38	6.41
24		0.50	0.62	71.59	5.96
25		0.59	0.70	71.43	5.89
26	1-naphthyl methacrylate (**8a**)	0.16	0.26	74.51	5.84
27		0.29	0.38	72.65	5.91
28		0.41	0.53	70.33	5.96
29		0.51	0.58	69.94	5.94
30	2-naphthyl methacrylate (**9a**)	0.25	0.34	73.22	5.89
31		0.40	0.52	70.16	5.87
32		0.49	0.57	69.88	5.93
33		0.58	0.64	69.08	5.91
34	4-biphenyl methacrylate (**10a**)	0.26	0.40	73.56	5.86
35		0.35	0.48	71.57	5.81
36		0.41	0.54	69.14	5.72
37		0.50	0.62	68.81	6.15
38	4-stilbenyl methacrylate (**11a**)	0.22	0.32	75.49	5.94
39		0.35	0.47	72.98	5.97
40		0.41	0.52	72.69	5.84
41		0.51	0.59	71.51	5.86
42	1-naphthylmethyl methacrylate (**8b**)	0.15	0.27	74.78	6.19
43		0.24	0.37	73.30	6.21
44		0.37	0.49	71.41	6.08
45		0.48	0.63	69.14	5.91
46	2-naphthylmethyl methacrylate (**9b**)	0.18	0.32	74.02	5.94
47		0.33	0.48	71.54	6.08
48		0.42	0.54	69.19	5.81
49		0.49	0.68	68.67	6.38
50	4-biphenylmethyl methacrylate (**10b**)	0.15	0.28	75.81	6.31
51		0.28	0.42	72.27	6.26
52		0.36	0.56	71.18	6.02
53		0.47	0.65	69.25	6.12
54	4-stilbenylmethyl methacrylate (**11b**)	0.20	0.32	76.36	6.38
55		0.27	0.43	74.46	6.32
56		0.39	0.58	71.92	6.21
57		0.50	0.67	70.37	6.24

and Fonds der Chemischen Industrie. The circular dichroism spectrometer was purchased with a research grant from Bundesministerium für Forschung und Technologie. P.K.D. is thankful to the Alexander von Humboldt Foundation, Bonn, for supporting him during the initial stage of this research.

Registry No. (1)(**2a**) (copolymer), 110590-46-0; (1)(**2b**) (copolymer), 110590-50-6; (1)(**3**) (copolymer), 123676-02-8; (1)(**4**) (copolymer), 123676-03-9; (1)(**5**) (copolymer), 123676-00-6; (1)(**6**) (copolymer), 123676-01-7; (1)(**8a**) (copolymer), 123676-04-0; (1)(**8b**) (copolymer), 123723-83-1; (**1**)(**9a**) (copolymer), 123676-05-1; (1)(**9b**) (copolymer), 123676-08-4; (1)(**10a**) (copolymer), 123676-06-2; (1)(**10b**) (copolymer), 123676-09-5; (1)(**11a**) (copolymer), 123676-07-3; (1)(**11b**) (copolymer), 123676-10-8; (1)(methacrylonitrile) (copolymer), 110590-41-5; **3**, 826-74-4; **4**, 827-54-3; **5**, 2350-89-2; **10b**, 54954-91-5; **11a**, 123675-98-9; **11b**, 123675-99-0; 1-naphthyl bromide, 90-11-9; 2-naphthyl bromide, 580-13-2; vinyl bromide, 593-60-2; 4-biphenylcarbaldehyde, 3218-36-8; methyltriphenylphosphonium bromide, 1779-49-3; 4-(hydroxymethyl)biphenyl, 3597-91-9; 4-(bromomethyl)stilbene, 50685-89-7.

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Quantitative Measurement of Chain Contraction in a Solid Blend of Two Incompatible Polymers: Poly(methyl methacrylate)/Poly(vinyl acetate)

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ABSTRACT: Electronic excitation transport among naphthyl chromophores in low concentration on isolated chains of poly(2-vinylnaphthalene-*co*-methyl methacrylate) dispersed in both poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) is monitored by time-resolved fluorescence depolarization spectroscopy. Analysis of the results with a theory for excitation transport in finite volume systems utilizing a Gaussian segment distribution function allows the quantitative determination of the root-mean-square radius of gyration ($\langle R_g^2\rangle^{1/2}$) of PMMA in the two hosts. The results for bulk PMMA agree with expected values for PMMA in a Θ solvent. The naphthyl groups do not perturb the average chain conformation. A significant decrease in $\langle R_g^2\rangle^{1/2}$ for isolated PMMA chains is observed in the PMMA/PVAc blend. These are the first measurements of $\langle R_g^2\rangle^{1/2}$ and chain collapse in a solid blend of two incompatible polymers. At higher concentrations of PMMA in PVAc, micro-phase separation on the order of aggregation of two or three chains is observed.

I. Introduction

There is significant interest in characterizing solid polymeric materials, especially blends, at the molecular level. This interest is due, in large part, to the tremendous technological importance of polymer blends. The bulk, macroscopic properties of such materials are determined by the microscopic structure which, in turn, is critically dependent on the degree of molecular mixing between blend components. The special properties of polymer materials arise from differences between the thermodynamic interactions in systems containing macromolecules and those in systems of only small molecules.

The nature of intermolecular interactions determines the microscopic structure in any condensed-phase system. However, when macromolecules are involved, there is additional complexity due to intramolecular considerations; the number of configurations available to a polymer chain, although restricted by covalent bond geometries, is vast. Thus, the morphology of a chain involves the interplay between the interactions of the polymer with its environment and the possible chain conformations. To understand these systems more fully, it is desirable to investigate quantitatively the interactions of isolated

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