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Chirality of Polyvinyl Compounds. 6.[1] Unusual Influences of the Comonomer Structures on the Chiroptical Properties of Optically Active Vinyl Copolymers with Chirality Arising from Configurational Relationships in the Main Chain

Günter Wulff* and Pradeep K. Dhal

Institute of Organic Chemistry and Macromolecular Chemistry, University of Düsseldorf, 4000 Düsseldorf, F.R.G.

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ABSTRACT: In contrast to appreciable negative optical rotations shown by most of the vinyl copolymers of 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (1) after removal of the D-mannitol template, copolymerizations of this monomer with styrene derivatives bearing functional groups in conjugation with the phenyl ring, viz., 4-cyano-, 4-formyl-, and 4-(methoxycarbonyl)styrene, yielded copolymers, which after removal of the D-mannitol template showed positive optical rotations. Copolymers obtained by using comonomers bearing the modified versions of these functional groups, viz., 4-(aminomethyl)- and 4-(hydroxymethyl)styrene, exhibited negative optical rotations. Interestingly, upon transforming the cyano, formyl, and methoxycarbonyl groups of the copolymers to the corresponding aminomethyl and hydroxymethyl groups by polymer analogue reactions, the formerly positively rotating polymers showed negative optical rotations. With the help of chiroptical techniques, particularly circular dichroism (CD), it has become possible to elucidate the unique role of the comonomer structures in this unusual behavior of the copolymers. While the absolute configuration of the distyryl diads generated from monomer 1 remains the same with all comonomers, in the case of the comonomers with conjugated chromophoric systems strong Cotton effects are induced, thus generating positively rotating polymers. These Cotton effects arise from asymmetric conformations of the atactic comonomeric part due to perturbation by chiral distyryl diads.

Introduction

Following a symmetry-based theoretical consideration of the possibility of the existence of optical activity in vinyl polymers due to chirality arising from configurational relationships in the main chain (so called main chain chirality),[2,3,3a] we have been developing synthetic methods to realize such structures. Toward this end, a polymerizable vinyl monomer linked to an appropriate chiral template (1) was synthesized and subsequently copolymerized by free radical initiation with another vinyl monomer. The resulting copolymer, after complete removal of the template molecules, showed strong negative optical rotations.[4] Mechanistic studies showed[1] that the polymerization proceeds through an asymmetric cyclopolymerization. The optical activity of the copolymer stems from the formation of chiral distyryl diads along the main chain. They are separated from one another by the comonomer units, but the chirality of the polymer is independent of the configuration at these centers. The absolute configuration of the asymmetric diad building block has been established to be *S*,*S* by synthesis of suitable well-defined oligomeric model compounds.[1]

In order to explore the potentialities of this new interesting copolymer system further, we have copolymerized the template monomer 1 with numerous vinyl comonomers. The resulting copolymers for the most part showed negative optical rotations with varying magnitudes depending on the structures of the comonomers and on the copolymer compositions. However, we encountered a startling situation when using 4-nitro- and 4-cyanostyrenes as comonomers, since we obtained optically active copolymers showing appreciable positive optical rotations.[1] We had no immediate explanation for this unusual observation, which apparently questioned the general validity of the proposed mechanism of the asymmetric induction and the absolute stereochemistry of the polymer chain. Therefore, it was an important task to pursue a detailed investigation for elucidating the role of these comonomers in the observed polymer chirality. Polymers showing positive optical rotations were transformed by analogous reactions to copolymers which could also be prepared by polymerizing preformed monomers bearing identical functionalities. Their chiroptical properties could then be compared. This enabled us to substantiate further the validity of the proposed mechanism of the asymmetric copolymerization. The results of this study are described in the present paper.

Results and Discussion

Synthesis and Characterization of the Polymers.

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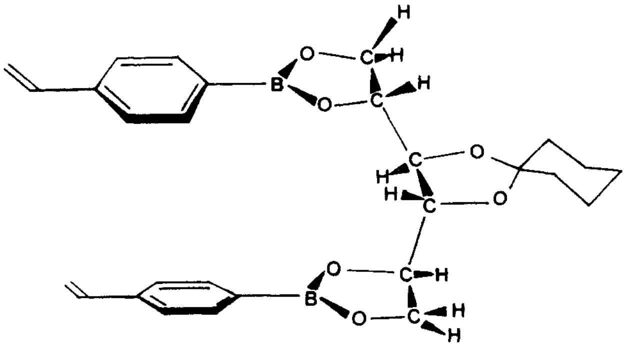
Table I
Optical Activity of 4-Cyanostyrene-Based Chiral Copolymers

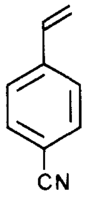
no.	mol frctn of the template monomer in the rctn mix	mol frctn of the template monomer in the resulting copolymer	$[\alpha]^{30}_{365}$[a]
1	0.16	0.22	+14
2	0.23	0.32	+19
3	0.31	0.40	+21
4	0.40	0.52	+27

[a] Optical rotations of copolymers prepared from 1 and 4-cyanostyrene after removal of the template; measured in dioxane/water (9:1 v/v) at a concentration of 0.2–0.3 g/100 mL.

Copolymerization of the template monomer, 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (1) with 4-cyanostyrene (2) by free radical initiation followed by removal of the D-mannitol template gave optically active copolymers showing positive optical rotations. Measurements of the optical rotations at different wavelengths (578, 546, 436, and 365 nm) showed an increasing order of optical rotations with decreasing wavelengths. No transition in the sign of the optical rotations was observed. Furthermore, synthesis of copolymers using varying mole ratios of the comonomers invariably resulted in positively rotating substances; however, like the other comonomer systems, the magnitude of the optical rotations was dependent on the copolymer compositions. These results on copolymer compositions and their optical rotations are summarized in Table I. This clearly shows the influence of 4-cyanostyrene on the observed positive optical rotations of these copolymers.



1



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In order to clarify the reason behind the observed positive optical activity of the copolymers, we sought to prepare corresponding copolymers with 4-(aminomethyl)styrene as the comonomer and compare these substances with those of the same constitution prepared by reduction of the positively rotating 4-cyanostyrene copolymers. This would enable us to compare two sets of optically active copolymers of identical chemical constitutions derived via different synthetic procedures. Comparison of the chiroptical properties of these two sets of copolymers would probably provide some information as to whether positively and negatively rotating polymers have the same absolute configuration and are produced through the same mechanism. Thus, copolymerizing the template monomer with 4-[(trifluoroacetamido)methyl]styrene (3) in different mole ratios and subsequent removal of the template molecules and trifluoroacetyl groups resulted in the desired copolymers showing negative optical rotations, similar to 4-methylstyrene-based copolymers.[1]

In order to introduce aminomethyl groups into the positively rotating 4-cyanostyrene-based copolymers, polymer analogue reduction reactions using $LiAlH_4$ resulted in complete transformation of the nitrile groups to aminomethyl functions, without affecting the boronic acid moieties. This is clearly evident from the infrared spectral patterns of the copolymers. After reduction, the absorption peak due to the nitrile group of 4-cyanostyrene at 2230 cm^{-1} completely disappeared but the B–O stretching band of the template monomer units at 1350 cm^{-1} remained unchanged. Interestingly, the modified products showed negative optical rotations having values close to the earlier mentioned synthesized 4-(aminomethyl)styrene-containing copolymers. The course of these chemical operations is represented in Scheme I and the results are summarized in Table II.

Since the modification procedure employed is specific to the nitrile group without involving the polymer backbone, any possibility of inversion of configuration of the polymer main chain is ruled out. Hence it appears the positive optical rotation is not a consequence of the opposite configuration of the main chain but, rather, is due to the influence of the benzonitrile group of the comonomer.

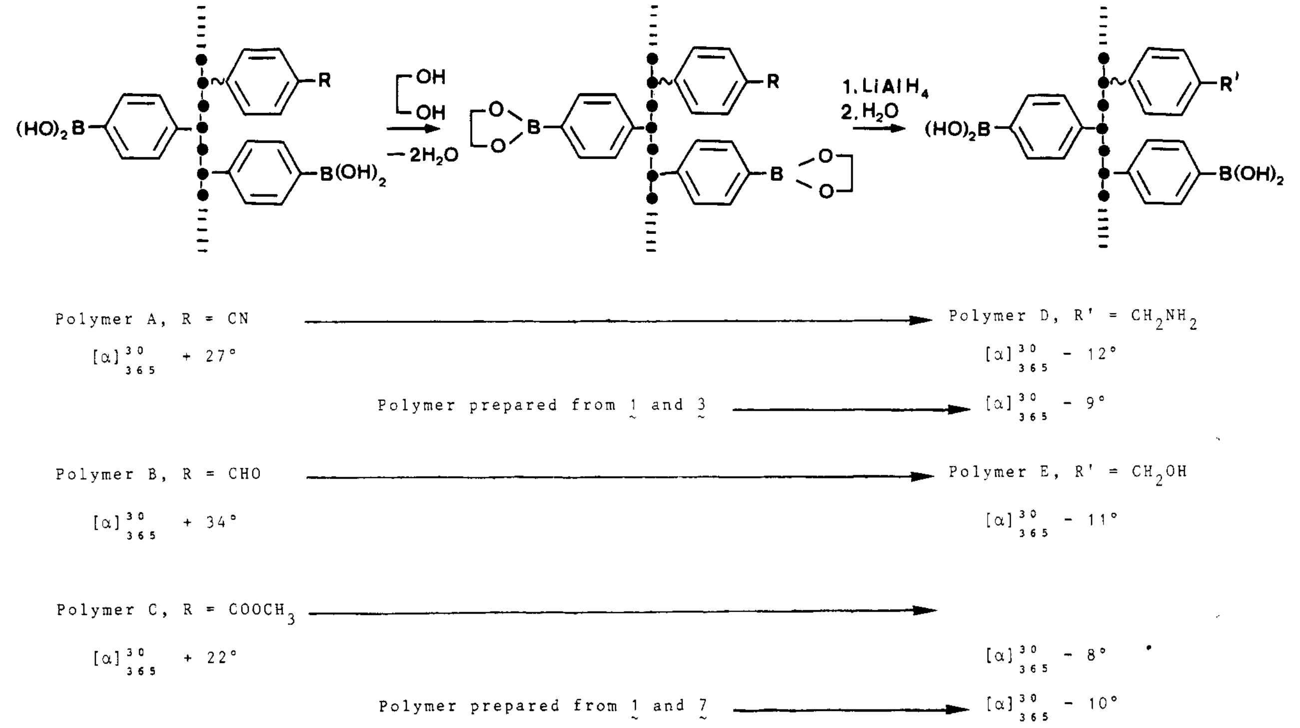
In order to ascertain whether this observation is a general phenomenon for comonomers bearing electron-withdrawing functional groups conjugated to the aromatic ring, we examined the copolymers of the template monomer 1 with other functional styrene comonomers possessing multiply bonded functional groups at the para position to the vinyl group. For this purpose, two comonomers, viz., 4-formylstyrene (4) and 4-(methoxycarbonyl)styrene (5), were copolymerized with the template monomer. Interestingly, all the copolymers thus obtained showed positive optical rotations of varying magnitudes depending on the copolymer compositions. Most notably, the copolymer

Table II
Comparison of the Optical Activities of 4-(Aminomethyl)styrene-Based Chiral Copolymers Obtained by Polymer Modifications and Copolymerization of Desired Comonomers[a]

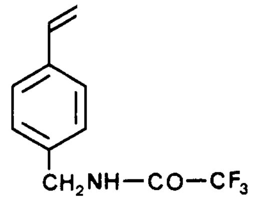
	opt act of 4-(aminomethyl)styrene-based copolymers from chem modif			opt act of 4-(aminomethyl)styrene-based copolymers from copolymeriztn		
no.	mol frctn of 1 in copolymer	$[\alpha]^{30}_{365}$[b] before modif	$[\alpha]^{30}_{365}$ after modif	mol frctn of 1 in init mix	mol frctn of 1 in copolymer	$[\alpha]^{30}_{365}$
1	0.32	+14	-8	0.14	0.20	-8
2	0.40	+21	-9	0.31	0.39	-9
3	0.52	+27	-12	0.40	0.49	-9

[a] For details please see Scheme I. [b] Same as in Table I.

Scheme I



obtained with ethylene glycol acetal derivative 6 of 4-formylstyrene showed positive optical rotations both before and after removal of the protecting groups. For comparison, the corresponding copolymer obtained with 4-methoxy styrene showed a low negative optical rotation of −3.5°.[1] The results on copolymer composition and optical rotations are summarized in Table III.



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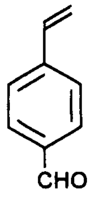

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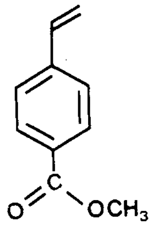

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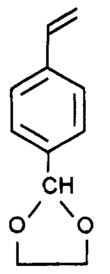

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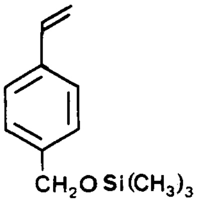


7

As in the previous case, for comparison purposes a copolymer was prepared which has a structure that can also be obtained by chemical modification of the positively rotating polymers. Copolymerization of 4-(hydroxymethyl)styrene (in the form of its trimethyl silyl ether 7) with the template monomer 1 yielded, after removal of the template and the protecting group, a copolymer containing 4-(hydroxymethyl)phenyl side groups showing negative optical rotations.

The previously mentioned copolymers with 4 and 5 as comonomers were reduced by using complex metal hydride for transforming the aldehyde and the ester group to 4-(hydroxymethyl) groups. Absence of infrared absorption bands due to the ester and the aldehyde groups at 1725 and 1695 cm^{-1}, respectively, in the resulting modified copolymers testified to the quantitative reduction of these functional groups. The resulting polymers exhibited negative optical rotation similar to that of the copolymer prepared from 7. The chemical modification procedures employed are illustrated in Scheme I and the results on optical rotations can be seen in Table III.

Table III
Comparison of Optical Activities of 4-Formylstyrene, 4-(Methoxycarbonyl)styrene, and Their Modified Analogues with 4-(Hydroxymethyl)styrene Copolymer Obtained by Copolymerization[a]

no.	mol frctn of 1 in reactn mixt	mol frctn of 1 in copolymer	$[\alpha]^{30}_{365}$ before modif	$[\alpha]^{30}_{365}$ after modif
	4-Formylstyrene-Based Copolymers			
1	0.15	0.23	+16°	−6°
2	0.24	0.37	+27°	−10°
3	0.41	0.51	+34°	−11°
4	0.49	0.62	+39°	
5	0.66	0.74	+21°	
	4-(Methoxycarbonyl)styrene-Based Copolymers			
1	0.21	0.32	+15°	−6°
2	0.32	0.41	+19°	−8°
3	0.45	0.53	+22°	−8°
	4-(Hydroxymethyl)styrene-Based Copolymers			
1	0.26	0.36	−6°	
2	0.35	0.48	−10°	
3	0.48	0.59	−7°	

[a] For detail please see Scheme I and Table I.

These results clearly show that the absolute configuration of the chiral distyryl units of the polymer main chain in all cases is the same and even the extent of asymmetric induction is apparently similar. It further shows that the comonomers being arranged presumably in atactic fashion along the chains influence the optical rotation either by their chemical nature or by adopting chiral conformations. The latter phenomenon has been reported in many in-

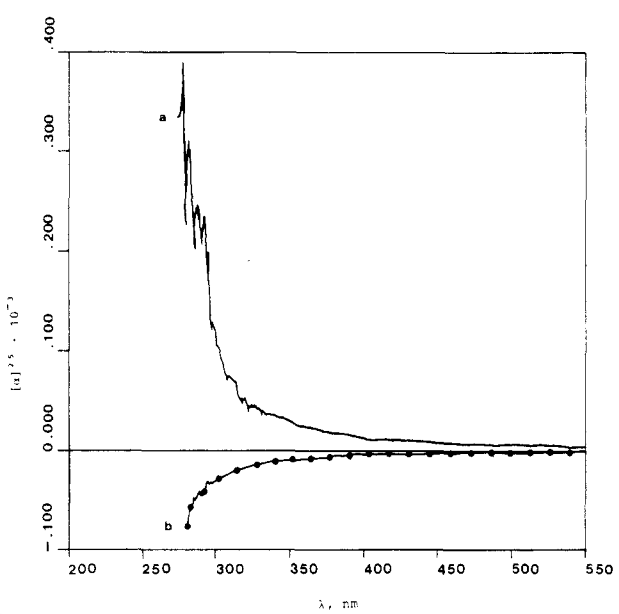


Figure 1. ORD spectra of the copolymer of 1 and 4-formylstyrene (a) and its reduced analogue (b).

stances for copolymers of optically active α-olefins with aromatic vinyl monomers. In these cases the aromatic rings show a chiral perturbation leading to specific chiroptical effects.[5]

ORD and CD Studies. Although the above-described synthetic and analytical procedures were helpful in assigning the significant role of comonomer structures in the observed surprising optical activities of chiral copolymers, the investigations were not sufficient to establish the exact mode of operation of the comonomer in inducing positive optical rotations. Therefore, we were prompted to utilize more sophisticated chiroptical techniques, viz., optical rotatory dispersion (ORD) and circular dichroism (CD), to probe further into this phenomenon.

In recent years, ORD and CD techniques have been successfully utilized in obtaining fruitful information regarding solution conformations of optically active synthetic polymers and biopolymers.[6,7] For synthetic vinyl polymers, by copolymerizing optically active vinyl monomers with nonchiral ones, modification of the chromophoric systems of the nonchiral monomers has furnished a good deal of information with regard to the dissymmetric interactions of these chromophores with the neighboring chiral comonomer units as well as among each other.[8,9]

The ORD curves for two sets of our copolymers, viz., copolymers containing 4-formylsytrene and 4-cyanostyrene, as well as their modified analogues are depicted in Figures 1 and 2. In all cases, the optical rotation dispersions measured between 500 and 275 nm show nearly plane curves with an increase in optical rotation with decreasing wavelength, roughly following a one-term Drude equation.

Figure 1a as well as Figure 2a shows some irregularities but they cannot be unambiguously assigned to Cotton effects. Strong absorptions in the chromophoric transition regions due to an unfavorable compromise between the optical rotations and UV absorption coefficients dampened further measurements at lower wavelength. Hence the ORD technique was not quite efficient in providing meaningful information on the comonomer-controlled variation of the sign of the optical rotations.

CD measurements in most cases provide more precise information on the configuration and conformation of chiral compounds.[10] In the present case the chiral diads of the copolymers consist of two (4-vinylphenyl)boronic acid units in the *S*,*S* configuration. This unit should be present in all the polymers. In order to analyze the electronic transitions of the chiral diads, the optically active copolymer of 1 with methacrylonitrile (after cleavage of the template) was first investigated, since the nitrile group of this comonomer should not interfere with the accessible electronic transitions of the aromatic rings. The UV and CD spectra of the copolymer with methacrylonitrile are shown in Figure 3. The aromatic chromophores of the (4-vinylphenyl)boronic acid units show absorption maximas at $\lambda = 230$ nm ($[\epsilon] = 1.26 \times 10^2$) and $\lambda = 280$ nm ($[\epsilon] = 7$) (this polymer contains 65.8 mol % aromatic units). The corresponding CD spectrum shows Cotton effects at 220, 233, and 240 nm with specific ellipticities of $+4.53 \times 10^3$, -3.24×10^3, and $+0.4 \times 10^3$, respectively. The polymer shows a negative optical rotation of $[\alpha]^{30}_{365}$ −73°. Without further detailed studies, it was not possible to assign these Cotton effects to definite UV transitions or exciton couplings.[11]

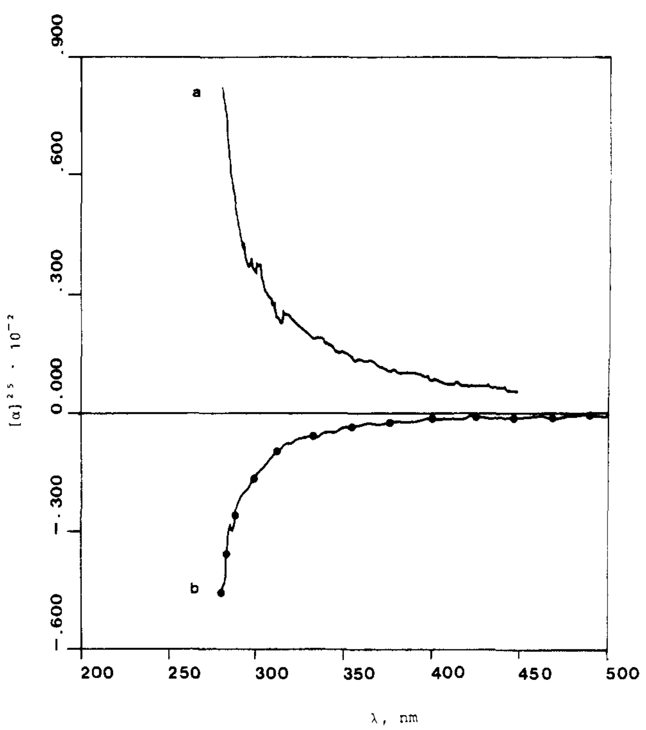


Figure 2. ORD spectra of the copolymer of 1 and 4-cyanostyrene (a) and its reduced analogue (b).

Further complicated are the CD spectra of the copolymers of (4-vinylphenyl)boronic acid with aromatic comonomers, since an overlap of the CD bands of the chiral bis(4-boronylstyryl) diads, as in the foregoing case, with an induced CD of aromatic nonstereoregular comonomeric units is expected. The CD and UV spectra of copolymers containing aromatic cyano and formyl substituents as well as their modified counterparts are illustrated in Figures 4–7.

Examination of the CD spectrum of the optically active copolymer containing benzonitrile chromophore (Figure 5a) reveals the presence of a strong positive Cotton effect at 244 nm, followed by a negative Cotton effect of somewhat lesser intensity at 232 nm. Upon modifying the nitrile group to an aminomethyl group, the CD spectrum of the resulting polymer, as can be seen from Figure 5b, does not give any indication of the presence of the positive Cotton effect at 244 nm. Furthermore, this spectrum closely resembles that of the reference copolymer, showing first a negative and then a positive Cotton effect; however, the Cotton effect extremas are slightly red-shifted. Examination of the UV spectrum (Figure 4a) of the positively rotating copolymer shows its maxima at 233 nm and a

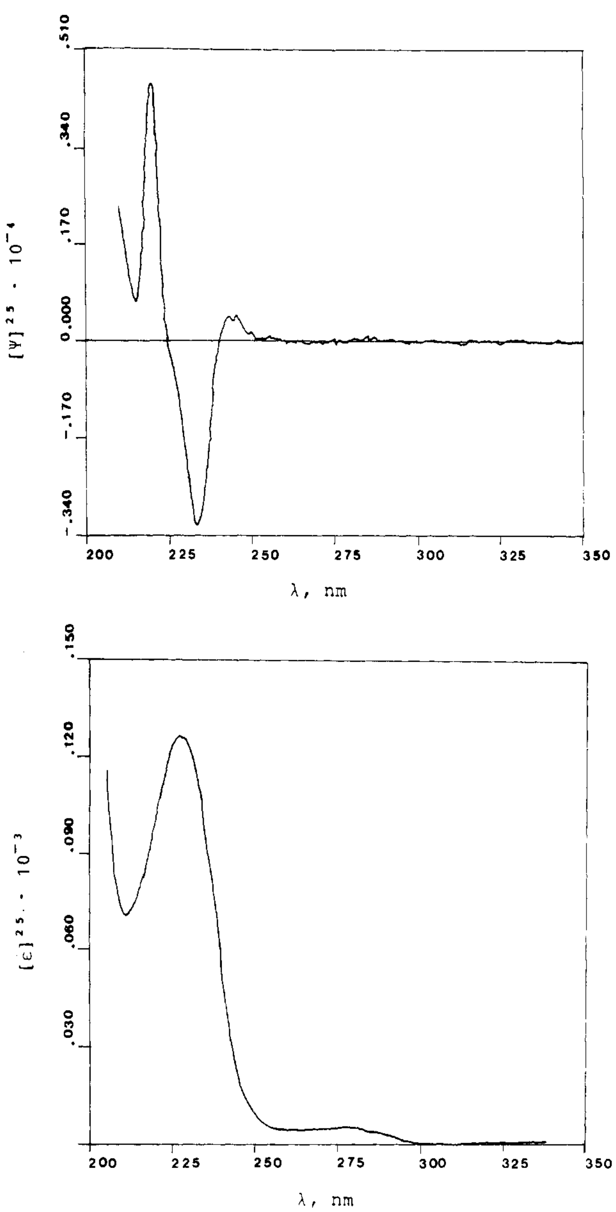


Figure 3. UV (bottom) and CD (top) spectra of the copolymer of 1 and methacrylonitrile. $[\epsilon]^{25}$ = specific extinction at 25 °C ⟨log (I_0/I)/(cm g/L)⟩; $[\Psi]^{25}$ = specific ellipticity at 25 °C ⟨(deg/dm)/(g/mL)⟩.

shoulder at 245 nm, the latter corresponding to π–π^* ^{1}La electronic transitions of 4-alkylbenzonitrile chromophoric systems.[12] The UV spectrum of the modified polymer shows the absence of a 245-nm shoulder.

The CD spectra of the chiral copolymer containing benzaldehyde chormophore and its modified counterpart are shown in Figure 7. For the former copolymer, the CD spectrum displays first a positive broad Cotton effect over the wavelength range of ca. 300–240 nm and second a negative cotton effect with its extrema at 234 nm. The positive cotton effect reveals a multiple structural pattern comprised of several overlapping peaks. The UV spectrum of this copolymer, shown in Figure 6a, shows two absorption peaks, the first one is relatively broad over 300–245 nm and the second stronger one with a maximum of 233 nm. The higher wavelength UV peak seems to be the combined absorption of several transitions of the aromatic ring and the carbonyl group of the 4-alkylbenzaldehyde chromophore. Probably, use of a polar solvent is responsible for the overlapping of these peaks. Comparison of the UV and CD spectra confirms that this positive Cotton effect is a consequence of chiral electronic transition of the 4-formylstyrene chromophoric system. As in the previous case, upon conversion of the aldehyde group to the hydroxymethyl group, the positive Cotton effect present in the aldehyde copolymer disappeared completely, and this CD spectrum (Figure 7b) shows the usual first negative and second positive Cotton effect in the lower wavelength region due to the phenyl boronic acid chromophoric systems. The CD behavior of the copolymers obtained by copolymerizing the preformed monomers bearing hydroxymethyl and aminomethyl groups is similar to that of their look-alike modified analogues. The results of these analyses are summarized in Table IV.

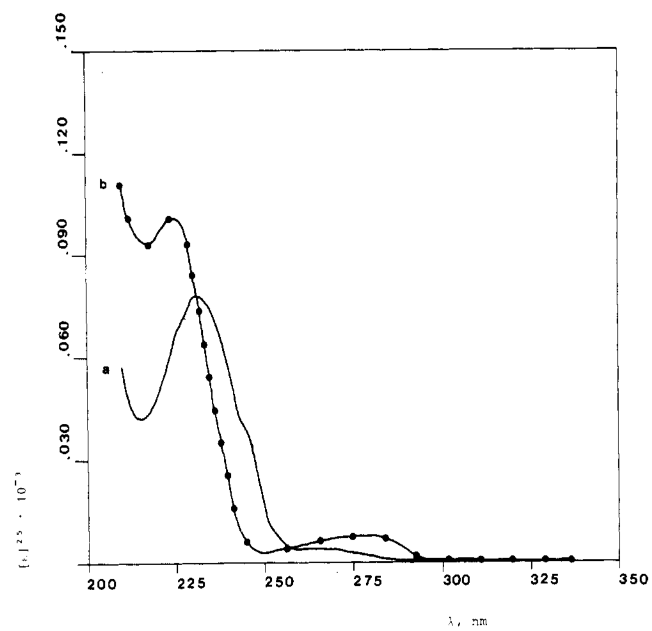


Figure 4. UV spectra of the copolymer of 1 and 4-cyanostyrene (a) and its reduced analogue (b).

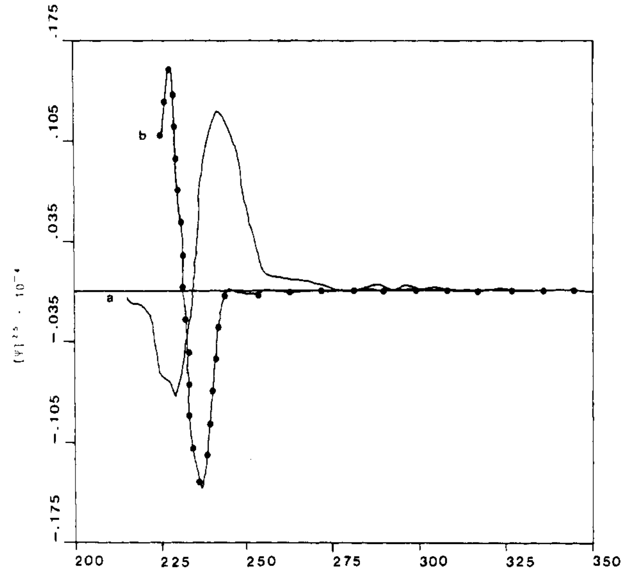
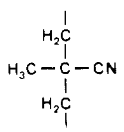
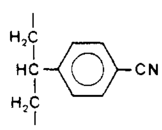
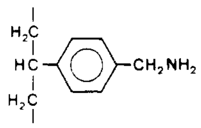
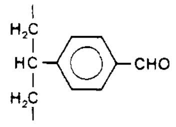
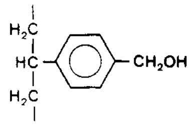


Figure 5. CD spectra of the copolymer of 1 and 4-cyanostyrene (a) and its reduced analogue (b).

On the basis of the above investigation, it has become possible to explain the chiroptical behavior of these optically active vinyl polymers containing aromatic comonomers with a functional group in conjugation with the phenyl ring. The findings of this study can be summarized in the following manner: In these asymmetric copolymerizations, chain growth always proceeds generating a polymer chain possessing distyryl diads with *S*,*S* absolute

Table IV

Results on UV and CD Absorption Features of 4-Cyanostyrene, 4-Formylstyrene, and Their Modified Analogues

no.	nature of functnl group in comonomer	mol frctn of 1 in copolymer	UV absorptn max				CD max			
			λ_1	$[\epsilon_1] \times 10^{-3}$ [a]	λ_2	$[\epsilon_2] \times 10^{-3}$	λ_1	$[\Psi_1] \times 10^{-4}$	λ_2	$[\Psi_2] \times 10^{-4}$ [b]
1		0.48	226	0.127			233	−0.318	220	+0.455
2		0.52	243	0.043	231	0.073	244	+0.133	231	−0.074
3		0.52	228	0.102			236	−0.136	229	+0.155
4		0.51	258	0.027	232	0.054	265 258 251 244	+0.082 +0.082 +0.045 +0.034	233	−0.119
5		0.52	229	0.112			236	−0.157	225	+0.139

[a] Specific extinction coeff: log (I_0/I)/(cm g/L). [b] Specific ellipticity (degr/dm)/(g/mL).

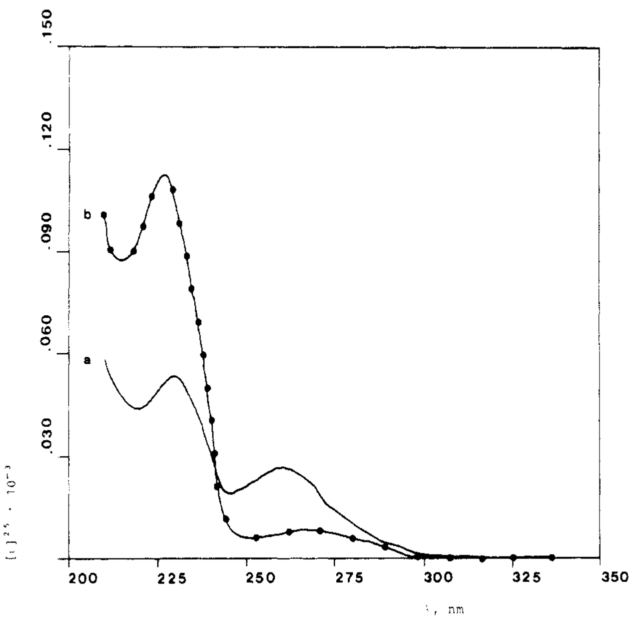


Figure 6. UV spectra of the copolymer of 1 and 4-formylstyrene (a) and its reduced analogue (b).

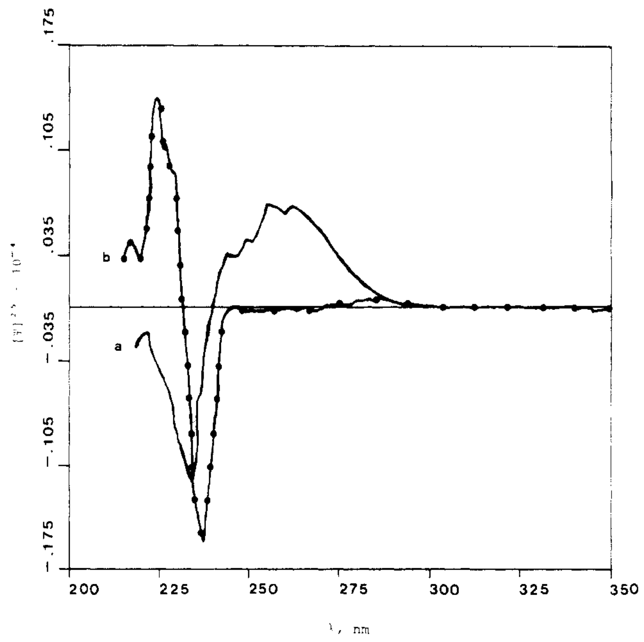


Figure 7. CD spectra of the copolymer of 1 and 4-formylstyrene (a) and its reduced analogue (b).

configuration. However, if a vinyl aromatic comonomer possessing an electron-withdrawing substituent in the para position is used, the usually negatively rotating polymers show positive optical rotations. This positive optical rotation is associated with a higher wavelength strong positive Cotton effect which apparently originates from a chiral conformation adopted by the comonomer units. Since the electronic transition of this aromatic comonomer producing the chiral conformation appears at higher wavelengths compared to those of the chromophores of the distyryl diad of the backbone, the positive optical rotation of conformational origin remarkably overshadows that due to the chiral configuration in the backbone of the copolymer. This can be clearly seen in the CD spectra where the original Cotton effects due to backbone chiral configuration are overruled by the stronger effects of the comonomers. The phenomenon of dissymmetric disposition of the chromophoric groups of nonchiral vinyl aromatic monomers, when copolymerized with optically active vinyl comonomers bearing side chain chiral centers, has been systematically investigated in recent years by Ciardelli and co-workers.[13] Even for nonregular copolymers obtained by free radical initiation, a short-range chiral perturbation of the aromatic chromophores was observed.[14]

After the modification of the comonomeric part of these chromophoric systems a similar chiral conformation might still be present but cannot easily be detected due to weaker Cotton effects at lower wavelengths. We are presently pursuing our studies with comonomers bearing other chromophoric systems to elucidate the possibility of any such effects. These studies should further be helpful in assigning the electronic transitions responsible for the CD effects.

Experimental Section

Solvents and Reagents. All the solvents were of reagent grade and were purified by standard procedures prior to their use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. All the reagents were of analytical grade, purchased from Fluka AG, and used as received.

Monomers. (i) Template Monomer (1). Details of the synthesis of the template monmer, 3,4-cyclohexylidene-D-mannitol 1,2:5,6-bis-*o*-[(4-vinylphenyl)boronate] have been reported elsewhere.[1]

(ii) 4-Cyanostyrene (2). This was prepared by Wittig reaction of 4-cyanobenzyl bromide, following a literature procedure.[15]

(iii) 4-Formylstyrene (4) and 4-(1,3-Dioxolan-2-yl)styrene (6). The monomer 4 was prepared by the Grignard reaction of 4-chlorosytrene following the method of Dale et al.,[16] and monomer 6 was obtained from 4 by using a reported procedure.[17]

(iv) 4-(Methoxycarbonyl)styrene (5). This monomer was prepared by following the procedure described by Letsinger et al.[18]

(v) 4-[(Trifluoroacetamido)methyl]styrene (3). To 1.55 g (11.64 mmol) of 4-(aminomethyl)styrene[19] in 20 mL of dry CH_2Cl_2, 2.7 g (12.8 mmol) of trifluoroacetic anhydride in 10 mL of dry CH_2Cl_2 was added dropwise at -10 °C under N_2. After it was stirred at this temperature for 2 h, the reaction mixture was slowly warmed up to 0 °C and stirred for another 2 h. The solvent was subsequently removed under reduced pressure and the residue was recrystallized from ether/hexane (1:4 v/v). Yield 55%; mp 106 °C, ^1H NMR δ 4.46 (d, 2 H, J = 7 Hz, $C_6H_4CH_2NH$), 5.2–5.8 (dd, 2 H, J = 10, 18 Hz, $CH_2{=}CH$), 6.5–6.83 (dd, br, 2 H, $CH{=}CH_2$ with submersed NH), 7.2–7.5 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.18; N, 6.11. Found: C, 57.23; H, 4.18; N, 5.92.

(vi) 4-[(Trimethylsiloxy)methyl]styrene (7). To 2.5 g (18 mmol) of 4-(hydroxymethyl)styrene[18] in 10 mL of dry THF, 4.1 g (25 mmol) of hexamethyldisilazane was added dropwise under N_2, while the temperature was maintained below 10 °C. Subsequently a few drops of trimethylchlorosilane was added and the reaction mixture was stirred at room temperature for 6 h under N_2. The solvent was removed under reduced pressure and the product was purified by vacuum distillation. Yield 60% (bp 68–70 °C/2 mbar); ^1H NMR δ 0.16 (s, 9 H, $-OSiCH_3$), 4.6 (s, 2 H, $C_6H_4CH_2OSi$), 5.2–5.9 (dd, 2 H, J = 10, 18 Hz, $CH_2{=}CH$), 6.5–6.83 (dd, 1 H, $CH{=}CH_2$), 7.28–7.5 (m, 4 H, C_6H_4).

General Methods of Polymer Synthesis. The copolymerization reactions were carried out by taking predetermined amounts of the template monomer and the respective comonomer in toluene (concentration of template monomer, 0.4 mol/L) and polymerizing at 70 °C under N_2 with AIBN as free radical initiator. Details of the synthesis, purification, and quantitative removal of the chiral template are being dealt with elsewhere.[1]

Removal of the Trifluoroacetyl Groups from 4-[(Trifluoroacetamido)methyl]styrene-Based Compolymers. To 0.5 g of the copolymer dissolved in 25 mL of dioxane/water (9:1 v/v), 10 mL of 1 N NaOH was added and the reaction mixture was stirred overnight at room temperature. At the end, the polymer solution was poured into an excess of CH_2Cl_2 with stirring and the precipitated polymer was isolated and dried to constant weight under vacuum.

Removal of the Ethylene Glycol Units from 4-(1,3-Dioxolan-2-yl)styrene-Based Copolymers. To 1 g of the copolymer dissolved in 20 mL of dioxane/water (9:1 v/v), 15 mL of 3:1 (v/v) mixture of dioxane and 90% CF_3COOH was added. The solution was stirred overnight at room temperature and finally poured into large volume of CH_2Cl_2 with stirring. the precipitated polymer was isolated and dried to constant weight under vacuum.

Table V
Results on the Elemental Composition Data of the Copolymers

no.	comonomer type	mol frctn of 1 in reactn mix	mol frctn of 1 in co-polymer	elem comp % N	% C	% H
1	4-cyanostyrene	0.16	0.22	7.62	76.18	5.71
2		0.23	0.32	5.60	72.41	5.66
3		0.31	0.40	4.68	66.13	5.36
4		0.40	0.52	3.02	66.56	5.86
5	4-(aminomethyl)-styrene	0.14	0.20	5.01	58.02	4.76
6		0.31	0.39	3.74	59.85	5.04
7		0.40	0.49	3.19	59.63	4.97
8	4-formylstyrene	0.15	0.23		71.65	5.88
9		0.24	0.37		69.88	5.76
10		0.41	0.51		68.42	5.81
11		0.49	0.62		67.56	6.24
12		0.66	0.74		66.63	5.78
13	4-(methoxy-carbonyl)-styrene	0.21	0.32		69.85	6.17
14		0.32	0.41		68.90	5.28
15		0.45	0.53		67.88	5.92
16	4-(hydroxy-methyl)styrene	0.26	0.36		71.97	5.66
17		0.35	0.48		70.14	5.16
18		0.48	0.59		68.66	6.08

Modification of Comonomer Chromophoric Systems in the Copolymers. In order to render the copolymers soluble in common organic solvents used for complex metal hydride reduction, the free boronic acid groups were at first esterified with ethylene glycol. For this purpose, 1.1 mol equiv (with respect to boronic acid groups) of ethylene glycol and the copolymer were refluxed in CH_2Cl_2 in the presence of a catalytic amount of triethylamine, with azotropic distillation of the formed water. The refluxing was continued for 6 h, during which period a clear solution was obtained. The polymer was purified by precipitating into a large excess of petroleum ether (40–60 °C) and dried under vacuum of constant weight. Reduction of the cyano, ester, and aldehyde groups in the copolymers was carried out following the procedure of Cohen et al.[20] During decomposition of the excess of unreacted $LiAlH_4$ at the end of the reactions, the boronic ester groups were hydrolyzed and the polymer precipitated out along with the inorganic salts. Isolation of the polymers was achieved by dissolving the solid mass in dilute acetic acid and dialyzing with water.

Analysis and Characterization. Elemental analysis was carried out at Faculty of Natural Sciences, University of Düsseldorf. Elemental composition of the copolymers is presented in summarized form in Table V. The melting point was measured with Büchi 510 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with Varian EM 390 and Varian XL 100 spectrometers, respectively, using $CDCl_3$ as solvent and TMS as internal standard. Infrared spectra were obtained with a Perkin-Elmer Model 1420 spectrophotometer in the form of clean KBr pellets.

UV spectra were recorded at 25 °C in dioxane/water (9:1 v/v by using a Varian CARY 2300 spectrophotometer interfaced with a Digital Equipment's Microvax-2 computer system. The path lengths of the cells were 1 and 0.1 cm for the wavelength regions 350–250 and 260–200 nm, respectively, and the concentrations of the polymer solutions were 2 mg/mL. Optical rotations were measured at 30 °C by using a Perkin-Elmer 241 polarimeter. The samples were examined as 0.2–0.3 g/100 mL solution in dioxane/water (9:1 v/v). ORD and CD spectral measurements were carried out at 25 °C in dioxane/water (9:1 at a concentration of 2 mg/mL by using a JASCO-J-20 automatic recording spectropolarimeter, interfaced with a Digital Equipment's Microvax-2 computer system. The path lengths of the cells were 1 and 0.5 mm for the 350–250 and 270–200 nm wavelength regions, respectively.

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A Kinetic Theory on Cationic Polymerization with Termination by Combination with a Negative Fragment

Gang-Feng Cai,[†] De-Yue Yan,[‡] and Morton Litt*[†]

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, and Department of Applied Chemistry, Shanghai Jiao Tong University, Shanghai 200030, P.R. China. *Received August 18, 1986*

ABSTRACT: The cationic polymerization with instantaneous initiation and termination by combination with a negative fragment, which is the product formed during initiation reaction with some component of the polymerization system, has been studied by means of a non-steady-state method. The molecular weight distribution function and a series of important molecular parameters of the polymer generated from mono-, bi-, and multifunctional initiators are rigorously derived. The theoretical results obtained are applicable to any ionic polymerization with second-order termination. A procedure is described for calculating the molecular weight distribution curve and the values of the various molecular parameters directly from the polymerization conditions.

Introduction

As we know, chain termination has an important effect upon the molecular weight distribution and other molecular parameters of the polymer formed in a polymerization system. Important work on chain termination has been done by Overberger,[1] Pepper,[2] Plesch,[3] and Szwarc,[4] etc. Generally speaking, chain termination is second order with respect to the propagating chains in free radical polymerization but first order with respect to the growing chains in ionic polymerization. The reason for this is that initiation of ionic polymerization usually leads to ion pairs, and termination arising from collapse of an ion pair is a first-order reaction. Formation of the free ions is feasible only if their combination into inactive product does not take place at every collision; otherwise the two oppositely charged species have no chance to separate after being formed. The termination in systems involving free ions is, of course, a second-order reaction.[3,4] There are, indeed, several cationic polymerization systems with termination involving counterions, such as the polymerization of the oxetane initiated by SnCl$_4$,[6] etc. It has also been reported that in a few sufficiently pure cationic polymerization systems, in which concentrations of water and other terminating agents are less than 10^{-7}–10^{-10} mol/L, termination of a propagating cationic chain occurs by combination with a negative fragment Y^-. Y^- is formed during an initiation reaction.[7-11]

$$...M^+ + Y^- \xrightarrow{k_t} ...M{-}Y$$

For many ionic polymerization systems with termination and transfer, such as monomer transfer,[12-19] monomer termination,[20-22] spontaneous termination,[22,23] impurity termination,[25,26] impurity transfer,[27] spontaneous transfer,[28] etc., the influences of termination and transfer on molecular weight distributions of the resultant polymers have been theoretically studied by means of non-steady-state analysis. For cationic polymerization systems with termination by combination with a negative fragment, the concentration of which is equal to that of the propagating species, $\sum N_n^+$, i.e., $Y^- = \sum N_n^+$, the termination rate should be

$$R_t = k_t(Y^-)\sum N_n^+ = k_t(\sum N_n^+)^2 \qquad (1)$$

if other terminations are absent.[3,4,7] Such a case is quite

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[*] To whom correspondence should be addressed.

[†] Case Western Reserve University.

[‡] Shanghai Jiao Tong University.

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